# ELECTROCHEMISTRY AND PHOTOCHEMISTRY OF SULPHONIUM SALTS

A Thesis Submitted to the Council for National Academic Awards in Partial Fulfilment of the Regulations for the Degree of Doctor of Philosophy

by

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Dedicated to my parents, family and Catherine

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## Statement of Advanced Studies Undertaken

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# ELECTROCHEMISTRY AND PHOTOCHEMISTRY OF SULPHONIUM SALTS

S.S. Parmar

## ABSTRACT

The cleavage in aqueous solution of the $C-\overset{+}{S}$ bond in a series of related sulphonium salts having a benzyl ligand has been investigated:

(i) electrochemically (ground state)

(ii) photochemically (excited state).

(i) Most of the sulphonium salts examined reduced in the same general manner: the polarographic wave forms were consistent with a 2-electron reduction, but analysis of the substituent effects supports a 1e + 1e continuous two step process. The macroscopic reductions are also in accord with the latter mechanism. The hydrocarbon/organomercury product ratios indicate that the radical giving rise to the products is $C_6H_5CH_2\dot{S}R_2$ rather than $C_6H_5CH_2^{\cdot}$. The product ratios could be selectively controlled by varying the applied cathode potential and temperature or a combination of both. The effect of substituents, both open chain and cyclic, directly bonded to the sulphur has been investigated and the electrolysis of the isomeric xylylenebis (dialkylsulphonium bromide) salts has been carefully examined.

(ii) The photolysis of 1-benzylthioniacyclopentane bromide affords products resulting from both homolytic and heterolytic cleavage of the benzyl carbon-sulphur bond. The photolysis of some xylylenebis (dialkylsulphonium bromide) salts has been investigated. This is the first report of the photolysis of bis-sulphonium salts.

The photolysis of some benzyltrialkylammonium salts has been examined and shown to be faster than the photolysis of the corresponding sulphonium salts.

# ELECTROCHEMISTRY

## Introduction

The electrochemical reduction in aqueous solution of the C-$\overset{+}{S}$ bond in sulphonium salts at a dropping mercury electrode (DME) has been investigated by various workers(1). A list of some half-wave potentials is given below.

TABLE 1

| sulphonium ion | - E½(V vs.SCE) |
|---|---|
| $(CH_3)_3\overset{+}{S}$ | 1.85 |
| $(C_2H_5)_3\overset{+}{S}$ | 2.00 |
| $(C_2H_5)_2\overset{+}{S}CH_2CH_2OH$ | 2.00 |
| $(C_2H_5)_2\overset{+}{S}CH_2CH=CH_2$ | 1.46 |
| $p\text{-}CH_3C_6H_4CH_2\overset{+}{S}(CH_3)_2$ | 1.55 |
| $(C_6H_5)_3\overset{+}{S}$ | 1.09 |
| $C_6H_5CH_2\overset{+}{S}(C_2H_5)_2$ | 1.30 |
| $C_6H_5CH_2\overset{+}{S}(CH_2CH_3)(CH_2CH_2OH)$ | 1.21 |
| $(C_6H_5CH_2)_3\overset{+}{S}$ | 0.65 |
| $C_6H_5COCH_2\overset{+}{S}(C_2H_5)_2$ | 0.63 |
| $C_6H_5COCH_2\overset{+}{S}(CH_3)(C_6H_5)$ | 0.41 |

The diffusion currents of these irreversible polarographic waves were found to obey the Ilkovic equation and were independent of the pH of the medium except where the substrate exhibited acid/base behaviour.

The E½ value is a measure of the ease of reduction at the DME: the easier the reduction the less negative the value of E½. Alkyl type sulphonium ions, for example $Me_3\overset{+}{S}$ ion, have been reported to reduce at potentials very close to the discharge voltage of the supporting electrolyte or solvent; as a result the polarographic waves are ill-defined or the sulphonium ion does not reduce under these conditions.

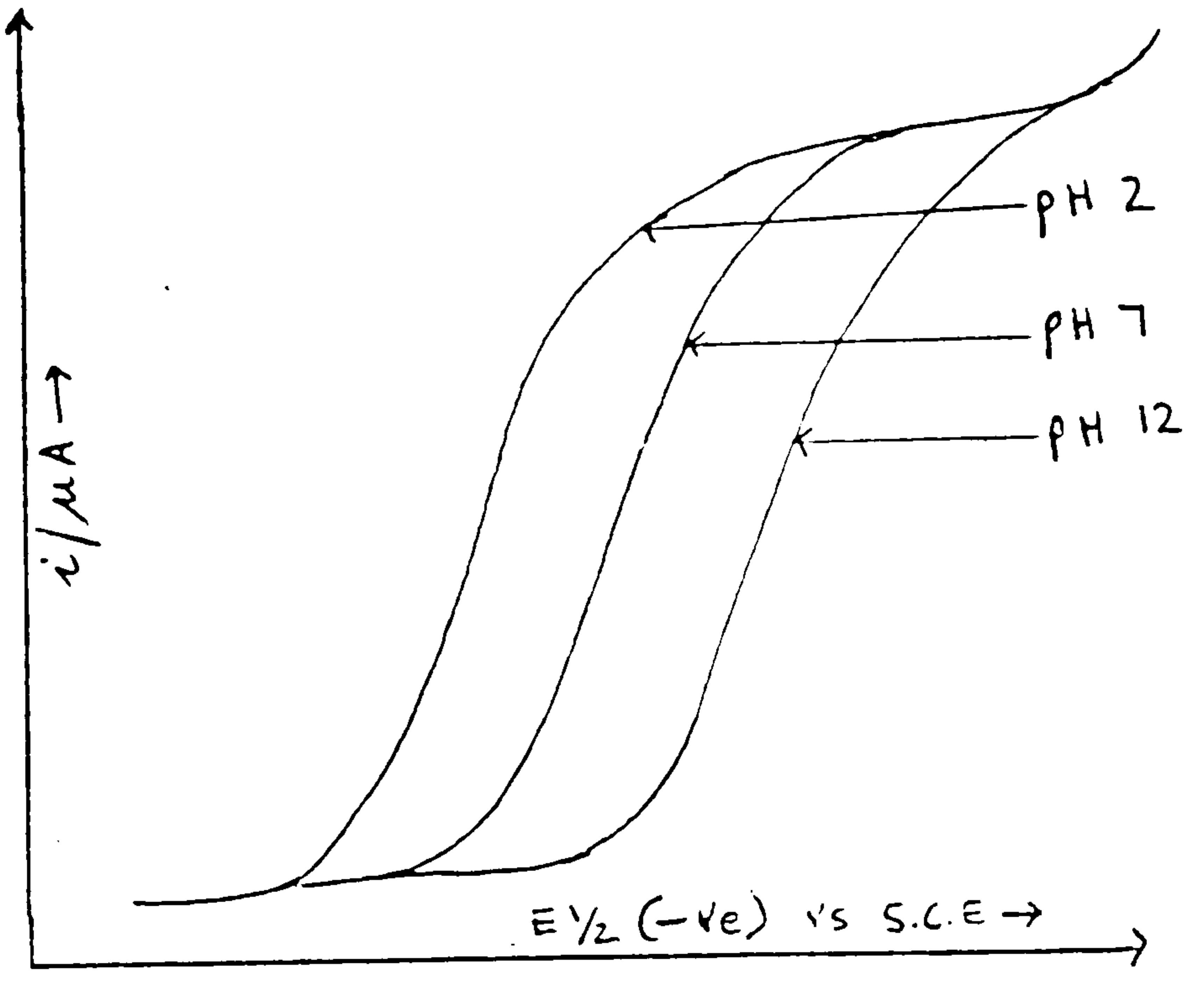
However, replacement of alkyl groups in trialkyl type salts by electronegative or benzyl substituents at the sulphur atom causes the half-wave potentials to shift to less cathodic values.

Phenacyl type sulphonium salts undergo electrochemical C-S bond cleavage at relatively low half-wave potentials (see Table 1), which are independent of pH over a wide range (pH 2.1 to 7.1)(2, 3). This ease of reduction is not unexpected because the electronegative carbonyl group can interact with the sulphur centre and can stabilise the intermediate resulting from an initial electron transfer to the sulphonium ion. Consequently, even the phenacyl ammonium salts undergo reduction at relatively low potentials, though higher than that for the sulphonium salt( 4 ). In more acid media protonation of the carbonyl group occurs, giving rise to a species which is reduced at a less negative potential than the non-protonated form. At high pH, the sulphonium ion is converted to the ylide, which is not reducible under polarographic conditions.

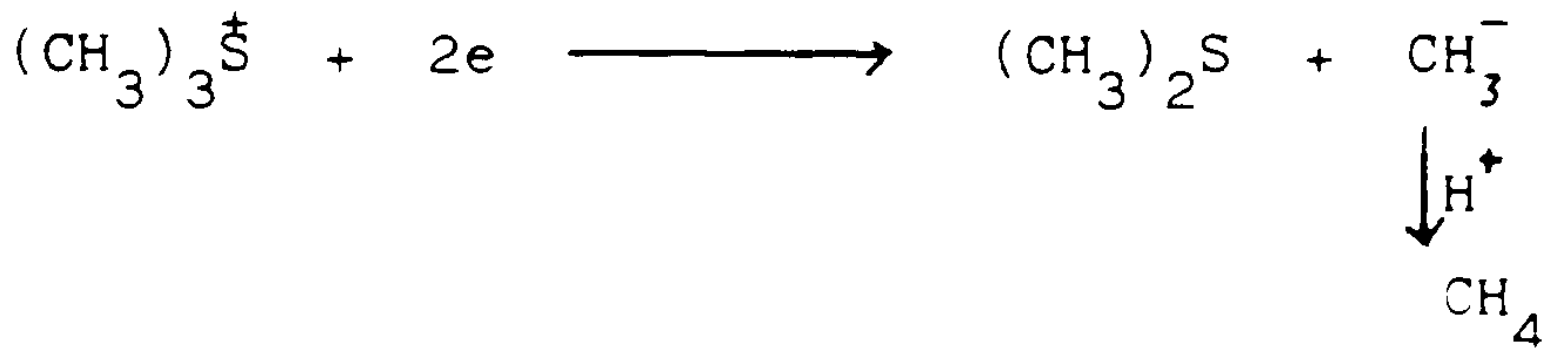
$$C_6H_5COCH_2\overset{+}{S}R_2 \xrightarrow{OH^-} C_6H_5CO\overset{-}{C}H\overset{+}{S}R_2$$

Ylide

With a decrease in the sulphonium ion concentration a greater electrode potential must be applied in order to maintain a given rate of electron transfer, thus the E½ shifts to more cathodic voltages with increasing pH.



Colichman and Love(5) reported on the polarographic reduction of trimethylsulphonium salts and o-, m- and p- cresyldimethylsulphonium salts. From the slopes of the waves they concluded that the reductions were irreversible. From the wave heights(current) of the trimethylsulphonium salts in alcohol solution compared with that of the first reduction wave of diphenyliodonium iodide, known to be due to one electron transfer, they concluded that the reduction required two electrons. This may be formulated:

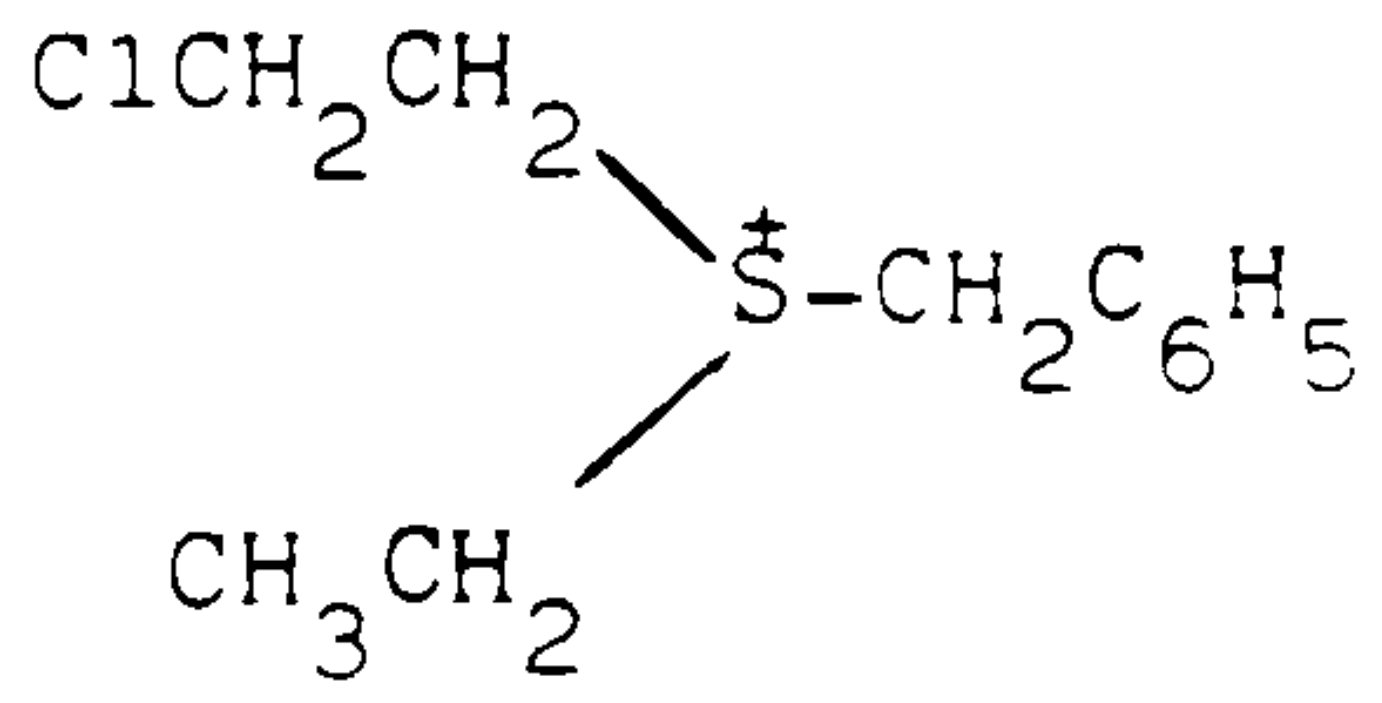


$$(CH_3)_3\overset{+}{S} + 2e \longrightarrow (CH_3)_2S + \underset{\substack{\big\downarrow H^+ \\ CH_4}}{CH_3^-}$$

although they did not complement their study with any preparative reductions and product analysis.

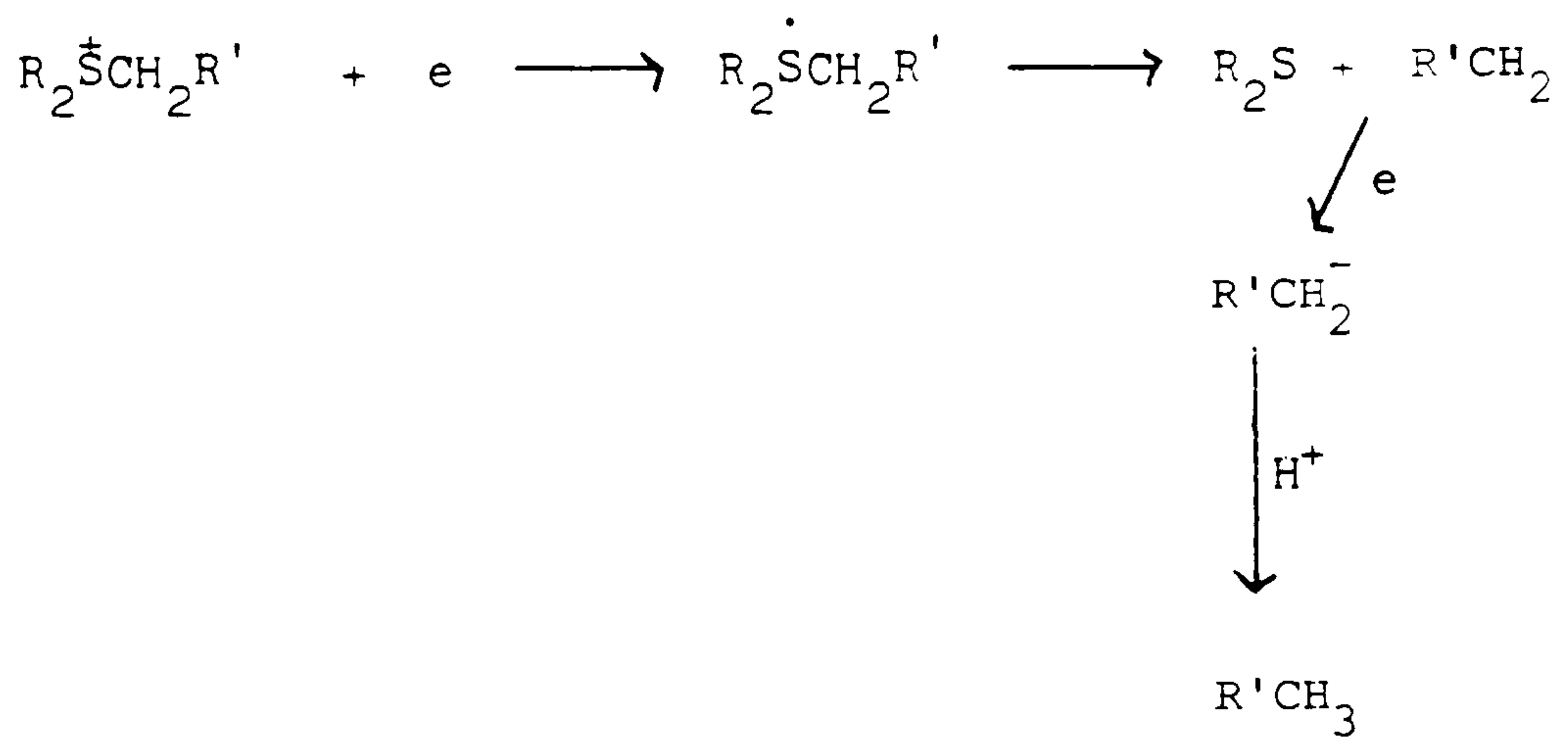
In connection with their studies of sulphonium salts as cytostatic agents, Lüttringhaus and Machatzke(6) examined the polarography of over 40 alkyl type sulphonium salts. Most of these had electronegative reducible functional groups in addition to the sulphonium group and since they reported no investigation of the products of reduction the polarograms do not allow an unambiguous assignment of the half wave potentials to particular processes. They found that electronegative groups lowered the half wave potentials, often quite markedly, as did allyl and benzyl ligands. They also reported that some sulphonium salts with two different activating ligands gave polarograms with two waves, each approximately half the height of a two electron reduction wave, thereby indicating two successive one electron steps.

e.g.



| | $E_{1/2}(V)_1$ | $E_{1/2}(V)_2$ |
|---|---|---|
| $ClCH_2CH_2(CH_3CH_2)\overset{+}{S}-CH_2C_6H_5$ | -0.89 | -1.20 |

They therefore proposed the following two step scheme for the reduction of sulphonium salts.



$$R_2\overset{+}{S}CH_2R' + e \longrightarrow R_2\dot{S}CH_2R' \longrightarrow R_2S + R'CH_2$$

$$R'CH_2 \xrightarrow{e} R'CH_2^- \xrightarrow{H^+} R'CH_3$$

While we agree with this mechanism, we do not regard their evidence as very strong. Indeed, the present study provides much better evidence for this mechanism, as will be discussed later.

The two-step reduction mechanism of Lüttringhaus was supported and extended by McKinney and Rosenthal( 7 ), in a detailed polarographic investigation of triphenylsulphonium bromide supplemented by macroscopic reduction studies. The polarographic reduction which was accompanied by strong adsorption phenomena, occurred in two steps: the first wave ($E_{1/2} = -1.09v$) was pH independent whilst the second wave was pH dependent (pH6, $E_{1/2} = -1.33v$; pH11, $E_{1/2} = -1.39v$). The products from macroscopic reductions at a mercury cathode were diphenyl sulphide, benzene and diphenylmercury. However, the reaction appeared to proceed via a complex mechanism involving the adsorption of the electro-reduced species on the mercury surface and a chemical reaction of the intermediate radical, $(C_6H_5)_3S{-}{-}{-}H\dot{g}$. The reaction pathway could be controlled by varying the applied working potential: electrolysis at the potential of the first polarographic wave, yielded quantitative amounts of diphenyl sulphide and diphenylmercury; no benzene or biphenyl was formed. At potentials more negative than the second wave, diphenyl sulphide and benzene were formed quantitatively, provided low substrate concentrations were used. With increasing substrate concentration the yield of diphenylmercury increased at the expense of benzene. The following reaction scheme was put forward to account for the products:

step 1

$$\left[(C_6H_5)_3\overset{+}{S}..Hg\right] + e \longrightarrow \left[(C_6H_5)_3S...Hg^{\cdot}\right]$$

$$2\left[(C_6H_5)_3S...Hg^{\cdot}\right] \longrightarrow 2(C_6H_5)_2S + (C_6H_5)_2Hg + Hg$$

step 2

$$\left[(C_6H_5)_3S...Hg^{\cdot}\right] + e \xrightarrow{\overset{+}{H}} (C_6H_5)_2S + C_6H_6 + Hg$$

This is an example of the importance of the applied potential in determining the course of a reaction pathway. It should be noted that the triphenylsulphonium ion is an aromatic sulphonium ion and differs from alkylsulphonium ions, mainly in the possibility of interaction between the aromatic $\pi$ electron system and the S atom , both in the ground state and in any transition state or intermediate formed in the reduction process. The C-S bonds also differ, involving $sp^2$ hybrid carbon orbitals in the aromatic salts and $sp^3$ hybrids in the alkyl sulphonium salts. These differences in structure suggest that the mechanism for the reduction of the aryl sulphonium salts may not necessarily be the same as for the alkyl salts (cf. the mechanisms of nucleophilic substitution of alkyl halides and aryl halides).

An investigation more closely related to the studies reported in this thesis was the reduction of tribenzylsulphonium hydrogensulphate(8). Bär found that the polarography showed two one electron reduction waves ($E_{1/2}$ = -0.65v, -1.15v) and proposed the following mechanism for the first step.

$$(C_6H_5CH_2)_3\overset{+}{S} \;+\; e \longrightarrow (C_6H_5CH_2)_2S \;+\; C_6H_5CH_2^{\bullet}$$

$$2C_6H_5CH_2^{\bullet} \;+\; Hg \longrightarrow (C_6H_5CH_2)_2Hg$$

This was supported by macroscopic reduction at -0.8v and isolation of the products, dibenzyl sulphide and dibenzylmercury. The coulometry of this reduction was consistent with a one electron transfer process. The second wave of the polarogram was more complex and exhibited both absorption effects and pH dependance. It was ascribed mainly to the reduction of dibenzyl sulphide although Bär was unable to carry this out. Macroscopic reduction of dibenzylmercury at -1.1v showed a weak current, due to reduction and this may account for part of the current in the second wave. While Bär's investigation throws some light on the first reduction step, it is vague about the second reduction step. We repeated Bär's polarography with essentially similar results.

There is evidence to indicate that addition of the first electron to a sulphonium ion causes carbon-sulphur bond cleavage to yield the most stable carbon moiety. When the electrolysis of the sulphonium salt is effected in acrylonitrile, the initially formed radical intermediate is trapped to form products(9), for example, cyanomethyldimethylsulphonium salts give glutaronitrile in 20% yield and benzyldimethylsulphonium salts give γ-phenylbutyronitrile in 29% yield.

$$C_6H_5CH_2\overset{+}{S}(CH_3)_2 \xrightarrow{CH_2=CHCN/e} C_6H_5CH_2CH_2CH_2CN + (CH_3)_2S$$

The following scheme was put forward to account for the products.

$$\begin{tikzcd}[column sep=small]
C_6H_5CH_2\overset{+}{S}(CH_3)_2 + e \arrow[r] & C_6H_5CH_2^{\bullet} + S(CH_3)_2 \\
C_6H_5CH_2^{\bullet} + CH_2{=}CHCN \arrow[r] & C_6H_5CH_2CH_2\dot{C}HCN \\
C_6H_5CH_2CH_2\dot{C}HCN + e \arrow[r] & C_6H_5CH_2CH_2\bar{C}HCN \arrow[d, "\overset{+}{H}"] \\
 & C_6H_5CH_2CH_2CH_2CN
\end{tikzcd}$$

A similar scheme can be formulated for an initial 2e transfer to give the benzyl anion, which could add to the acrylonitrile in the same way.

In a related reaction, reduction of dimethyl(3-cyanopropyl)-sulphonium salts in dimethyl sulphoxide containing styrene at a mercury cathode lead to di(3-cyanopropyl) mercury and 6-phenylhexanenitrile by reaction of the first formed 3-cyanopropyl radical(10). The following scheme was put forward:

$$\begin{tikzcd}[column sep=small]
(CH_3)_2\overset{+}{S}CH_2CH_2CH_2CN + e \arrow[r] & (CH_3)_2S + {}^{\bullet}CH_2CH_2CH_2CN \\
2\ NCCH_2CH_2CH_2^{\bullet} + Hg \arrow[r] & Hg(CH_2CH_2CH_2CN)_2 \\
NCCH_2CH_2CH_2^{\bullet} + CH_2{=}CHC_6H_5 \arrow[r] & NCCH_2CH_2CH_2CH_2\dot{C}HC_6H_5 \arrow[d, "+e/H^+"] \\
 & NCCH_2CH_2CH_2CH_2CH_2C_6H_5
\end{tikzcd}$$

More recently Settineri(11,12) and co-workers have developed the work on sulphonium salts with the aim of utilising them for preparative industrial processes: for example, coating of metals in semi-conductor work, formation of polymers and fungicides; consequently most of their work is published in patents.

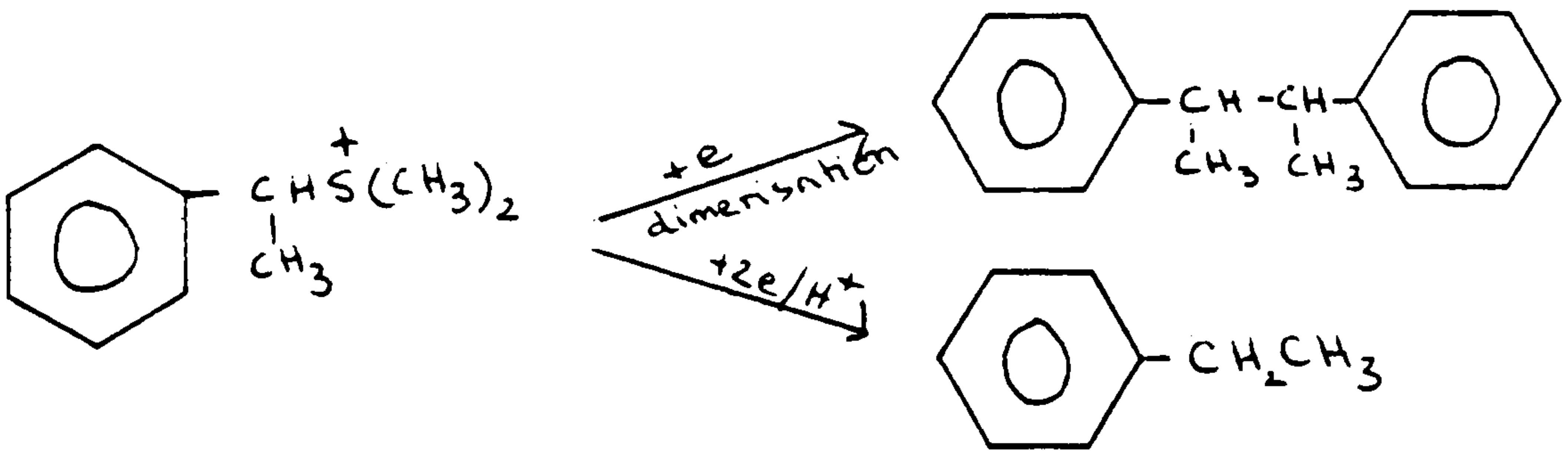
They reported that many benzylic sulphonium ions when reduced at a mercury cathode yield the corresponding organometallic product, for example:

$$C_6H_5CH_2\overset{+}{S}(CH_3)_2 \xrightarrow[-0.92\ \text{V vs SCE}]{+e/Hg} (C_6H_5CH_2)_2Hg + S(CH_3)_2$$

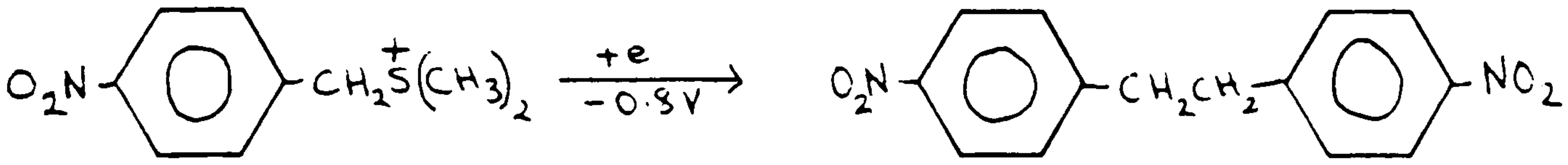
94%

$H_2O$ solvent (90°C)

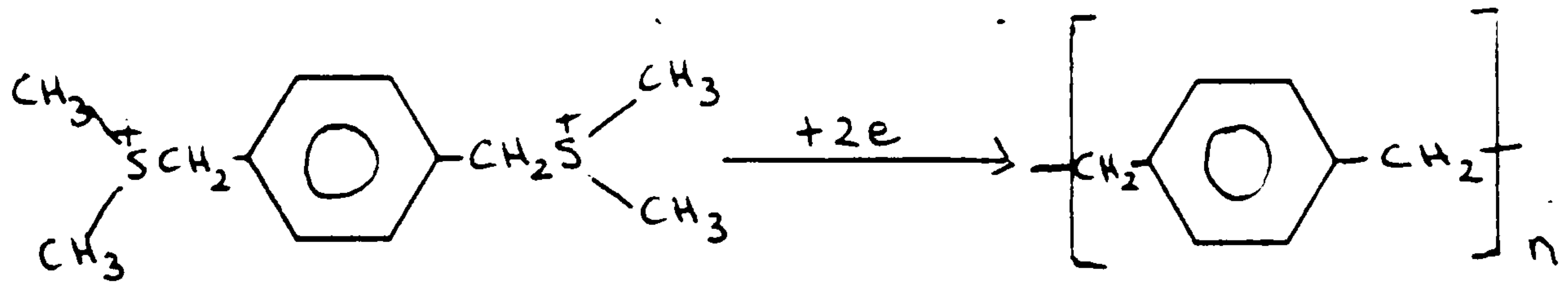
This process was reported to be dependent upon both the temperature and the applied potential. Whereas low potentials and high temperatures favoured mainly organomercury compounds, high potentials gave good yields of the corresponding hydrocarbon. The product dependence on applied potential was also applicable to the α-substituted benzyl salts: for example, α-methylbenzyldimethylsulphonium bromide, at low cathode voltage gave the one electron transfer coupled product, 2,3-diphenylbutane, and at a more cathodic voltage the two electron transfer product, ethylbenzene, was formed.



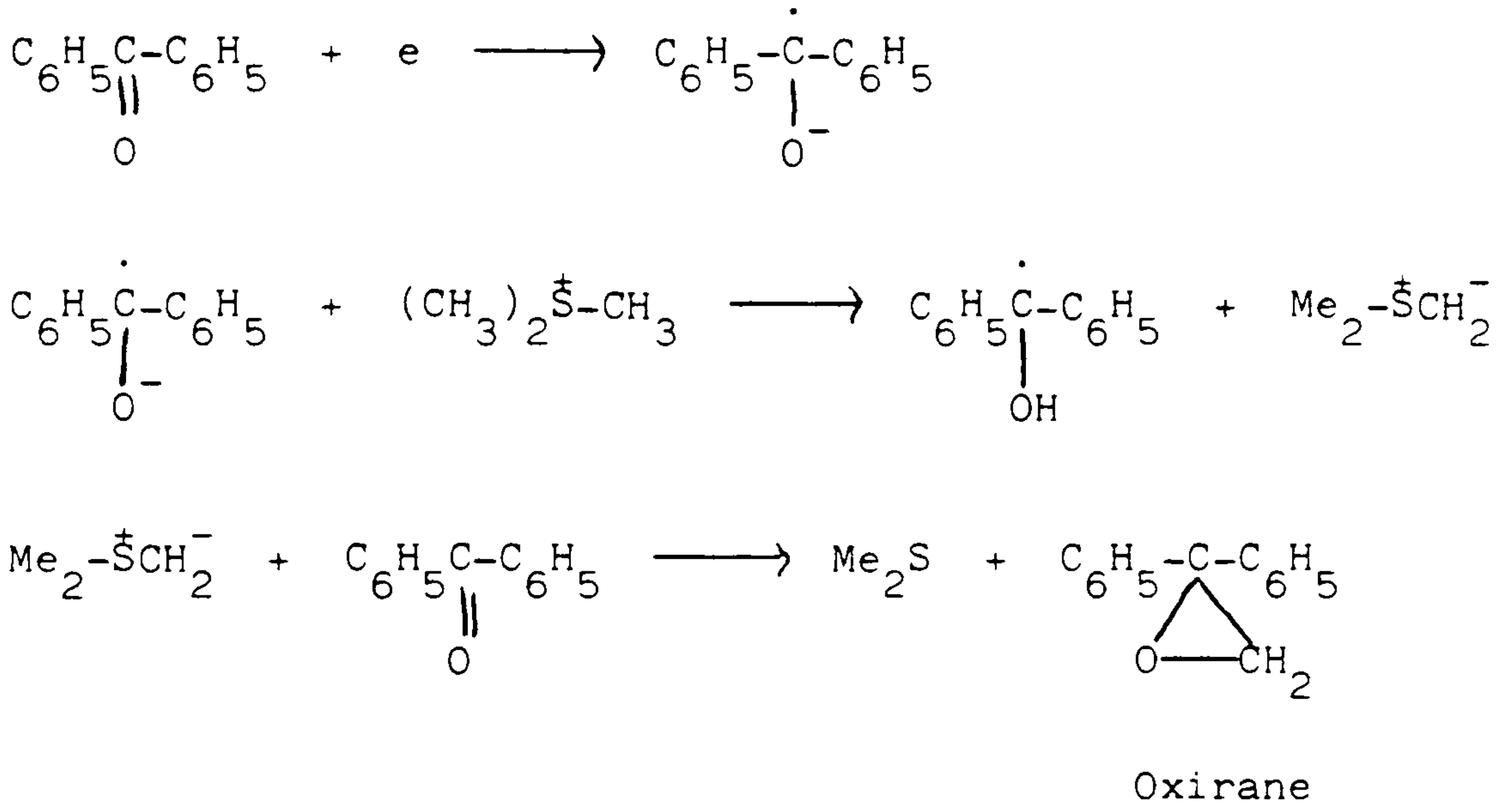
The steric effects of the α-methyl groups, resulting in unfavourable geometry at the mercury surface was proposed for the absence of organomercury compounds. 4-Nitrobenzyldimethylsulphonium bromide gave good yields of 4,4'-dinitrobibenzyl on reduction at a mercury cathode in aqueous solution, whereas the meta-isomer was reported not to reduce under the same conditions.



Reduction of the p-xylylenebis(dimethylsulphonium) salts at a number of cathodes gives the polymer, p-xylylene$^{(13)}$. This is the subject of patents reporting the use of this reaction to apply polymer coatings.



Sulphonium salts are reported by Shono et alia to form the corresponding ylides upon electrolysis in aprotic solvents at carbon electrodes$^{(14)}$. The following scheme could account for the products: for example benzophenone, to form the oxiranes. The following scheme could account for the products:



$$C_6H_5\underset{\overset{\|}{O}}{C}-C_6H_5 + e \longrightarrow C_6H_5-\overset{\bullet}{\underset{O^-}{C}}-C_6H_5$$

$$C_6H_5\overset{\bullet}{\underset{O^-}{C}}-C_6H_5 + (CH_3)_2\overset{+}{S}-CH_3 \longrightarrow C_6H_5\overset{\bullet}{\underset{OH}{C}}-C_6H_5 + Me_2-\overset{+}{S}CH_2^-$$

$$Me_2-\overset{+}{S}CH_2^- + C_6H_5\underset{\overset{\|}{O}}{C}-C_6H_5 \longrightarrow Me_2S + C_6H_5-\underset{O-CH_2}{C}-C_6H_5$$

Although this is reported as the reduction of the sulphonium group, it is in fact the indirect reduction involving a base, which gives rise to the sulphonium ylide. Similar results were reported by Utley$^{15,16)}$ on the indirect reduction of phosphonium salts to afford Wittig reagents. The Japanese workers rejected this scheme because they were able to form the ylide at potentials lower than that necessary to reduce the carbonyl compound, and they proposed a single step reduction of the sulphonium salt to the ylide.

$$R_2\overset{+}{S}CH_2R' \xrightarrow{1e} R_2\overset{+}{S}\overset{-}{C}HR' + (H^{\bullet})$$

## Summary

The polarography of a considerable number of sulphonium salts has been reported but few of the investigations have been supplemented by other studies, e.g. macroscopic reductions, to ascertain the products.

Two mechanisms for the reduction have been proposed:

a) a one step two electron transfer to give an anion which then reacts chemically to give products.

b) a one electron transfer to give a radical which may react chemically to give products or add another electron to give an anion.

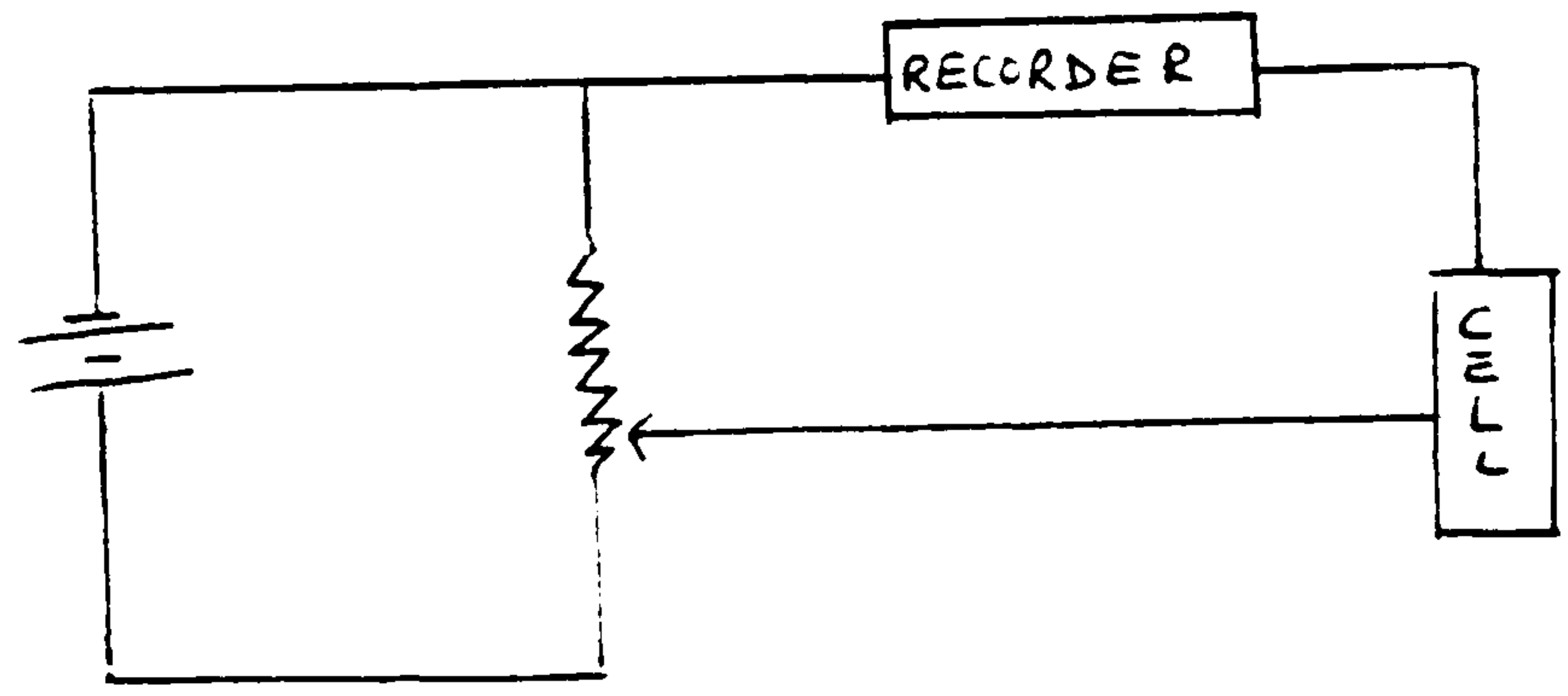
In macroscopic reductions, the applied potential can have a considerable effect on the relative amounts of one electron/two electron reduction products. The solution temperature may also influence this ratio.

Polarographic studies showed that benzyl substituents markedly reduced the potential necessary for the reduction and favoured benzyl-$\overset{+}{S}$ bond cleavage presumably due to the delocalisation of electrons in the transition state leading to the benzyl radical or anion. It was this enhancement of reduction, together with the ease of studying the effect of ring substituents on the processes and the desire to correlate electrochemical reduction with other means of reduction of sulphonium salts carried out in this laboratory(17) which led us to investigate benzyl sulphonium salts in this study. These salts allowed us to work in aqueous solutions at a working cathodic potential well below that for the discharge of the supporting electrolyte. This system also allowed us to investigate the effect of open chain and cyclic ligands on the reduction process and probe more deeply into the problem of the one electron versus two electron processes.

## Techniques

The cleavage of the C-$\overset{+}{S}$ bond in 'onium salts can be achieved and effectively studied by reduction at a mercury cathode. In particular such reductions can be studied by polarography which gives useful information on the ease of reduction and some insight into the mechanism of electron transfer. It has been widely used in the present study and in this section the main principles and conditions of use are outlined.

This technique involves the electrolysis of solutions of electro-reducible or electro-oxidizable materials between a dropping mercury electrode (DME) and some reference electrode, usually a saturated calomel electrode (SCE) or a mercury pool. The potential applied between them is varied and the consequent changes in the flow of current are measured. The DME consists of a fine capillary attached to a reservoir containing mercury. Mercury passes down the capillary and emerges in the form of small drops, where either reduction or oxidation processes can occur. In polarography the situation is so arranged that the reducible/oxidizable ions arrive at the DME by natural diffusion alone and, to make this possible, a 'supporting' electrolyte is added to the solution so that electrical migration has a negligible effect. In addition the solution is kept quiescent to avoid convection effects. Since the mercury drops grow to a maximum size and then fall there is a constantly changing area of the drop and this causes a varying size of the current. To minimise this fluctuation the recording system is heavily damped by a capacitive circuit so that a mean current can be read.



Essential Polarographic Circuit

Using Fick's laws of diffusion, Ilkovic derived an expression for the mean current in a diffusion controlled process:

$$\bar{I}d = 607\ n\ D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} C$$

where $\bar{I}d$ = diffusion current ($\mu$A)

m = mass of mercury flowing/sec(mg/s)

t = drop time (s)

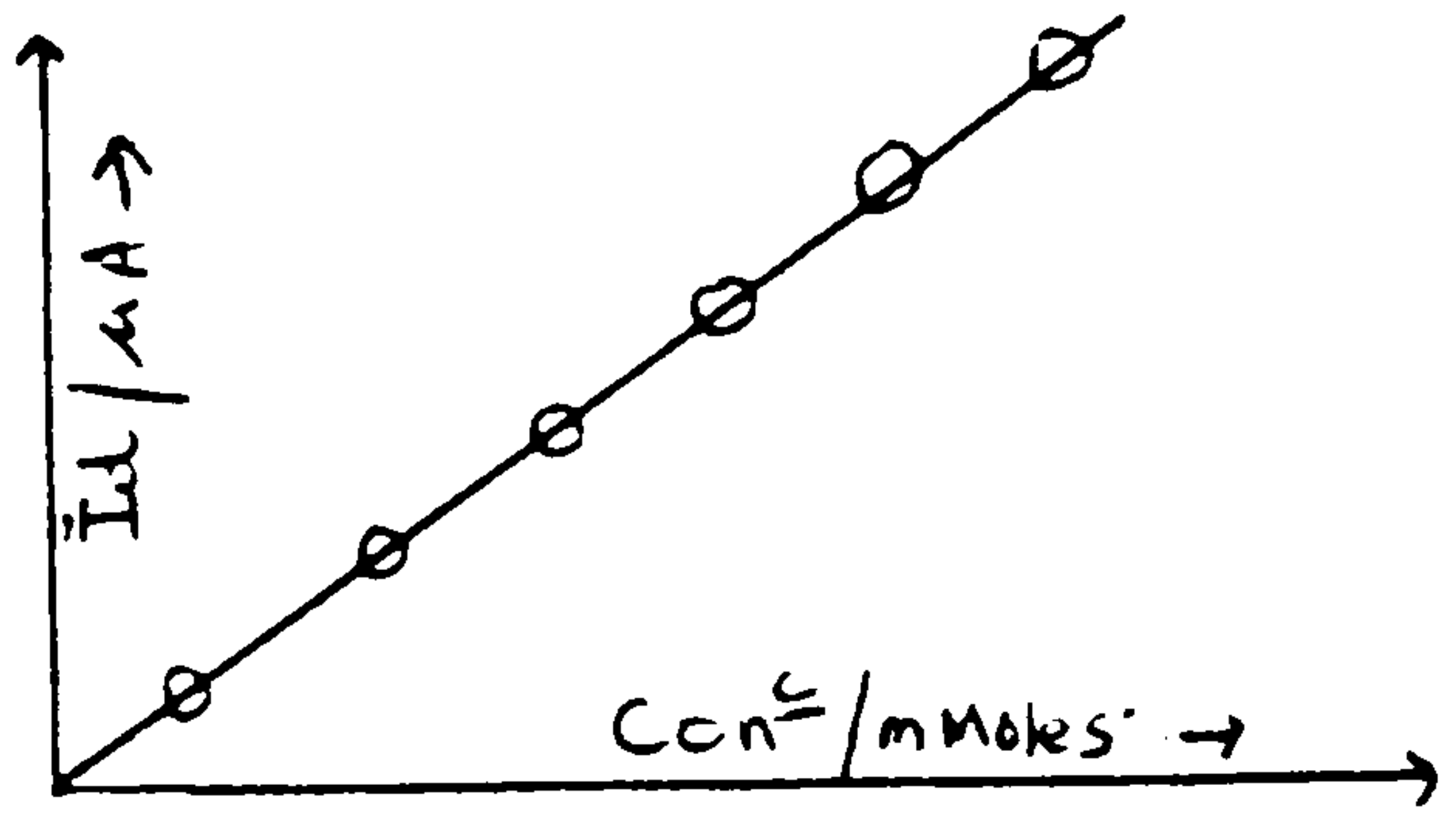
C = concentration (mMoles/litre)

D = diffusion coefficient ($cm^2$/sec)

Rewriting the equation in form:

$$\bar{I}d = \underbrace{607\ n\ D^{\frac{1}{2}} C}_{\text{solution factors}} \times \underbrace{m^{\frac{2}{3}} t^{\frac{1}{6}}}_{\text{electrode factors}}$$

a division into variables concerned with the solution and electrode is apparent. If the electrode factors are maintained constant then $\bar{I}d \propto C$, i.e. there is a linear relationship between current and concentration. This is the basis of the polarographic method for quantitative analysis:



The upper range of concentration used is approximately $10^{-2}$M, a limit imposed by migration effects. The lower range is approximately $10^{-5}$M and is governed by the difficulty in measuring $\bar{I}d$ apart from the residual current. For most analytical purposes a range of $10^{-3}$ to $10^{-4}$M is used.

If the solution is maintained constant, then $\bar{I}d \propto m^{\frac{2}{3}} t^{\frac{1}{6}}$.

By Poiseuilles equation the rate of flow of liquid through a capillary under a head (h) of liquid is given by

$$\text{volume v flowing in unit time} = \frac{\pi r^4 p}{8l\eta}$$

where p = pressure, r = capillary diameter, l = length of capillary and $\eta$ = viscosity of liquid.

$$\text{as } p \propto h, \qquad v \propto h.$$

$$\text{as } m \propto v, \qquad m \propto h.$$

$$t \text{ (drop time)} \propto \frac{1}{m}, \text{ so } t \propto \frac{1}{h}$$

then the terms $m^{2/3}\ t^{1/6}$ in the Ilkovic equations

become $\propto h^{2/3}\ h^{-1/6}$

i.e. $\propto h^{1/2}$ .

The importance of maintaining electrode conditions constant is thus apparent, particularly when using the technique for analytical purposes. The two conditions $\bar{I}d \propto C$ and $\bar{I}d \propto h^{1/2}$ are used as criteria for diffusion controlled processes, when examining a system of unknown behaviour. Another type of current sometimes exhibited by redox systems is a kinetic current ($i_k$) which is independent of the height of the mercury reservoir. In this investigation kinetic currents were not encountered. Finally there is always present a residual current which arises from the changing surface area of the drop. Such a surface acquires an electrical double layer i.e. it is a charging process; since this process is continuous there is a continuous residual or charging current. This effect cannot be eliminated in classical polarography and must therefore be substracted from the total current flowing.

Other factors which affect the normal recording of a polarogram are: (a) dissolved oxygen, (b) maxima and (c) drop-time.

(a) Since oxygen is easily reduced at the dropping mercury electrode dissolved oxygen must be removed from the solution prior to the recording of a polarogram. For this purpose nitrogen is bubbled through the solution for several minutes. The gas stream must be stopped during the recording of the polarogram, otherwise the resultant stirring causes irregular dropping of the mercury from the capillary, and introduces a strong convection effect.

(b) Polarograms are frequently complicated by maxima. The waves for the reduction of a substrate may exceed the height of the true wave and then decrease, giving rise to a sharp peak or a hump on the curve, in most cases making measurements uncertain. Maxima are believed to be due to a tangential streaming motion of the solution past the surface of the mercury drop and are eliminated by using organic surfactants, for example gelatine or Triton X100 in small amounts, usually not greater than 0.01% of the test solution. Gelatine was used in this study.

(c) The optimum drop-time (t) should be between 3 and 7 seconds; below 3 seconds the rapid flow of mercury causes a stirring effect which results in irregular drop-times and consequently a fluctuation in the recorded current. A drop-time greater than 7 seconds results in unduly large oscillations in the observed current, which makes capacitance damping difficult since it approaches the response time of the recording system.

## Summary of Conditions Employed in Polarography

(i) depolariser concentration between $10^{-3}$ to $10^{-4}$ M;

(ii) supporting electrolyte (approx 0.1M). Buffer solutions were used in this investigation;

(iii) elimination of oxygen by purging with nitrogen gas;

(iv) elimination of maxima by suppressors (gelatine);

(v) drop-time; 3 - 7 seconds.

## Polarographic Determination of E½ and n(18)

Automatic polarography is used to record approximate values of the half-wave potential (characteristic of the depolariser) E½; more accurate values of E½ can be obtained by manual logarithmic wave analysis, using a modification of the Nernst equation. For an irreversible reduction process

$$E = E_{\frac{1}{2}} + \frac{RT}{\alpha nF} \ln \frac{\bar{I}d-i}{i} \qquad (1)$$

where F is the Faraday charge, i is the current at an applied voltage E and $\bar{I}d$ is the diffusion current. It is evident that when $i = \frac{1}{2}\bar{I}d$, $E = E_{\frac{1}{2}}$.

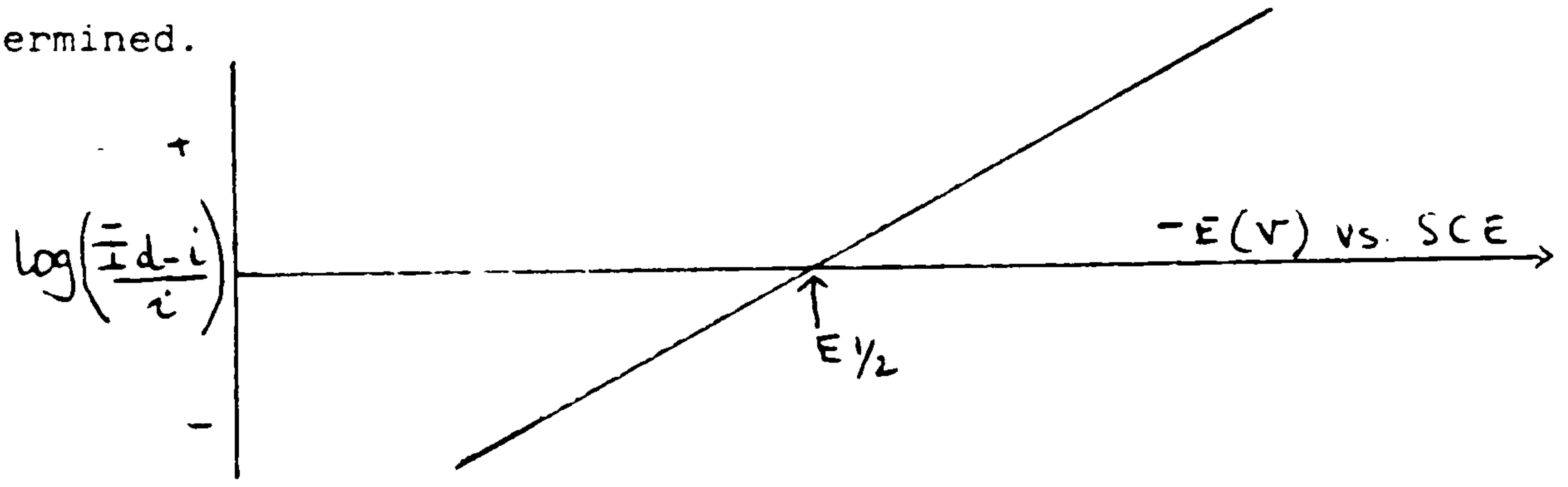
Using this equation and knowing the transference coefficient ( $\alpha$ ), the number of electrons (n) involved in a reaction can be determined. Since $\alpha$ values are difficult to determine, it is common practice to find n by coulometry at constant potential or to calculate it from current-time plots. The former method is more accurate and was used in this work.

Alternatively the Ilkovic equation may be solved for n under stated conditions provided that a suitable value of D can be found. A value of D for a similar size species can be used and assumed to be sufficiently close for this purpose.

Rearrangement and differentiation of equation (1) gives

$$\frac{d\left(\log \frac{\bar{I}d - i}{i}\right)}{dE} = \frac{\alpha n F}{2.303\,RT} \quad \text{at} \quad 25^{\circ}C$$

A plot of log $\left[(\bar{I}d - i)/i\right]$ vs. E gives a straight line graph with a slope of $\alpha nF/2.303$ RT. From the plot both E½ and n values can be determined.



The participation by hydrogen ions, in the primary process, can be tested by measuring the E½ values dependence on pH:

$$\frac{E_{1/2}}{pH} = \frac{-0.0591m}{n} \text{ volts/pH at } 25^{\circ}.$$

(m is number of protons involved per species reduced).

A shift of 59 millivolts per pH unit is indicative of a single hydrogen ion involvement for a reversible one electron change. Since the types of changes involved in the present studies are irreversible this change becomes

$$\frac{E_{1/2}}{pH} = \frac{-0.0591m}{\alpha n} \text{ volts/pH at } 25^{\circ}C.$$

Once again the problems of $\alpha$ arise so that $\alpha n$ is required before m can be solved. With only one exception (dibenzylmethylsulphonium bromide), all the sulphonium salts used in this study gave polarographic waves which were independent of pH.

## Determination of n Values by Coulometry

The usual method for determining the number of electrons (n) in polarographic reduction, assuming both micro and macro-scale reduction are the same, was to measure the number of coulombs consumed in reducing a known amount of material. The method proposed by Lingane(19) consisted of a cell having a stirred mercury cathode, placed in series with a coulometer, to determine the number of coulombs used. In the present studies, electrolyses were carried out at a constant applied working potential whose values were selected from the polarogram usually at some point on the current plateau. The electrolyses were allowed to continue until complete, or rather until the current was practically zero in each case.

A known volume of solution was placed in a two-compartment cell incorporating a three electrode system; a stirred mercury cathode, reference electrode (SCE) positioned with its tip as close as possible to the cathode surface and an auxiliary electrode. The solution was de-aerated and a selected voltage was applied by a potentiostat. The number of coulombs was recorded by a coulometer. The completion of the electrolysis was taken to be the point at which the current fell to a constant low value. This low current is called the residual current and was assumed to be present throughout the electrolysis. The correction for this term was made by calculating the coulombs for the residual current and subtracting this value from the observed coulometry value. From this corrected coulometric value and the amount of salt electrolysed, n can be calculated. An example of this calculation is given on page 68 .

## Instrumentation and Techniques

Unless otherwise stated, infra-red spectra of solids were determined as nujol-mulls, and liquids as thin films on either a Perkin-Elmer 237 grating spectrophotometer or Perkin-Elmer 298 spectrophotometer. Ultra-violet spectra were determined on a Unicam SP1800 spectrophotometer using 1 cm quartz cells.

Nuclear magnetic resonance (nmr) spectra of the salts were determined in deuterium oxide ($D_2O$) solution, unless otherwise stated, on a Jeol 60 MHz spectrometer. Chemical shifts are given in $\delta$ with sodium trimethylsilylpropanesulphonate as the internal standard; splitting patterns are designated as: s, singlet; d, doublet; t, triplet; q, quartet; b, broad singlet; m, multiplet; um, unresolved multiplet; $^{13}C$ spectra were recorded using a Jeol 100 MHz Fourier transform spectrometer. Mass spectra were recorded on the Jeol JMS-DX300 low/high resolution spectrometer.

Polarograms were automatically recorded on a P04 Radiometer Polariter, using a saturated calomel electrode (sce) as the reference electrode.

More accurate determinations were carried out by manually varying the applied potential, using the Polariter and measuring the corresponding current on a galvanometer.

Potential controlled electrolysis (pce) were carried out using a TA 251 ministat and a Wenking SS 170 coulomb integrator.

Gas liquid chromatography (glc) was determined on the Pye series 104 chromatograph, with a nitrogen flow rate of 60 $cm^3$/minute, linked to a Servoscribe mK 11 integrator, using either OV1, OV101, or Silar 5 cp columns.

## Preparation of Sulphonium Salts

These were made, with few exceptions, by reaction of the corresponding benzyl halide with a sulphide.

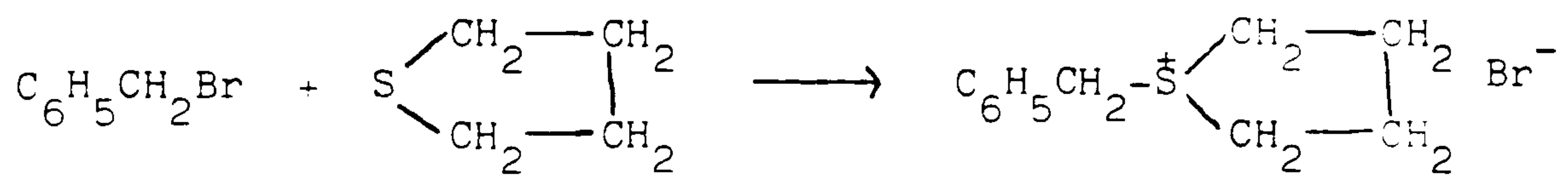
$$XC_6H_4CH_2Hal \quad + \quad R_2S \quad \longrightarrow \quad XC_6H_4CH_2\overset{+}{S}R_2Hal^-$$

$X \;=\; H, Br, Cl, CH_3, NO_2$

$Hal = Cl, Br$

The structures of new compounds were established by analysis and $^1H$ nmr spectra. Although the salts are often hygroscopic and sometimes difficult to precipitate from solution, this method was generally found to be satisfactory although some difficulties in the xylylene series were encountered. An example of the general method is the preparation of 1-benzylthioniacyclopentane bromide:

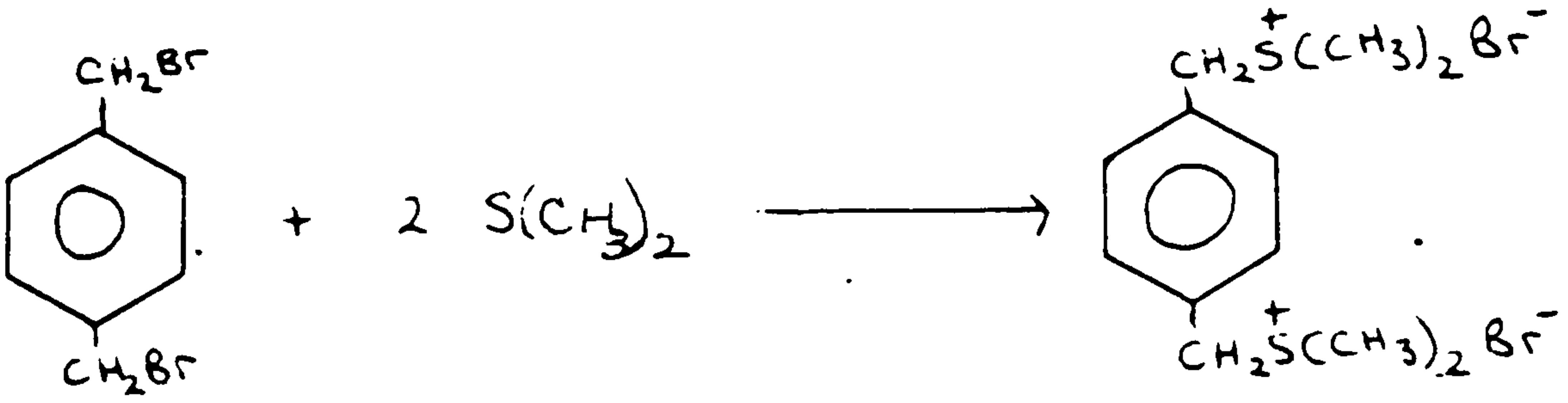
Benzyl bromide (1.71 g) was added to a solution of thiacyclopentane (0.98 g) in absolute alcohol (5 cm$^3$). No warming up was detected and the colourless mixture was left for six days. Sodium dried ether (25 cm$^3$) was added, and the white precipitate was filtered off using a Schlenk filter under nitrogen. The solid was purified by successive dissolution in alcohol (5 cm$^3$), and reprecipitation with excess of ether. The salt was dried under nitrogen. The salt was non-deliquescent, and was stored in the dark to prevent photochemical decomposition. Yield 2.5 g (96%), mp. 107°.



Analysis: calculated: C, 50.96%; H, 5.79%; Br, 30.89%
found: C, 50.99%; H, 5.85%; Br, 30.81%

|  | Aromatic(5H) | benzyl$CH_2$(2H) | $CH_2$(4H) | $CH_2$(4H) |
|---|---|---|---|---|
| $^1H$ $\delta$ values(ppm) | 7.63(s) | 4.58(s) | 3.54(m) | 2.31(m) |
| $^{13}C$ $\delta$ values(ppm) | 130.99, 130.67<br>130.29, 128.88 | 46.27 | 28.83 | 17.44 |

In some preparations ether was used instead of alcohol. This is useful to avoid disproportionation, as the salt, once formed, is precipitated thus minimising the reverse reaction. This method was used in the alkylation of thietanes (see later section). Trichloromethane was found to be superior to alcohol or ether for the preparation of all the xylylene salts.



p-Xylylene dibromide (3.88 g) was dissolved in trichloromethane (30 $cm^3$) and dimethyl sulphide (1.90 g) was added dropwise. After 30 minutes a fine solid precipitated out. The mixture was left for a day to ensure completion of reaction and went almost solid. More trichloromethane (30 $cm^3$) was added to assist filtration and the solid was filtered off using a Schlenk filter, washed with trichloromethane, and dried under nitrogen.

Yield 4.9 g (84%), mp. 99-101°C.

The ortho- and meta-isomers were prepared similarly.

The xylylenebis(1-thioniacyclopentane bromide) salts were also synthesised by the same method, using thiacyclopentane in place of dimethyl sulphide. This reaction was significantly faster than the reaction with dimethyl sulphide.

Attempts to prepare the related bromomethylsulphonium salts were unsuccessful even when a three fold excess of the xylylene dihalide was used. In all cases a mixture of the mono and bis-sulphonium salts was obtained, from which the mono-sulphonium salt could not be purified.

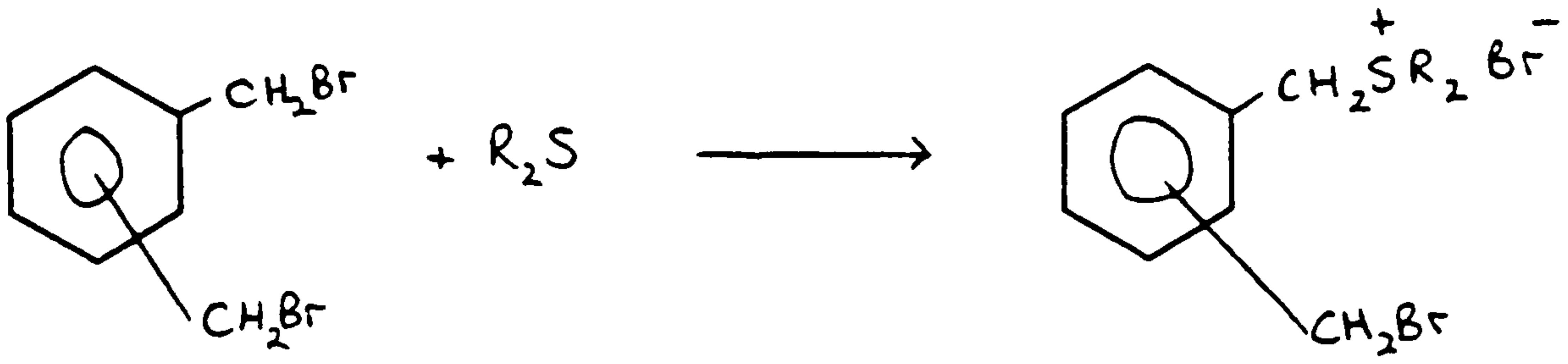


TABLE 2 Substituted Sulphonium Salts $XC_6H_4CH_2\overset{+}{S}R_2Y^-$

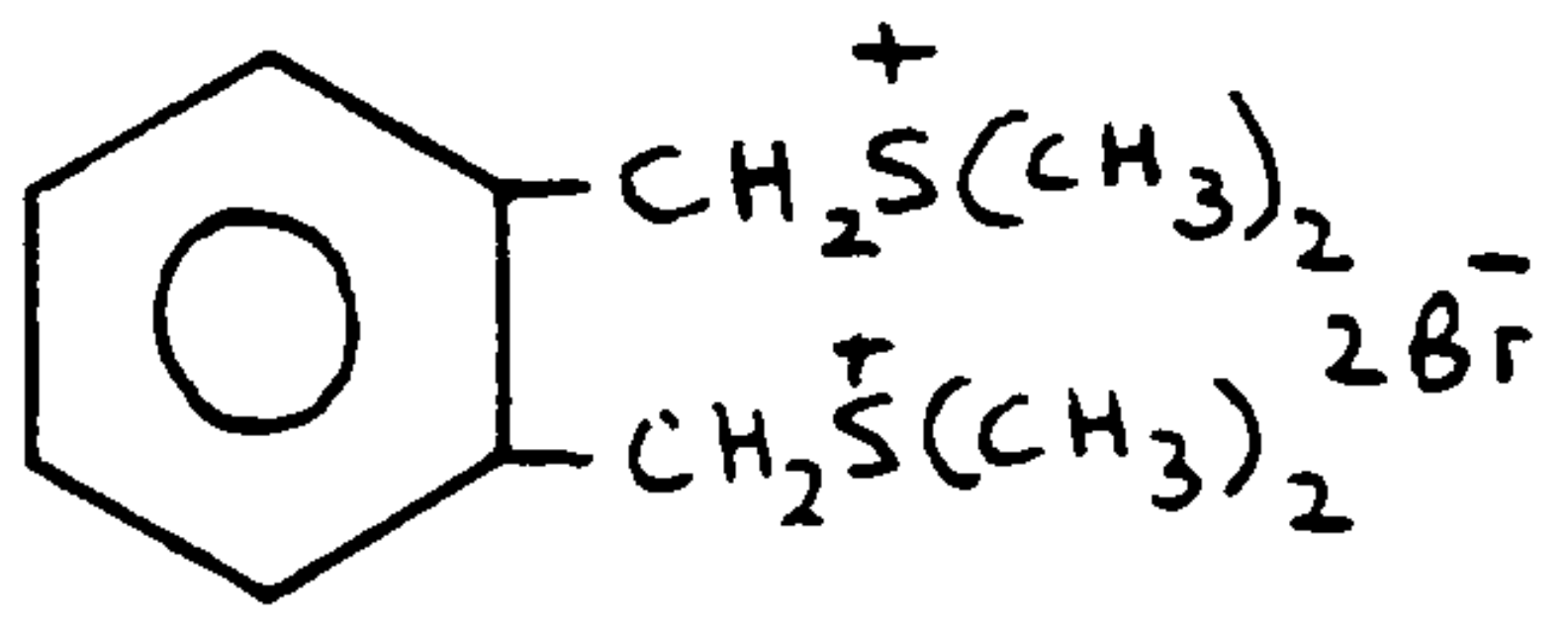
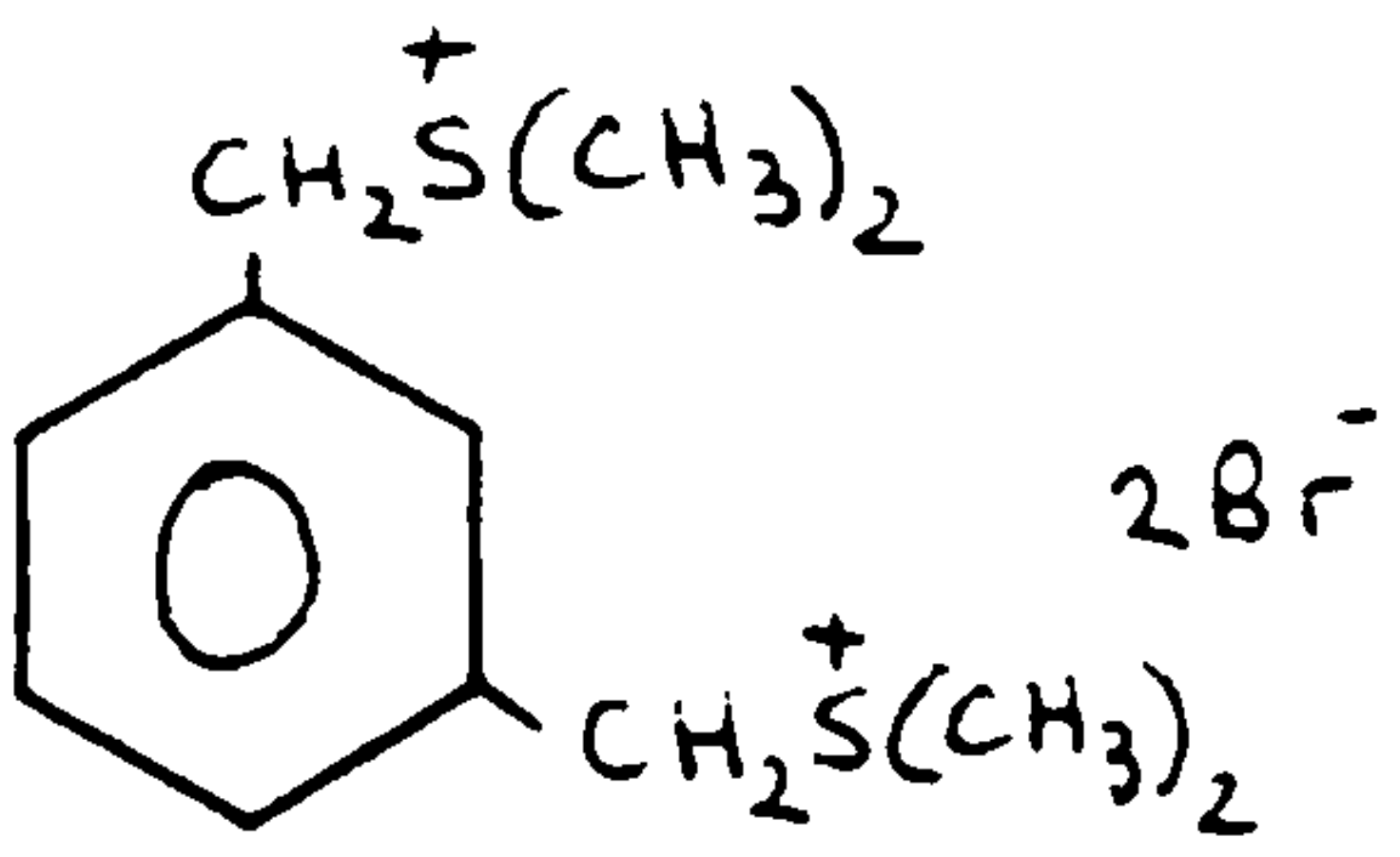
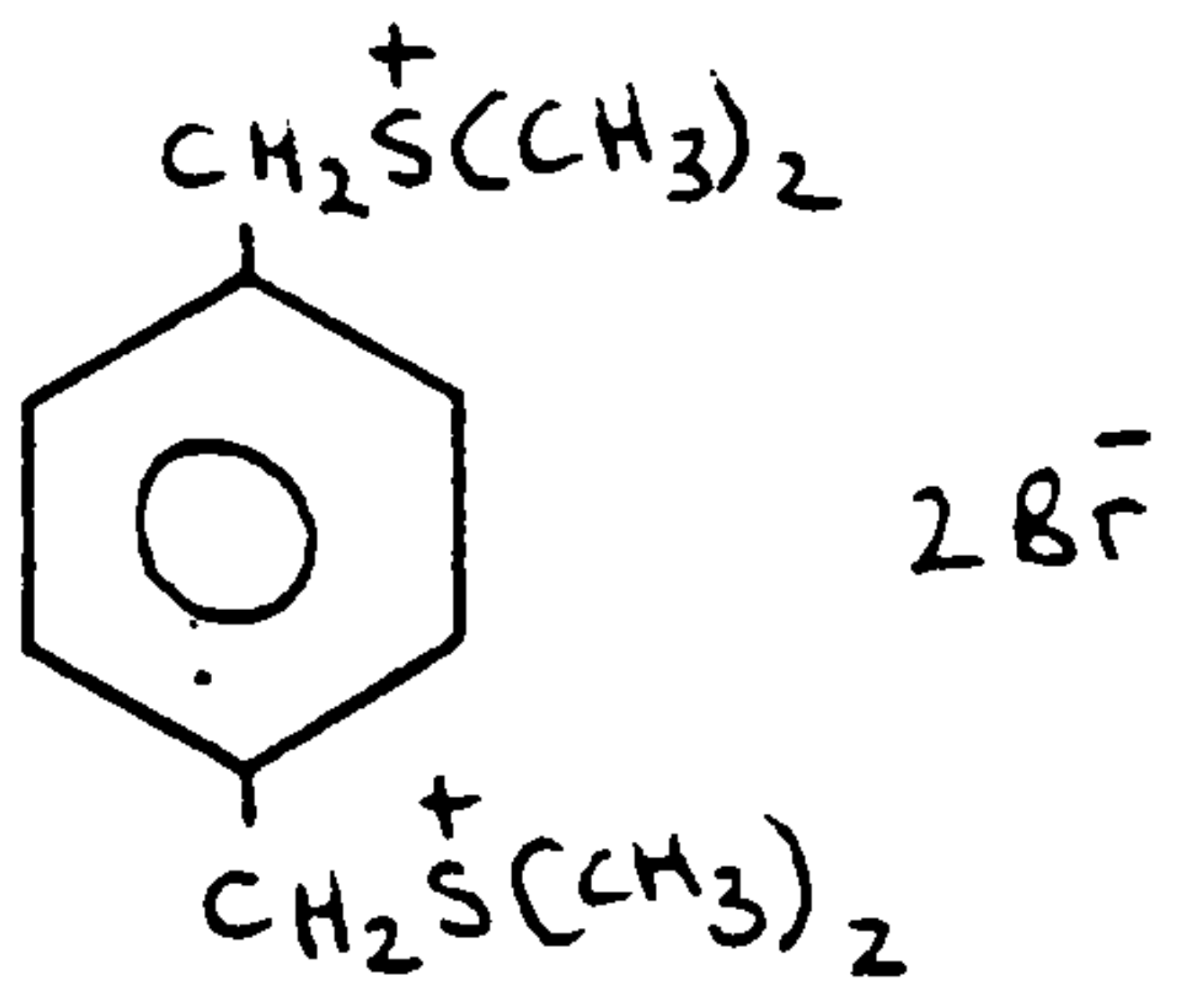
| X | R | $Y^-$ | mp(°C) | lit mp(°C) |
|---|---|---|---|---|
| H[a,b] | $CH_3$ | Br | 99 | 99-95.5 |
| 2-$CH_3$[a,b] | $CH_3$ | Br | 124-126 | |
| 3-$CH_3$ | $CH_3$ | Br | 142 | |
| 4-$CH_3$[a,b] | $CH_3$ | Br | 116 | 109-110<br>121-122 |
| 4-Br[b,c] | $CH_3$ | Br | 136 | 135-136 |
| 4-Cl[b,c] | $CH_3$ | Cl | 119-120 | 119-120 |
| 4-F | $CH_3$ | Br | 107 | |
| 4-$NO_2$ | $CH_3$ | Br | 113 | 112-113 |
| H | $(CH_2)_4$ | Br | 107 | |
| 4-$CH_3$ | $(CH_2)_4$ | Br | 127 | |
| 4-Br | $(CH_2)_4$ | Br | 139-140 | |
| 4-Cl | $(CH_2)_4$ | Cl | 131 | |
| H | $(CH_2)_5$ | Br | 151-152 | |
| H | $(C_6H_5CH_2)$ | $HSO_4$ | 171 | |
| 2-$CH_2\overset{+}{S}(CH_3)_2$ | $CH_3$ | 2Br | 163 | |
| 3-$CH_2\overset{+}{S}(CH_3)_2$ | $CH_3$ | 2Br | 131-132 | |
| 4-$CH_2\overset{+}{S}(CH_3)_2$ | $CH_3$ | 2Br | 99-101 | |

references:
a P. Mamalis, J. Chem. Soc., 4747, (1960).
b G. Walcott, MSc Thesis, (London University) 1965)
c F. Fichter and P. Sjostedt, Chem. Ber., 43, 3425, (1910), O. Haas and G. Dougherty, J. Amer. Chem. Soc., 65, 1238, (1943).

## Characteristics of bis-sulphonium salts

Both nmr spectra and elemental analysis were consistent with the proposed structures.

$^1H$ Chemical shifts ($\delta$) ppm.

| Salt | | Aromatic | CH$_2$ | CH$_3$ |
|---|---|---|---|---|
| 1. |  | 7.86(s) | 5.06 | 3.09 |
| 2. |  | 7.99(s) | 4.83 | 2.96 |
| 3. |  | 7.88(s) | 4.85 | 2.97 |

Elemental Analysis

| Salt | Found |  | Calculated |  |
|---|---|---|---|---|
|  | %C | %H | %C | %H |
| 1 | 37.14 | 5.13 | 37.11 | 5.16 |
| 2 | 37.14 | 5.13 | 37.11 | 5.16 |
| 3 | 36.91 | 5.17 | 37.11 | 5.16 |

## Preparation of Tribenzylsulphonium Hydrogensulphate

Preparation of the tribenzylsulphonium salt by the 'normal' method proved unsuccessful. This point was also noted by Dougherty and Lee(20) but our attempts to synthesise the tribenzyl salt using their method, involving aluminium chloride as a catalyst, also proved unsuccessful. The salt was finally made by using Haas and Dougherty's method(21).

Dibenzyl sulphide (3 g) was added to concentrated sulphuric acid (6 g). Little solution occurred at room temperature, but on warming to 70-80°C and shaking vigorously, solution of the sulphide was complete in ten minutes. The dissolution was accompanied by the evolution of sulphur dioxide. After the reaction mixture had cooled, it was poured into water (25 $cm^3$) causing precipitation of a white crystalline solid, which was washed with water. The product was crystallised from alcohol. Yield 2.3 g, mp. 173°C.(21)

The $^1H$ nmr spectrum was consistent with the structure; $\delta$ values (ppm): 4.89 (s), 7.33 (s).

## Test for Sulphonium Salts(22)

All the sulphonium salts, including the xylylene-bis-salts gave a blue colouration/precipitate in aqueous solution when treated with the cobaltous ammonium thiocyanate complex. This reaction was used as a qualitative test for the sulphonium ion. To 0.5 $cm^3$ of slightly acidic cobalt nitrate solution was added two drops of 10% aqueous ammonium thiocyanate; followed by a few drops of trichloromethane and the mixture shaken vigorously. In the presence of a sulphonium ion the trichloromethane layer became blue and in some cases a blue precipitate was formed.

## Preparation of sulphides

### Preparation of benzyl n-butyl sulphide

$$C_6H_5CH_2SH \; + \; CH_3(CH_2)_3Br \xrightarrow{NaOH} C_6H_5CH_2\text{-}S(CH_2)_3CH_3$$

Sodium hydroxide (2.0 g) was dissolved in freshly boiled distilled water (10 $cm^3$) (to avoid oxidation of the thiol to the sulphide). To this benzyl thiol (6.20 g) was added which dissolved readily, yielding a pale yellow solution. The addition of ethanol (20 $cm^3$) resulted in the mixture becoming turbid, which increased with the dropwise addition of n-butyl bromide (7.0 g) and after two minutes an oily layer formed at the bottom of the flask. The mixture was refluxed for two hours, then cooled in an ice bath and poured into water (200 $cm^3$). The mixture was extracted with ether (3 x 30 $cm^3$) and the combined ethereal extracts were washed successively with 2 M sodium hydroxide (20 $cm^3$) and water (20 $cm^3$) to remove unreacted thiol. After drying over calcium chloride for one hour, the ether was removed by distillation and the residue vacuum distilled.

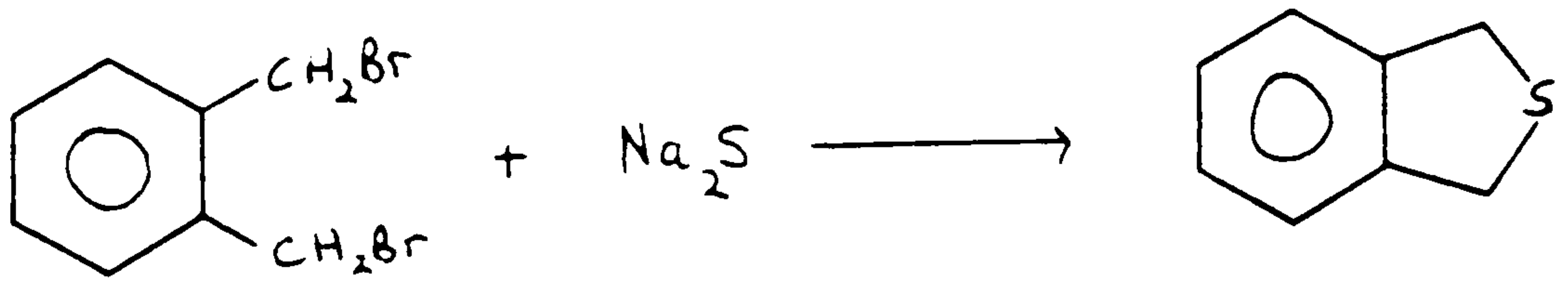
Yield 7.9 g (88%), bp. 130° (18 mm Hg)

The $^1H$ nmr spectrum was consistent with the structure.

$\delta$ values (ppm): 0.84(t), 2.0(m), 2.29(t), 3.65(s), 7.7-7.5(um)

### Preparation of 2,5-dihydrobenzo-[c]thiophene

A modification of Oliver and Ongley's method was used for the preparation of this cyclic sulphide:(23)



An alcoholic solution (100 $cm^3$) of o-xylylene dibromide (12.0 g) and an excess of dried sodium sulphide ($Na_2S.3H_2O$)* (6.50 g) was refluxed for one-and-half hours. The mixture was allowed to cool, the alcohol removed in vacuo at 50°C and the black residue was steam distilled to give the pale yellow liquid sulphide.

Yield 3.0 g (48%).

The $^1H$ and $^{13}C$ nmr spectra were consistent with this structure.

$^1H$ $\delta$ values (ppm): 4.14(s), 7.11(s).

$^{13}C$ $\delta$ values (ppm): 140.20, 126.49, 124.49, 37.87.

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*Sodium sulphide nonahydrate was dried over phosphorus pentoxide in a desiccator. The trihydrate formula is approximate.

## Preparation of thietanes

### Preparation of 3,3-dimethylthietane

The approach adopted was the conversion of the commercially available 2,2-dimethyl-1,3-propanediol (DPD) to the dibromide and cyclisation of the latter to the sulphide.

### Preparation of 1,3-dibromo-2,2-dimethylpropane

The method of Perkin and Simonsen(24) involved the conversion of the DPD to the diacetate by refluxing with acetic anhydride for three hours: 5.4 g of DPD gave 8.5 g of the acetate. Attempted conversion of this to the dibromide with hydrogen bromide was unsuccessful; treatment with hydrogen bromide gave only the monobromide. The following method was found to be successful.

The diol (20 g) was placed in a three-necked flask fitted with a reflux condenser to which was fitted a guard tube filled with glass wool to minimise the loss of hydrogen bromide. Freshly distilled phosphorus tribomide (45 g) was added dropwise over a period of 20 minutes: a vigorous reaction set in immediately and was controlled by cooling in an ice bath. The pale yellow mixture was heated to 150°C. During the first ten minutes, copious fumes of hydrogen bromide were given off and more phosphorus tribromide was added to counteract the loss. After 20 minutes the mixture became deep orange and as the reaction proceeded a red suspension formed, causing bumping. After cooling, the reaction mixture was poured into water and extracted with ether (3 x 30 $cm^3$). The combined ether extract was dried over anhydrous calcium chloride. The ether was removed by distillation and the residue vacuum distilled and the fraction between 85-90°C (30 mm Hg) collected.

Yield 26 g (59%), bp. 90°(24).

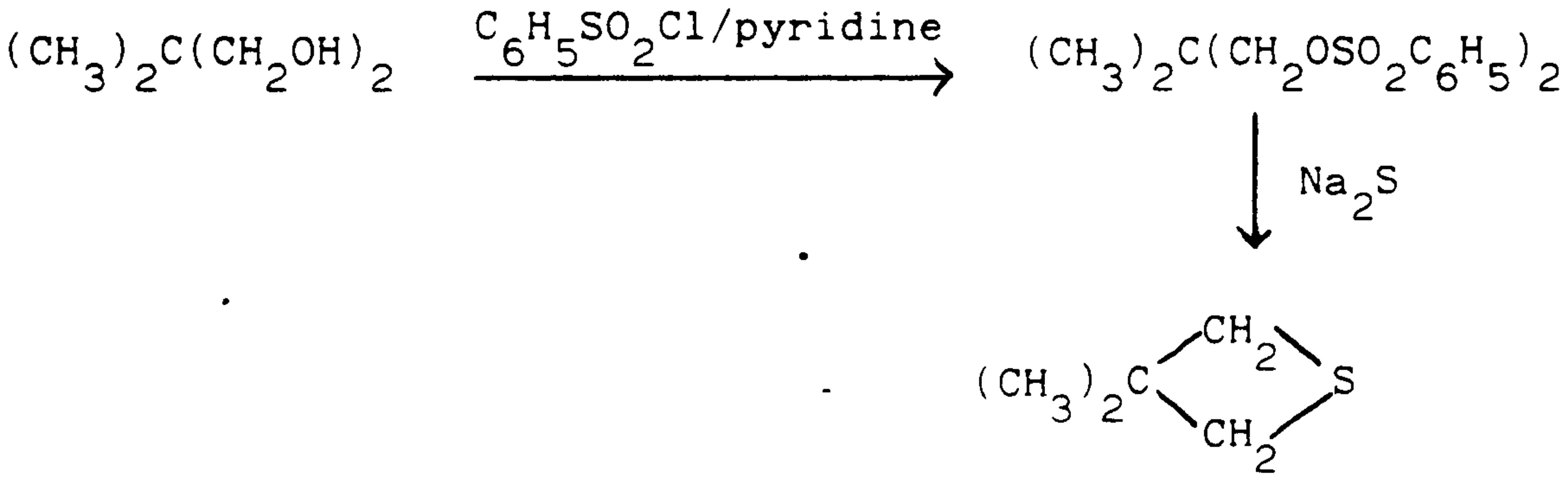
The infra-red spectrum showed a C-Br band (625 $cm^{-1}$) and the absence of an OH group absorption.

$^1H$ nmr $\delta$ values (ppm): 1.17(s), 3.41(s).

## Attempted conversion of the dibromide to the cyclic sulphide

The method of Backer and Keuning( 25 )to convert the dibromide to the cyclic sulphide involved refluxing the dibromide with sodium sulphide in alcohol for 12 hours, then pouring the mixture into saturated brine, and extracting the sulphide with ether. However, we repeated this procedure three times without success. The $^1H$ nmr and infra-red spectra showed the final product to be the dibromide.

The 3,3-dimethylthietane was finally obtained using Buza's method( 26 ). The diol is first converted to the dibenzenesulphonate and this is reacted with sodium sulphide nonahydrate.



## Preparation of 1,3-bis(benzenesulphonyloxy)-2,2-dimethylpropane

Benzenesulphonyl chloride (38.94 g) was added to a stirred, cold (ice-bath) solution of the diol (10.4 g) in dry pyridine (160 $cm^3$) at such a rate that the temperature remained below 15°C. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured into distilled water (1 litre) with vigorous stirring. The white precipitate was filtered off and successively washed with water, 2 M hydrochloric acid (2 x 25 $cm^3$), water and then air dried to yield the crude dibenzenesulphonate (36.9 g) which was recrystallised from aqueous ethanol.

Yield 34.5 g (90%), mp. 53-55°.

$^1H$ nmr $\delta$ values (ppm): $CH_3$; 0.92(s), $CH_2$; 3.85(s), $C_6H_5$; 7.96(s).

## The preparation of 3,3-dimethylthietane

To 100 $cm^3$ of stirred dimethylsulphoxide (DMSO) at an initial temperature of 60°C was added over a period of one hour, a thoroughly blended mixture of the dibenzenesulphonate of DPD (23.6 g) and finely divided dried sodium sulphide (approx. $Na_2S.2H_2O$) (8 g). The temperature was raised slowly during the addition, so that at completion the temperature was 90°C. The mixture was stirred at this temperature for two hours then poured into water (50 $cm^3$). The products were extracted with n-pentane (3 x 30 $cm^3$); the combined n-pentane extracts were washed with water (50 $cm^3$) and dried over anhydrous magnesium sulphate. Distillation of the mixture using a 15 cm Vigreux column, gave three fractions.

Fraction (i) : was shown to be n-pentane

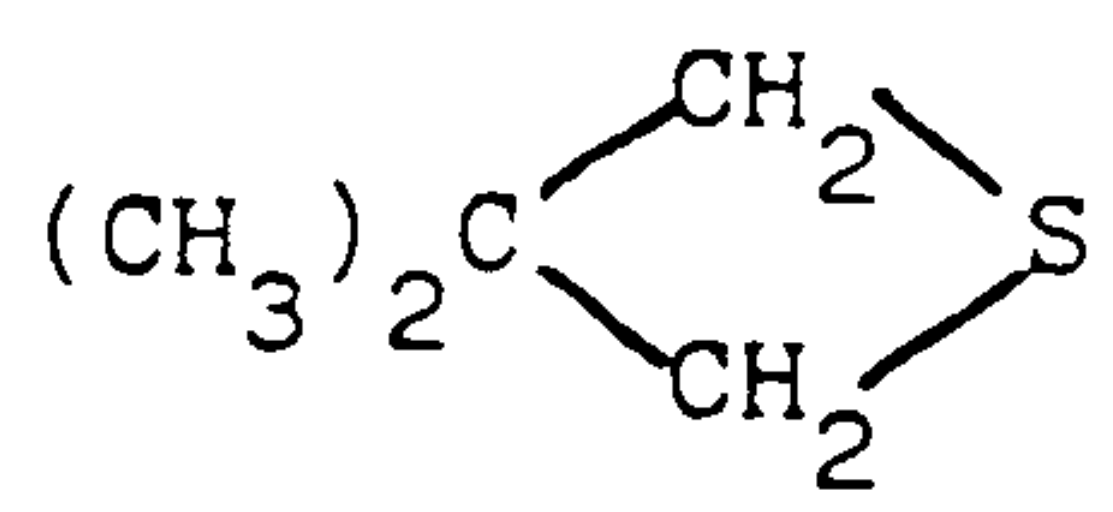
Fraction (ii) : bp. 82°C was shown by nmr spectrum to be a mixture of the thietane and water.

Fraction (iii) : bp. 119°C was the substituted thietane.

Further evidence for fraction (iii) was obtained from its infra-red spectrum which showed a band at 1175 $cm^{-1}$. This, according to Buza, is a characteristic of all thietane systems, (see spectrum p 139).

Yield 1.38 g (22%), bp.119°C.

The $^1H$ and $^{13}C$ nmr spectra were both consistent with the structure.



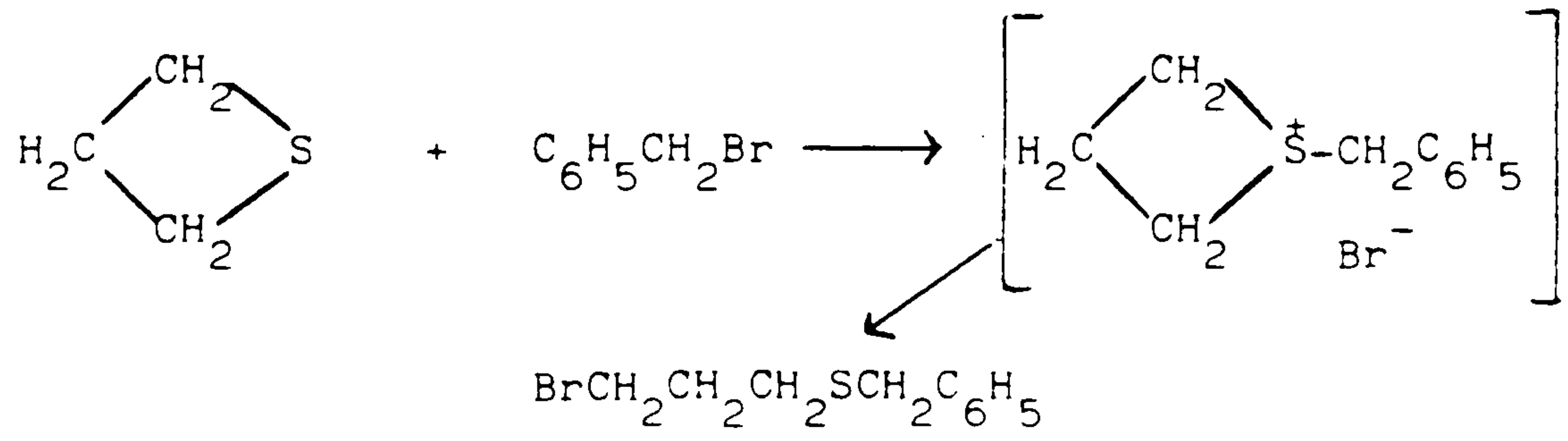
$^1H$ $\delta$ values (ppm): ($CH_3$): 1.25(s), $CH_2$: 2.93(s)

$^{13}C$ $\delta$ values (ppm): 29.36, 38.19, 41.55.

## Reactions of thietanes with alkylating agents.

### Benzyl bromide and thietane

Equimolar quantities of benzyl bromide (0.86 g) and thietane (0.37 g) were mixed at room temperature. There was no apparent sign of reaction. The solution was then transfered to an nmr tube and the spectrum recorded. No shift of the benzylmethylene group signal expected for salt formation was detected even after one hour; but on allowing the mixture to stand overnight the shift of the methylene protons had changed from 4.6 to 3.57. The latter value is too low for a benzyl sulphonium group but consistent with an open chain benzyl sulphide.



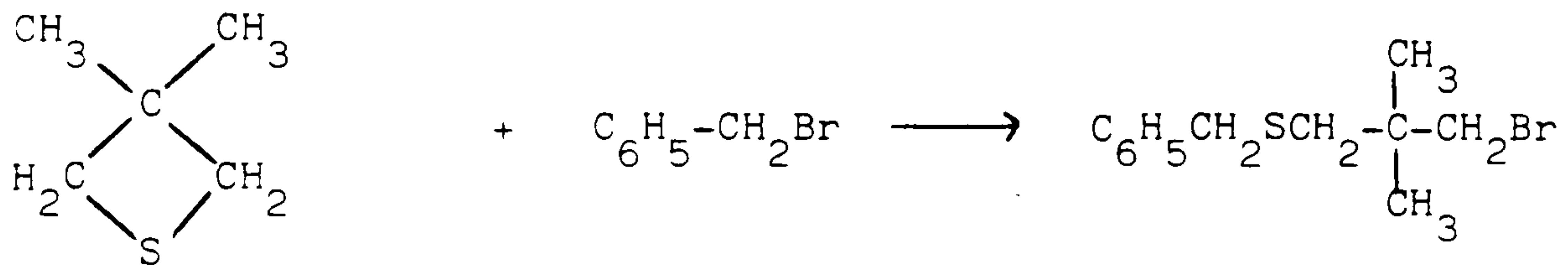
None of the open chain sulphonium salt, $Br(CH_2)_3\overset{+}{S}(CH_2C_6H_5)_2Br^-$ was detected even after long standing with excess benzyl bromide (spectra p.136-8) We found this surprising and therefore tested the reaction between benzyl n-butyl sulphide (1.79 g) and benzyl bromide (1.71 g) at room temperatures. Even after 28 days there was no evidence of any reaction, suggesting that the alkyl group was having a significant steric effect, because benzyl bromide reacts readily with benzyl methyl sulphide to give the sulphonium salt.

### Benzyl bromide, thietane and silver tetrafluoroborate

Equimolar quantities of benzyl bromide (0.57 g) and thietane (0.25 g) were mixed at room temperature and the nmr spectrum recorded. On addition of silver tetrafluoroborate the mixture instantly became hot with slight colouration. After a half mole equivalent of the silver salt (0.65 g) had been added, the mixture was cooled and dichloromethane added to dissolve non salt like material and any excess of silver tetrafluoroborate. The mixture was centrifuged and the solid residue isolated. The solid was treated with deuterium oxide to dissolve any sulphonium salts. No signals were detected by $^1H$ nmr spectroscopy in the deuterium oxide extract.

Benzyl bromide and 3,3-dimethylthietane

Equimolar quantities of benzyl bromide (0.57 g) and 3,3-dimethylthietane (0.34 g) were mixed at room temperature. There was no apparent reaction and the solution was transferred to an nmr tube and the $^1H$ nmr spectrum recorded; no shift in the benzylmethylene signal due to salt formation was detected even after one hour; but on allowing the mixture to stand overnight a reaction had occurred. A down-field shift of approximately 1 ppm of the benzyl group predicted for a sulphonium salt was not detected, but the spectrum was consistent with the open chain sulphide shown below (see p 142). This product could have only arisen from the cyclic sulphonium salt intermediate.

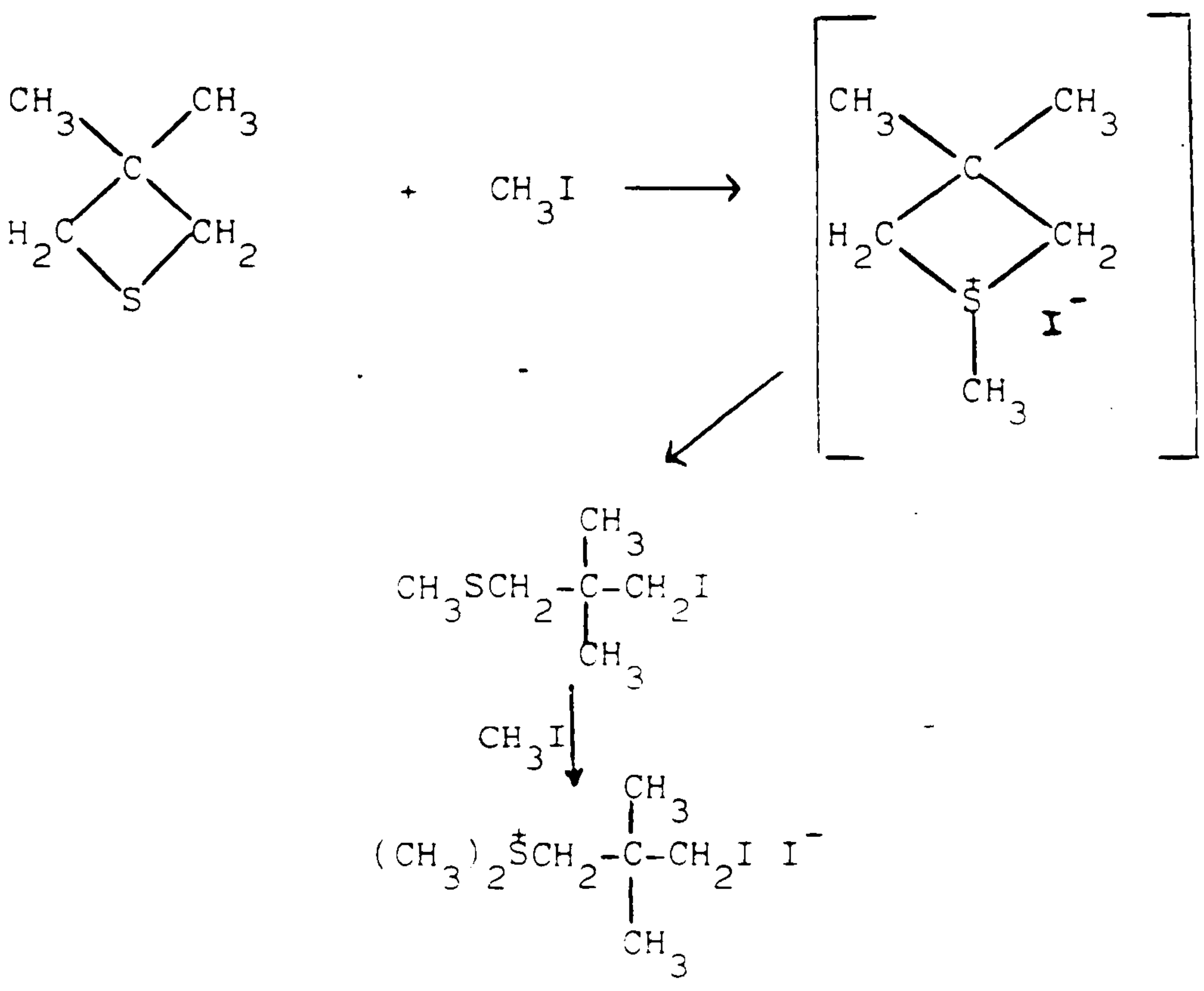


$$C_6H_5CH_2SCH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}CH_2Br$$

None of the expected open chain sulphonium salt, $(C_6H_5CH_2)_2\overset{+}{S}CH_2C(CH_3)_2CH_2Br\ Br^-$ was detected even after long standing with excess benzyl bromide.

### Methyl iodide and 3,3-dimethylthietane

Methyl iodide (0.5 g) was added to 3,3-dimethylthietane (0.34 g). There was no apparent reaction. The mixture was transferred to an nmr tube and the spectrum recorded: no shift of signals due to salt formation was detected, but on allowing the mixture to stand for 8 hours, signals due to the presence of a sulphonium salt were observed. Analysis of the spectrum showed it to be the open chain sulphonium salt. The following scheme is suggested.

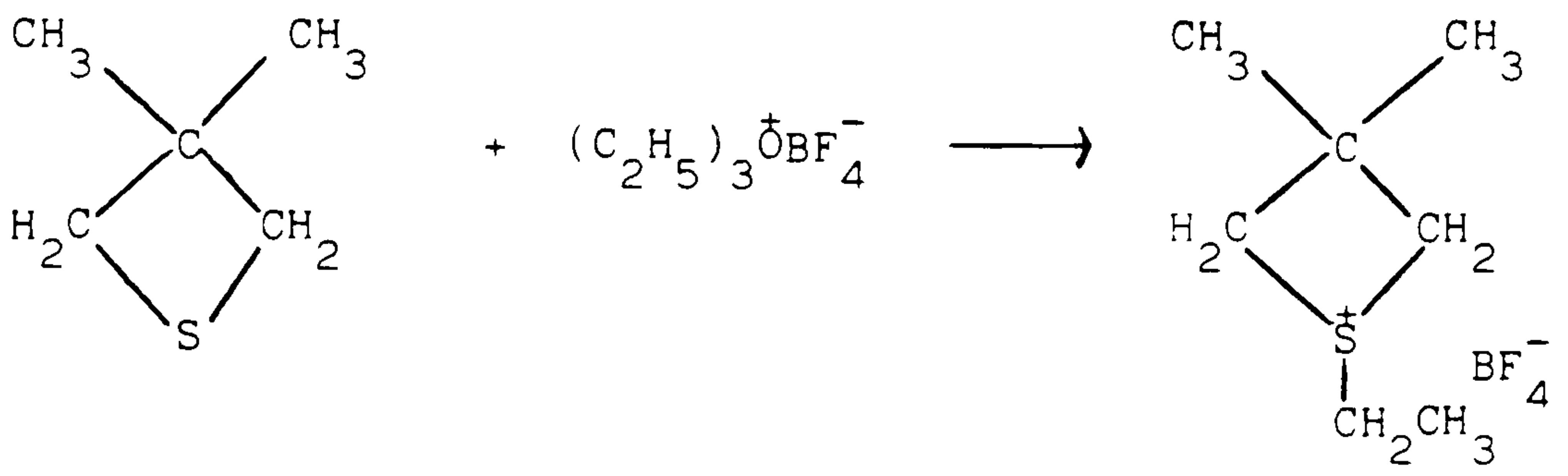


$^1$H nmr $\delta$ values (ppm) : 1.31(s),6H; 3.04(s),6H; 3.42(s),2H; 3.56(s),2H.

### Dimethyl sulphate and 3,3-dimethylthietane

The reaction between 3,3-dimethylthietane and dimethyl sulphate is vigorous and results in the formation of polymeric product.

## Preparation of 1-ethyl-3,3-dimethylthioniacyclobutane tetrafluoroborate



3,3-Dimethylthietane (0.5 g) was slowly added, with agitation, to a solution of triethyloxonium tetrafluoroborate (1.06 g) in dichloromethane at 0°C. After addition, the mixture was left for five minutes. The salt was precipitated by adding sodium dried ether and purified by successive dissolution in methanol and precipitation with ether.

Yield 0.7 g, (65%); mp. 92°(27).

The $^{1}H$ nmr spectrum was the same as that reported in the literature.(27)

$^{1}H$ $\delta$ values (ppm): 1.5(m), 3.8(m).

## Preparation of 1,3,3-trimethylthioniacyclobutane fluorosulphonate

Methyl fluorosulphonate (0.42 g) was added dropwise to a solution of 3,3-dimethylthietane (0.34 g) in dichloromethane at 0°C. After standing for five minutes excess ether was added to precipitate the salt which was purified by successive dissolution in methanol and reprecipitation with ether.

Yield 0.52 g (73%); mp. 95°C.

$^{1}H$ nmr $\delta$ values (ppm): 1.41(s), 3.21(s), 3.73(s).

This nmr spectrum is the same as that reported for the tetrafluoroborate salt(28).

## Preparation of ammonium salts

The following quaternary ammonium salts were prepared.

$$YC_6H_4CH_2\overset{+}{N}R_3X^-$$

| Y | R | X | mp ($^{o}$C) |
|---|---|---|---|
| H | $CH_3$ | Br | 242 |
| H | $C_2H_5$ | Br | 232 |
| H | $(CH_2)_5, CH_3$ | I | 131-132 |
| H | $(CH_2)_5, C_6H_5CH_2$ | Br | 128 |
| H | $(CH_2)_4, CH_3$ | I | 141 |
| H | $(CH_2)_4, C_6H_5CH_2$ | Br | 135 |
| $2\text{-}\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br | 179-180 |
| $3\text{-}\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br | 200-202 |
| $4\text{-}\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br | 254 |
| $4\text{-}CH_2Br$ | $C_2H_5$ | Br | 172 |

Most of these salts were prepared by reaction of the corresponding benzyl halides with a tertiary amine.

$$C_6H_5CH_2Hal + NR_3 \longrightarrow C_6H_5CH_2\overset{+}{N}R_3Hal^-$$

An example of the general method is the preparation of benzyltrimethylammonium bromide:

To benzyl bromide (8.55 g), cooled in an ice bath, was added, over a period of five minutes, an ethanolic solution of trimethylamine (5.4 g). After 30 minutes excess anhydrous ether was added, causing precipitation of the salt which was purified by repeated dissolution in ethanol and reprecipitation with ether and finally filtered and dried under nitrogen, using a Schlenk filter.

Yield 11.8 g (92%), mp. 242°C(17).

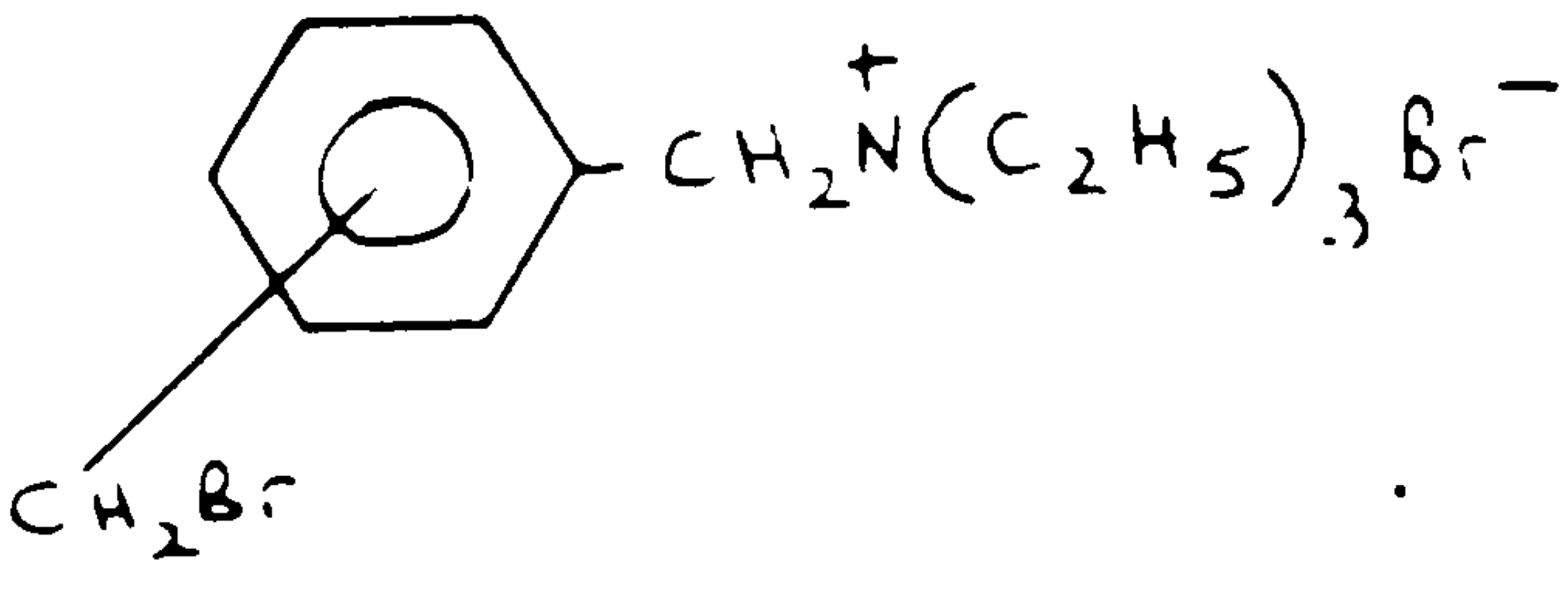
$^1$H nmr spectrum was consistent with the proposed structure.

δ values (ppm): 1.41(t), 3.28(q), 4.53(s), 7.71(s)

The following ammonium salts were prepared by the above method, using an excess of triethylamine and trichloromethane as solvent.

| xylylenebis(triethylammonium bromide) | | $^1$H nmr δ values (ppm) |
|---|---|---|
| o-bis-salt | mp 179-180°C | 1.37(t), 3.36(q), 4.67(s), 7.76(s) |
| m-bis-salt | mp 200-202°C | 1.45(t), 3.29(q), 4.54(s), 7.72(s) |
| p-bis-salt | mp 254°C | 1.44(t), 3.29(q), 4.52(s), 7.69(s) |

The syntheses of the bromomethylbenzyltriethylammonium salts was attempted.



To a stirred solution of p-xylylene dibromide (5.0 g) in trichloromethane (50 $cm^3$) was slowly added triethylamine (1.85 g). After addition the mixture was stirred for 20 minutes at room temperature, then excess sodium dried ether (50 $cm^3$) was added, causing precipitation of an amorphous white solid. This was purified by repeated dissolution in ethanol and reprecipitation with ether, and finally filtered and dried under nitrogen using a Schlenk filter.

Yield 6.2 g (93%), mp. 170-173°C$^{(29)}$

$^1H$ nmr $\delta$ values (ppm): 1.39(t), 3.23(q), 4.39(s), 4.64(s), 7.55(m).

However the preparation of the corresponding ortho- and meta-isomers gave mixtures of the mono-and bis-salts, from which the mono-salt could not be purified.

The cyclic quaternary ammonium salts were prepared by alkylating the corresponding tertiary amines which were prepared as follows:

Preparation of N-benzylpiperidine

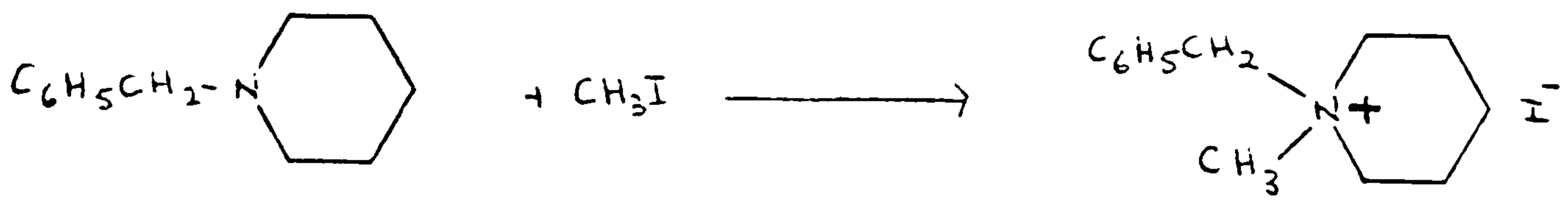
Piperidine (15.60 $cm^3$; 17.0 g) was dissolved in ethanol (50 $cm^3$) and to this benzyl chloride (11.80 $cm^3$; 13.0 g) was added in two equal portions. The mixture warmed up considerably and after ten minutes became dark yellow. When the reaction subsided the mixture was refluxed for 40 minutes, during which time it became an orange-red colour. The mixture was added to ice cold sodium hydroxide (300 $cm^3$). The resulting mixture was extracted with ether (2 x 30 $cm^3$) dried over powdered potassium hydroxide, filtered through glass wool and vacuum distilled.

Yield 16 g (68%), bp. 120°C (20 mm Hg).

The $^1H$ nmr spectrum was consistent with the structure.

$\delta$ values (ppm) 1.40(m), 2.23(m), 3.23(s), 6.98(m).

## Preparation of N-benzyl-N-methylpiperidinium iodide



N-Benzylpiperidine (3.5 g) was added to a solution of methyl iodide (2.8 g) in anhydrous ether (10 $cm^3$). A yellow solid precipitated and after one hour excess ether was added to the mixture. The pale yellow salt was filtered off and purified by dissolution in alcohol and reprecipitation with ether. The salt was dried in a vacuum desiccator at 40°C.

Yield 1.3 g (21%), mp. 131-132°C.

The $^1H$ nmr spectrum was consistent with the structure.
$\delta$ values (ppm): 1.78(m), 2.88(s), 3.28(m), 4.38(s), 7.35(s).

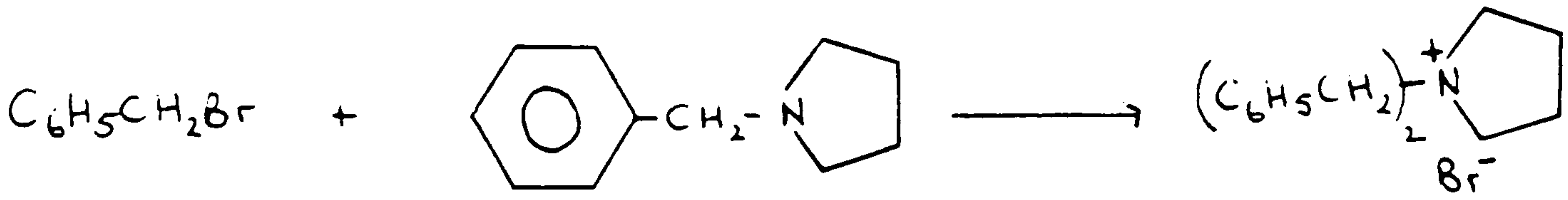
## Preparation of N,N-dibenzylpiperidinium bromide

This compound was made by the same method, using benzyl bromide in place of methyl iodide.

Yield 3.4 g (49%); mp. 128°C.

The $^1H$ nmr spectrum was consistent with the structure.
$\delta$ values (ppm): 1.53(um), 2.06(um), 3.29(m), 4.52(s), 7.52(s).

Preparation of N,N-dibenzylpyrrolidinium bromide



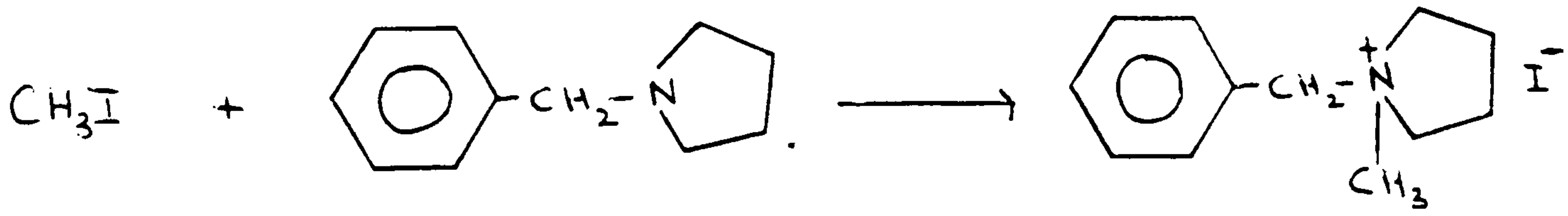
Adding benzyl bromide (2.42 g) to a solution of N-benzylpyrrolidine (2.40 g) in anhydrous ether (10 $cm^3$), immediately gave a milky solution with a suspension of fine particles. After one hour excess ether was added and the salt filtered off. The crude salt, which was very hygroscopic, was purified by dissolution in ethanol and precipitation with ether. The pure salt was non-hygroscopic.

Yield 1.2 g (25%), mp. 135°C.

The $^1$H nmr spectrum was consistent with the structure.

$\delta$ values (ppm): 2.09(um), 3.48(um), 4.52(s), 7.55(s).

Preparation of N-benzyl-N-methylpyrrolidinium iodide



This salt was prepared by the same procedure, using methyl iodide.

Yield 1.5 g (35%), mp. 141°C.

The $^1$H nmr spectrum was consistent with the structure.

$\delta$ values (ppm): 2.26(um), 2.96(s), 4.95(s), 7.59(s).

## Preparation of benzyl p-toluenesulphonate

Since the simple method of mixing together the alcohol and toluene-p-sulphonyl chloride in the presence of pyridine failed, the method described by Kochi(30) was used. This method allows the preparation of otherwise inaccessible tosylates of benzyl alcohol. Benzyl alcohol (5 cm$^3$) was dissolved in anhydrous ether (50 cm$^3$) and sodium hydride (2.21 g) added. The sodium hydride was crushed in situ to promote reaction. The mixture was refluxed for 12 hours under nitrogen. The mixture was cooled to -20°C using a dry ice bath, and toluene-p-sulphonyl chloride (9.75 g) in ether (50 cm$^3$) was added dropwise over a period of half-an-hour. The mixture was stirred for two hours at -10°C and for an additional hour at room temperature. The resulting suspension was filtered to afford a clear ethereal solution which after cooling for 30 minutes in the dry ice bath, yielded an amorphous solid. This was quickly filtered and recrystallised from 40-60°C petroleum ether giving needle shaped crystals.

Yield 2.55 g (20%), mp. 58°C(30).

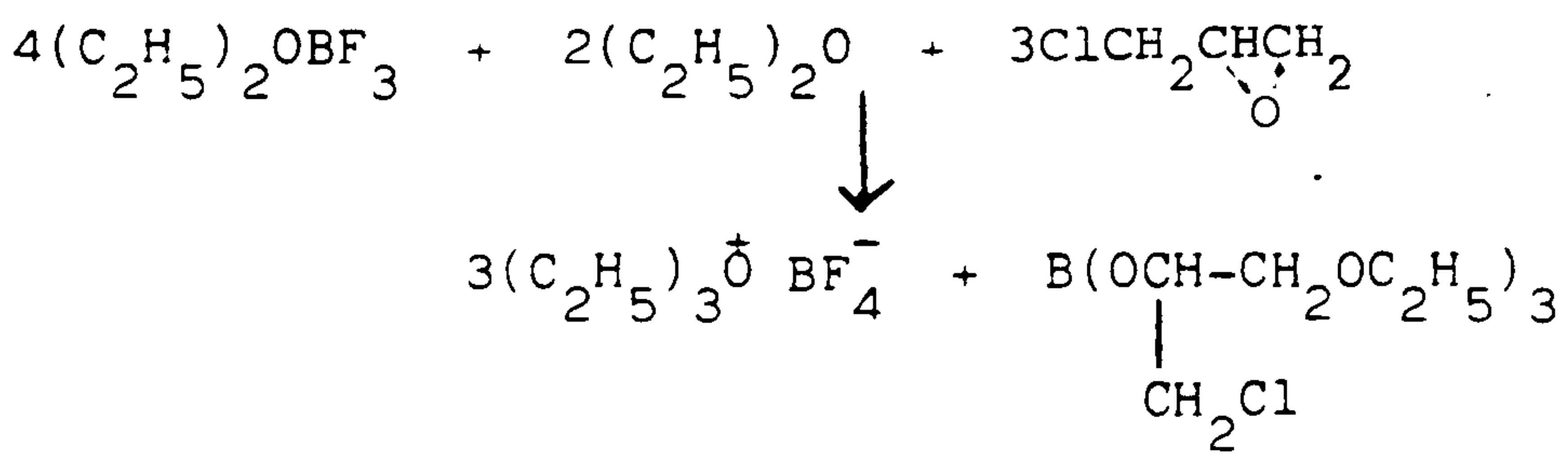
## Preparation of triethyloxonium tetrafluoroborate

The method described in Organic Syntheses(31) was used. A three-necked flask, a dropping funnel and a condenser fitted with a calcium chloride drying tube were dried in an oven at 100°C, assembled while hot and cooled in a stream of nitrogen. The flask was charged with dry ether (25 cm$^3$) and freshly distilled boron trifluoride etherate (12.5 g). Epichlorohydrin (6 cm$^3$) was added dropwise to the solution at a rate to maintain vigorous boiling (20 minutes). The mixture was refluxed for an additional hour and allowed to stand at room temperature overnight. The solid was filtered, washed with dry ether (3 x 25 cm$^3$) and dried under nitrogen using a Schlenk filter.

Yield 17 g, mp. 92°C (lit m.p 91-92°C)(31)

$^1$H nmr spectrum was consistent with the structure.

δ values (ppm): 1.59(t), 4.73(q), : J = 7Hz



$$4(C_2H_5)_2OBF_3 + 2(C_2H_5)_2O + 3ClCH_2CHCH_2O \longrightarrow 3(C_2H_5)_3\overset{+}{O}\,BF_4^- + B(OCH(CH_2Cl)\text{-}CH_2OC_2H_5)_3$$

<u>Preparation of dibenzylmercury compounds</u>

Symmetrical dibenzylmercury compounds were prepared in order to characterise mercury products formed during electrolyses of the sulphonium salts.

These compounds were prepared by a two-stage synthesis involving Grignard reagents(32).

(a) $RMgX + HgCl_2 \longrightarrow RHgCl + MgXCl$

(b) $RMgX + RHgCl \longrightarrow R_2Hg + MgXCl$

$R = C_6H_5CH_2$, $p\text{-}BrC_6H_4CH_2$, $p\text{-}ClC_6H_4CH_2$, $p\text{-}CH_3C_6H_4CH_2$

(a) <u>Preparation of benzylmercuric chloride</u>(33)

A solution of benzylmagnesium chloride was prepared in the normal manner from benzyl chloride (20 g) and a slight excess of magnesium (4.0 g) in anhydrous ether (140 $cm^3$). The reaction mixture was filtered through glass wool and the pale green solution was stirred mechanically and refluxed on a water bath. Finely powdered mercuric chloride (48.7 g) was added in about 2 g portions over a period of 40 minutes. Refluxing and stirring was continued for a further two hours. As the reaction proceeded a white solid separated from the reaction mixture and the green colour faded. After reflux the reaction mixture was allowed to stand overnight. A colour test with pp'-tetramethyldiamino-benzophenone was negative (no greenish-blue colour), showing that all the Grignard reagent had been consumed. The mixture was then decomposed with ice and 2M sulphuric acid. The crude product, a white solid, was filtered off. This was washed with dilute sulphuric acid (20 $cm^3$), hot water, ethanol (30 $cm^3$) and finally with ether (50 $cm^3$). Crystallisation from ethanol afforded colourless plates of benzylmercuric chloride.

Yield 23 g, mp. 105°C (lit 104°C)(34).

The $^1H$ nmr spectrum was consistent with the structure (see page 50).

## (b) Preparation of dibenzylmercury

An ethereal solution of benzylmagnesium chloride was prepared (see above). The filtered solution was cooled in an ice/salt bath and stirred mechanically with the addition of finely powdered benzylmercuric chloride in portions of about 2 g over a period of two hours. The mixture was cooled and stirred for a further 7 hours. As the reaction proceeded a white solid separated out. After the stirring period the reaction mixture was left in the dark overnight and was then decomposed with ice and 2M sulphuric acid. The crude product, an off white solid, was filtered, washed successively with sulphuric acid (dil. 20 $cm^3$), to remove inorganic salts, hot water (50 $cm^3$ at 80°C), alcohol (20 $cm^3$). The crude product was dried and recrystallised from an alcohol/chloroform mixture (1:1) and filtered hot to yield colourless needles of dibenzylmercury.

Yield 12 g, mp. 110°C (lit m.p 110°C)(34).

The $^1H$ nmr spectrum was consistent with the structure.

The substituted dibenzylmercury compounds were made by the same method.

| | Compound | |
|---|---|---|
| $(p\text{-}ClC_6H_4CH_2)_2Hg$ | 1. | mp 169°C (lit 169-170°C)(35) |
| $(p\text{-}BrC_6H_4CH_2)_2Hg$ | 2. | mp 160°C (lit 160°C)(35) |
| $(p\text{-}CH_3C_6H_4CH_2)_2Hg$ | 3. | mp 114°C (lit 113-115°C)(35) |
| $(C_6H_5CH_2)_2Hg$ | 4. | mp 110°C (lit 110°C)(35) |

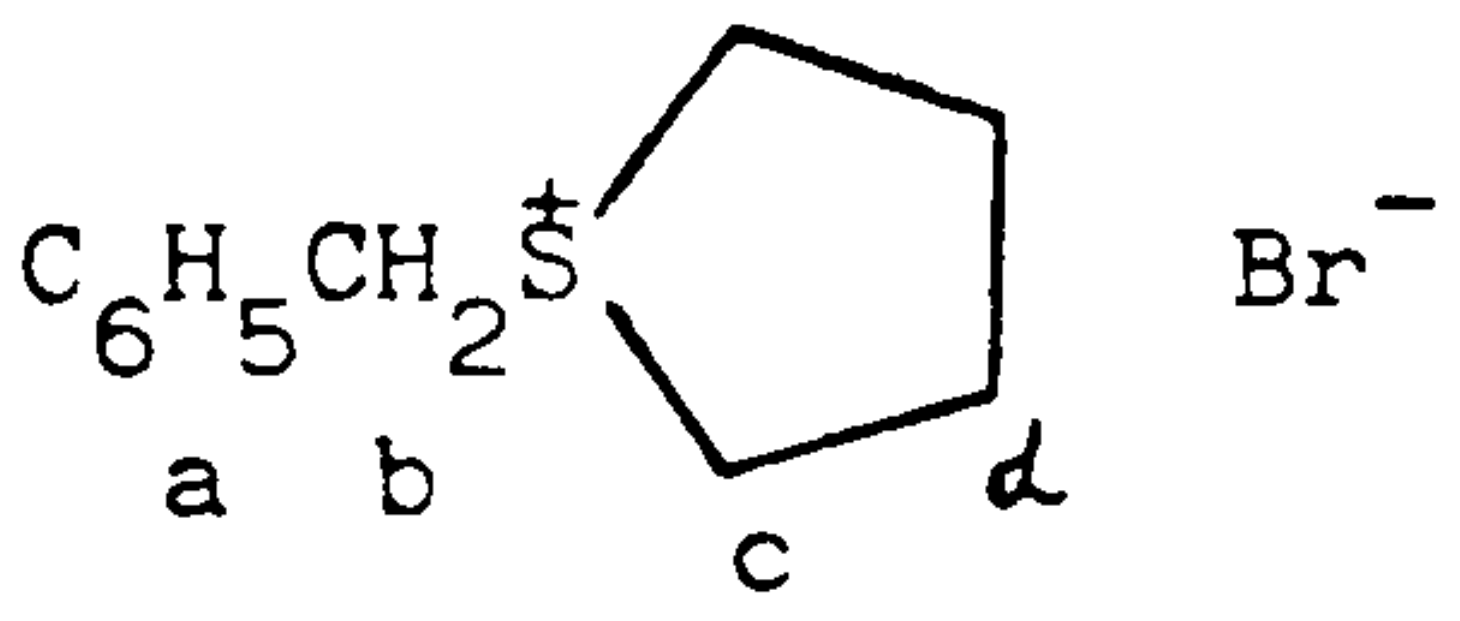
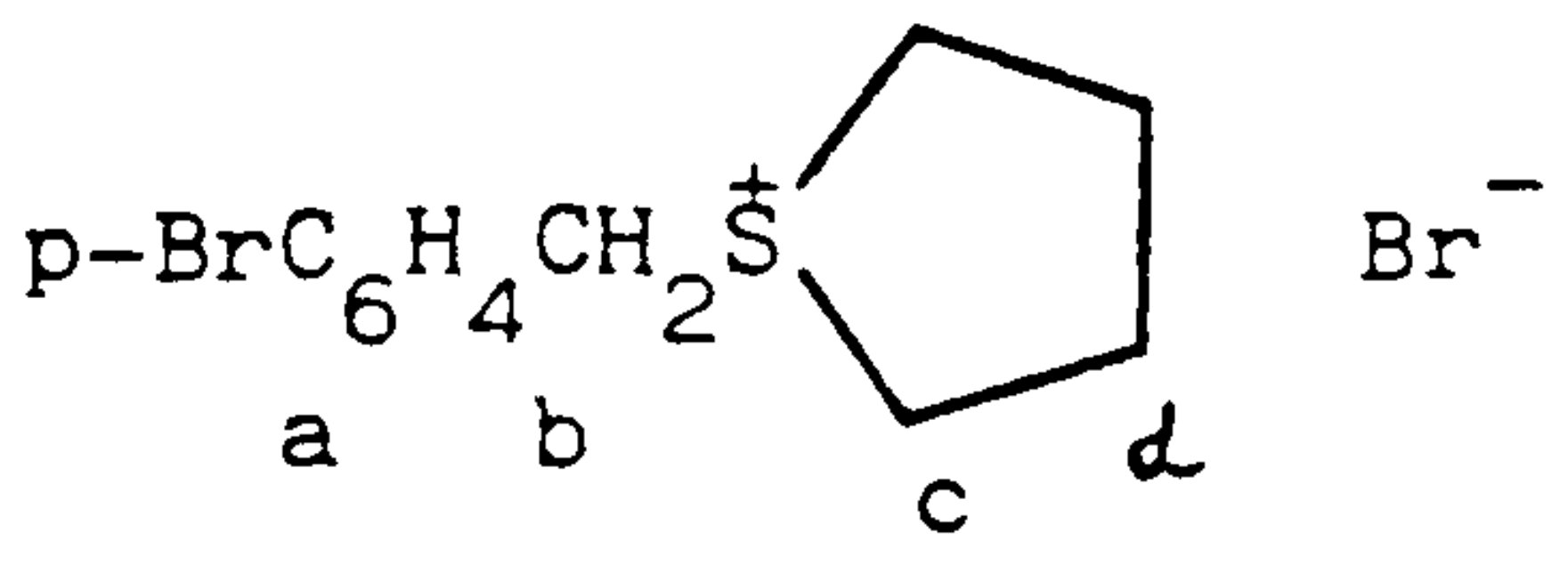
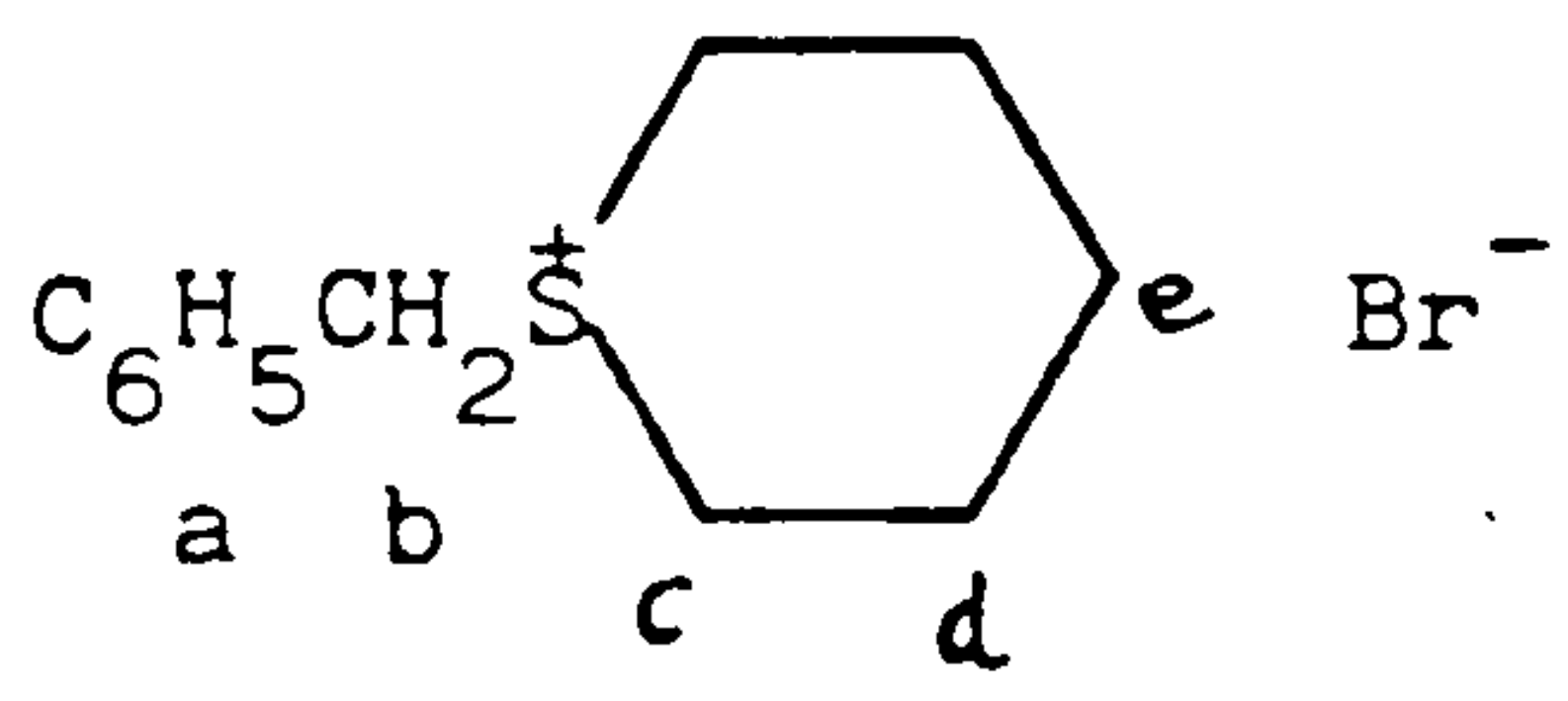
Elemental analysis data

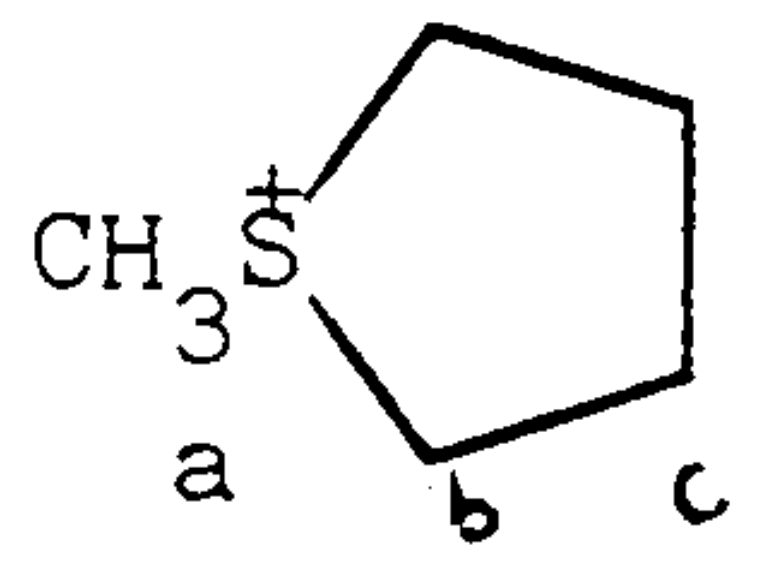
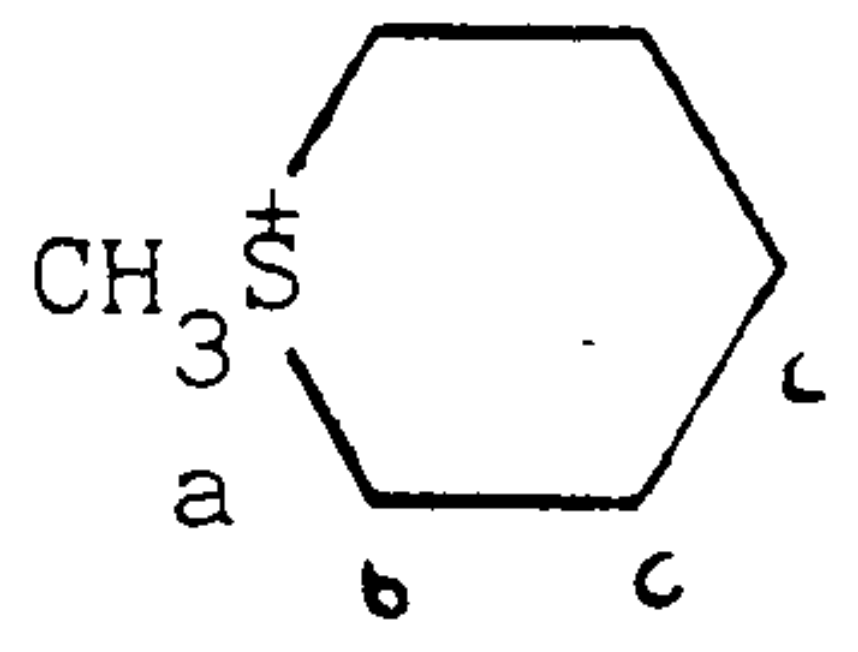
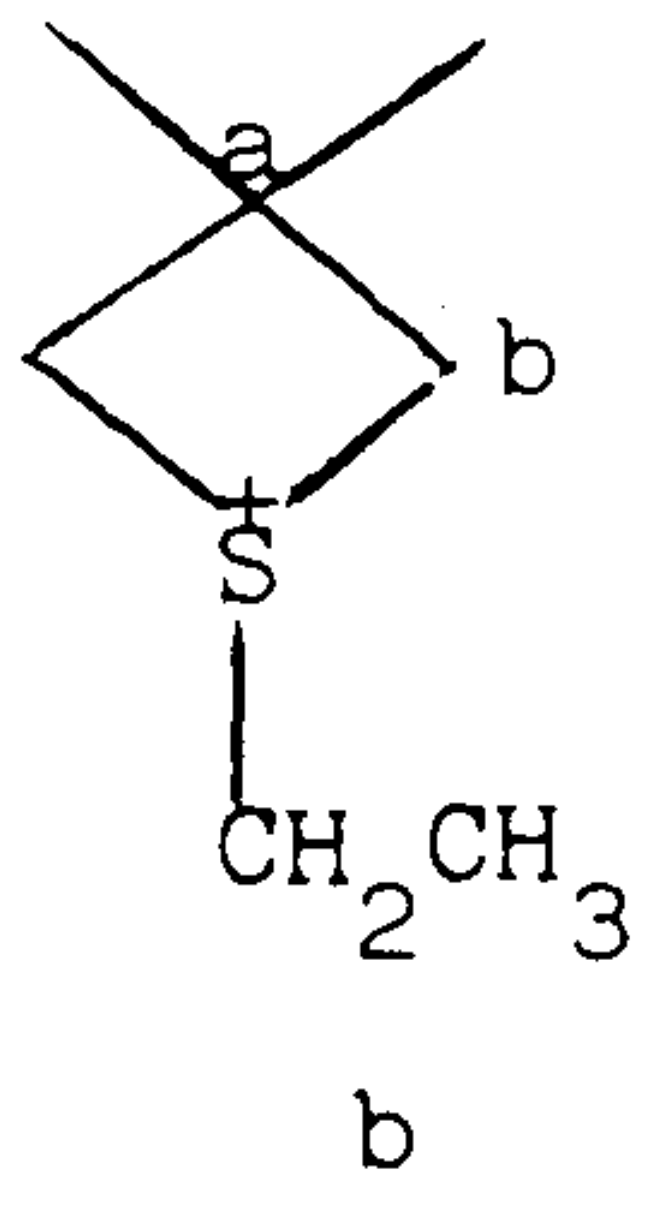
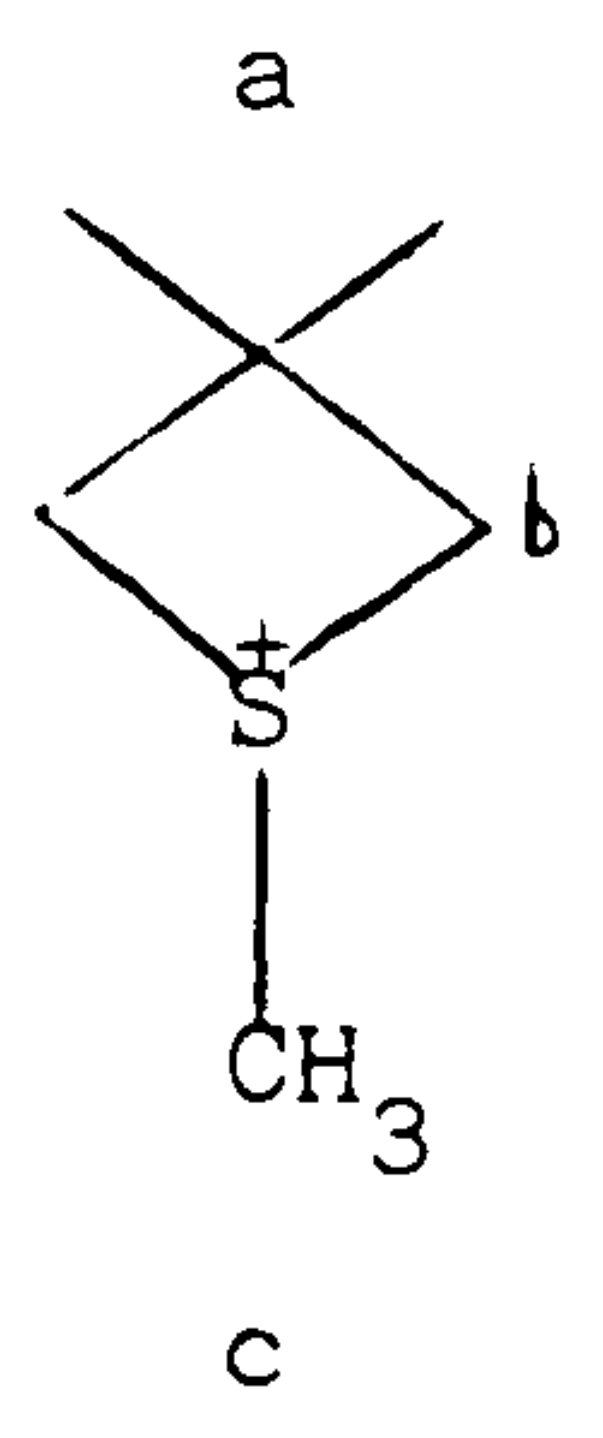
| | calculated | | found | |
|---|---|---|---|---|
| Compound | %C | %H | %C | %H |
| 1 | 37.17 | 2.66 | 37.14 | 2.62 |
| 2 | 31.08 | 2.22 | 31.17 | 2.26 |
| 3 | 46.72 | 4.38 | 46.77 | 4.30 |
| 4 | 43.91 | 3.66 | 43.90 | 3.68 |

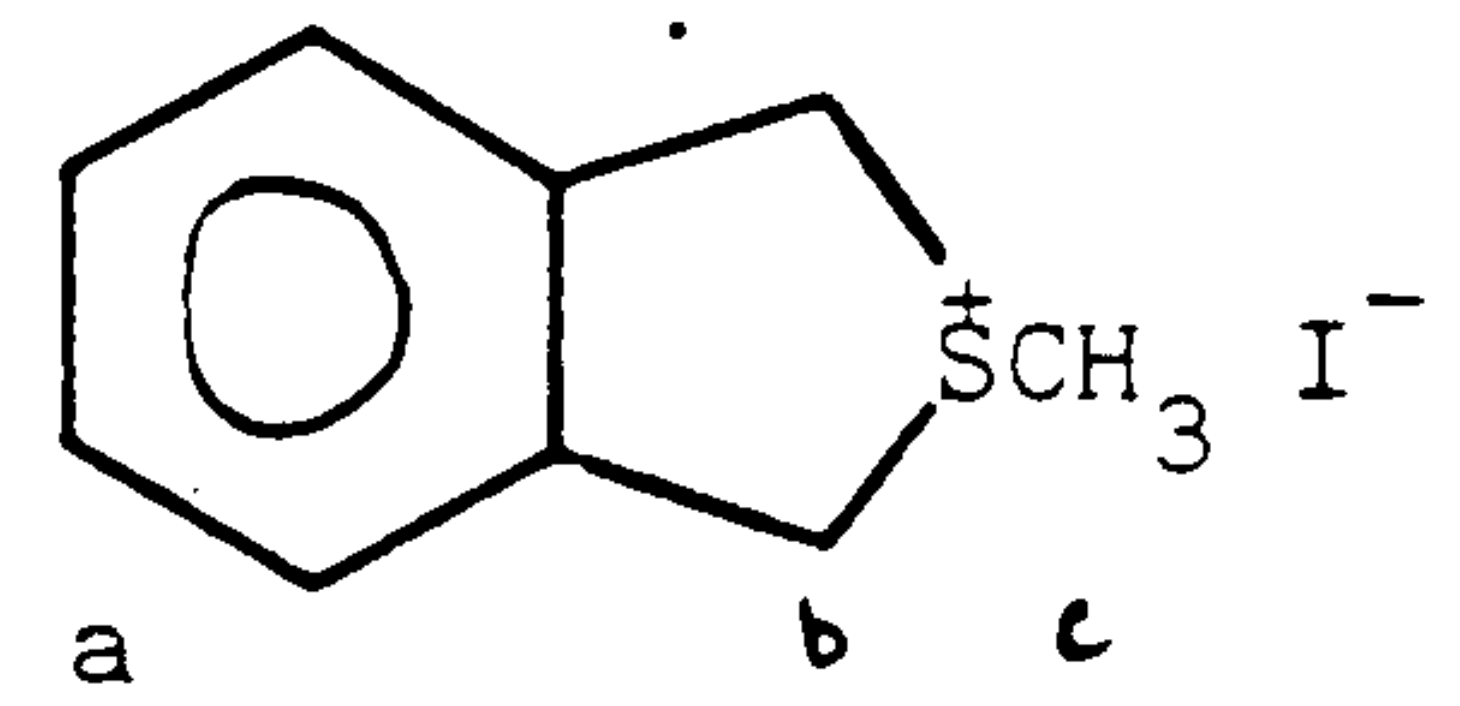
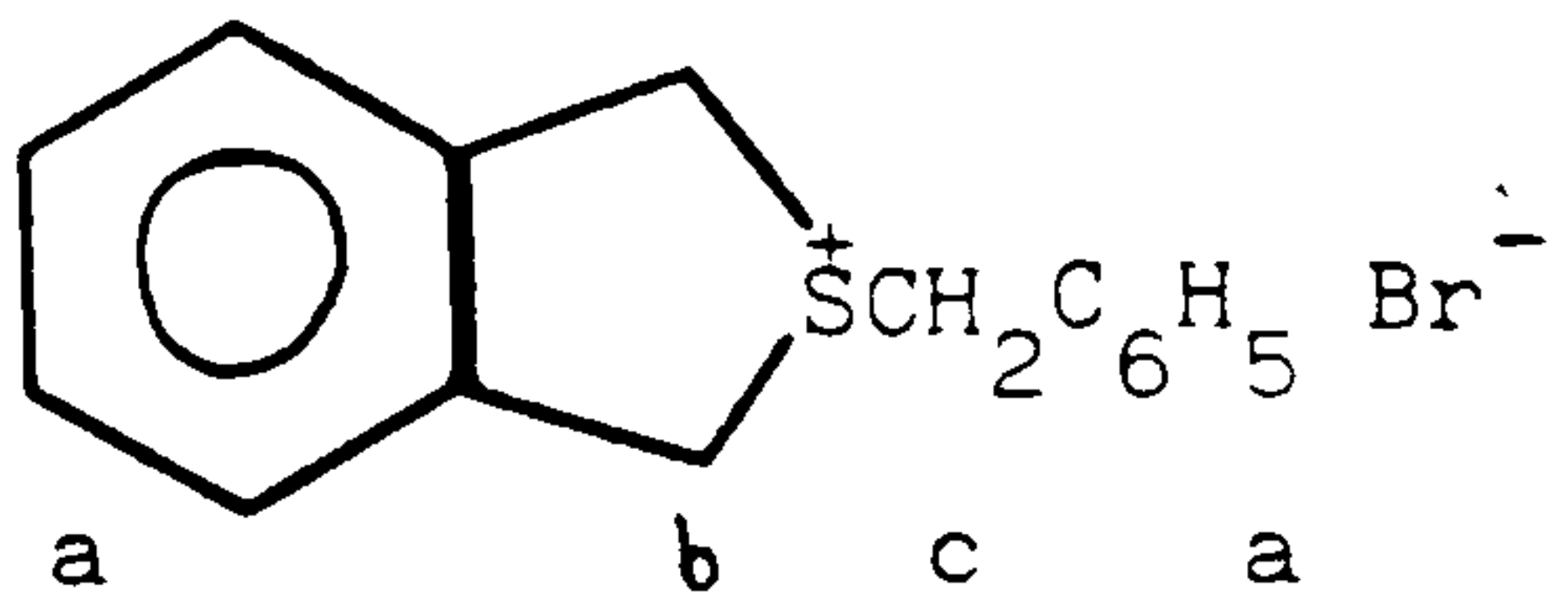
$^1H$ chemical shifts (δ) ppm.

| | | | $J_{CH_2\text{-}Hg}$(Hz) |
|---|---|---|---|
| 1 | 2.43(s) | 7.10(s) | 145 |
| 2 | 2.31(s) | 7.05(s) | 140 |
| 3 | 2.37(s) | 7.0(s) | 140 |
| 4 | 2.42(s) | 7.10(s) | 133 |

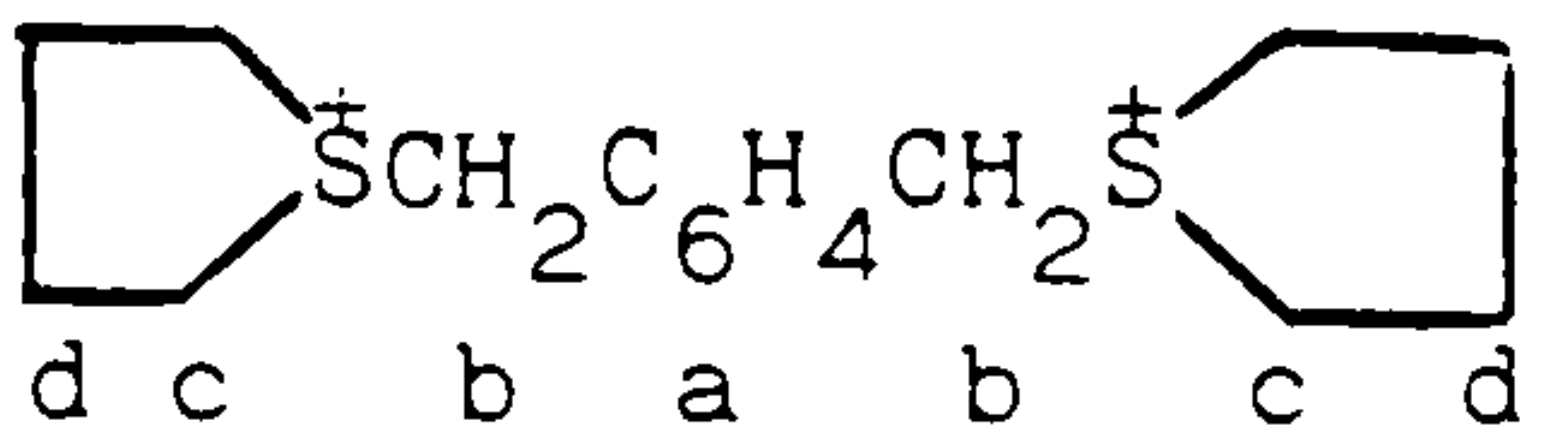
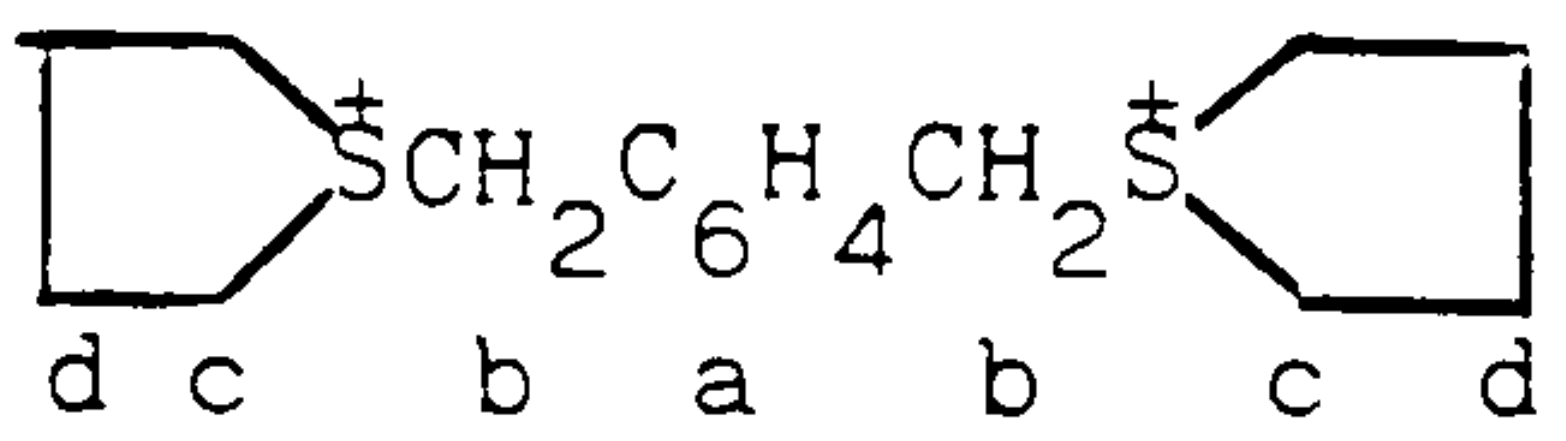
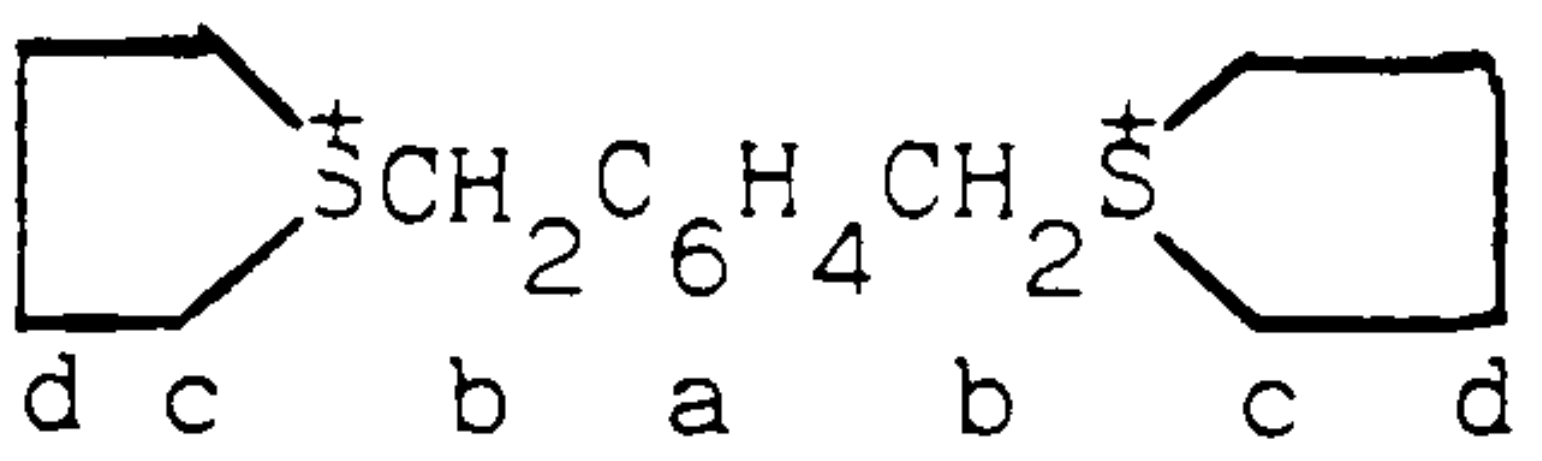
$^1$H nmr shifts of sulphonium salts

| | a | b | c | d | e |
|---|---|---|---|---|---|
| $C_6H_5CH_2\overset{+}{S}(CH_3)_2\ Tos^-$<br>a b c d | 7.8(bs) | 4.5(s) | 2.7(s) | 2.43(s) | |
| $C_6H_5CH_2\overset{+}{S}(CH_3)_2\ Br^-$<br>a b c | 7.59(bs) | 4.65(s) | 2.81(s) | | |
| $C_6H_5CH_2-\overset{+}{S}(CH_2CH_3)_2\ Br^-$<br>a b c d | 7.50(s) | 4.21(s) | 4.71(q) | 1.53(t) | |
| $C_6H_5CH_2\overset{+}{S}(CH_2CH_2CH_3)_2\ Br^-$<br>a b c d e | 7.53(s) | 4.64(s) | 3.19(t) | 1.76(m) | 1.03(t) |
| $C_6H_5CH_2\overset{+}{S}(CH_2CH_2CH_2CH_3)_2\ Br^-$<br>a b c d d e | 7.51(s) | 4.65(s) | 3.24(t) | 1.61(um) | 0.92(um) |
|  | 7.63(s) | 4.58(s) | 3.54(m) | 2.31(m) | |
|  | 7.54(s) | 4.64(s) | 3.5(um) | 2.3(um) | |
|  | 7.6(s) | 4.88(s) | 3.44(bm) | 2.02(bm) | |

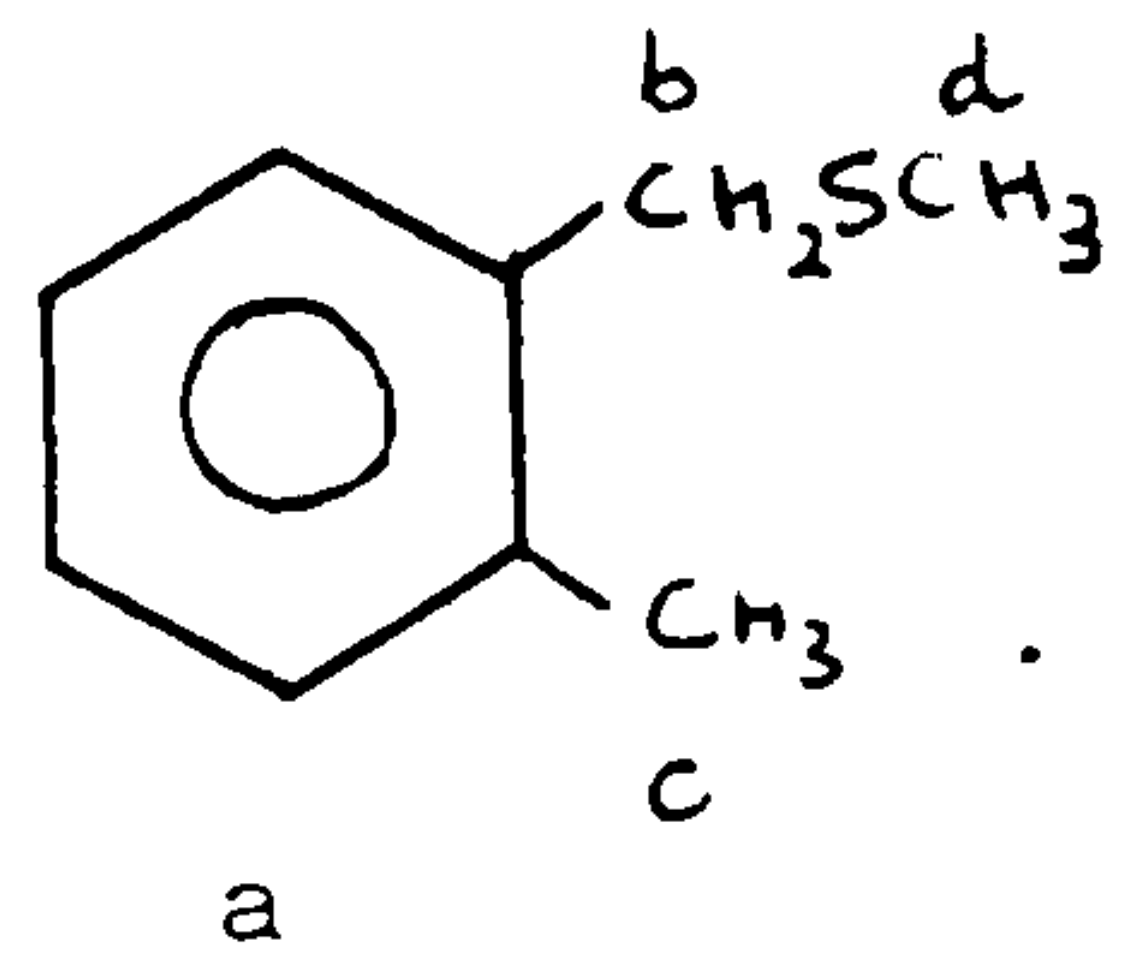
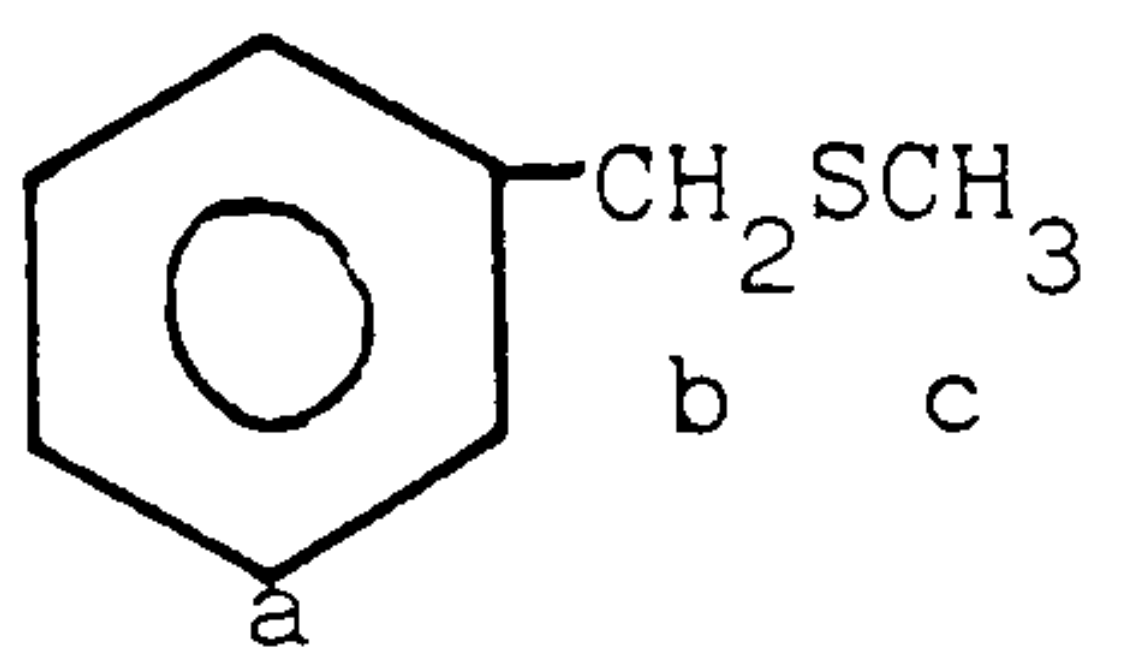
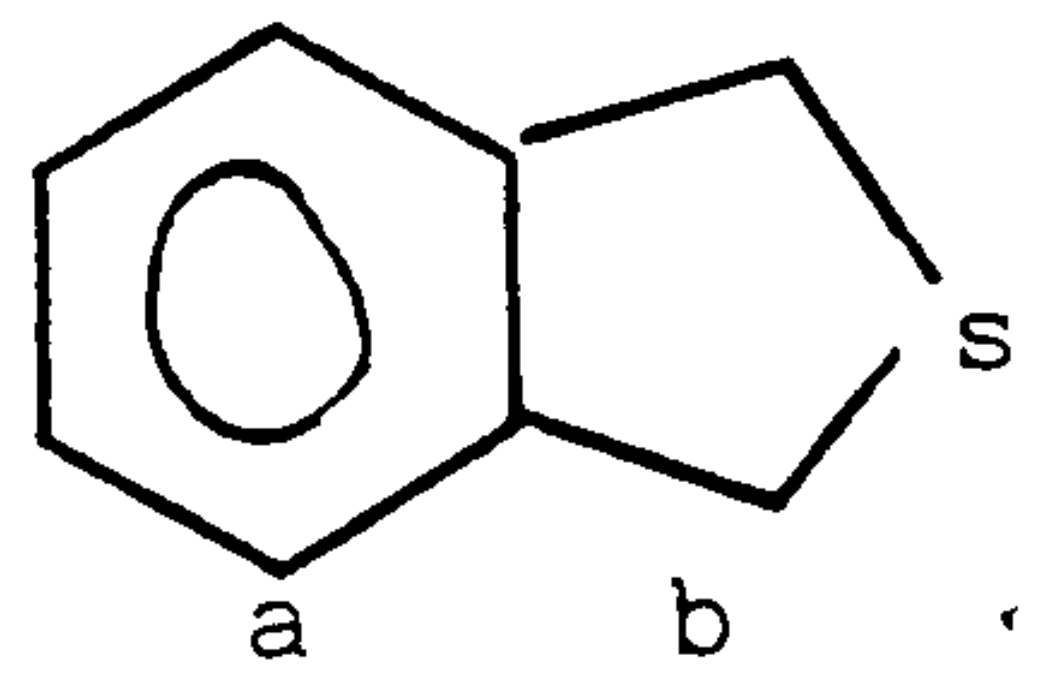
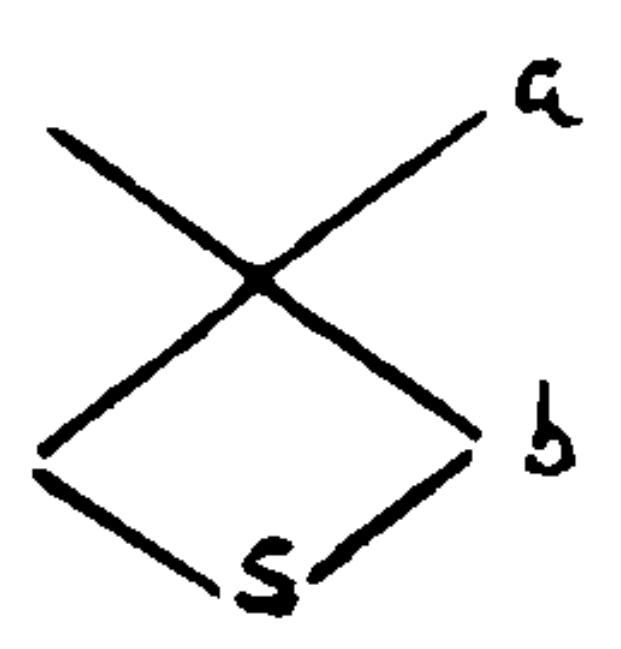
| | a | b | c |
|---|---|---|---|
| $(\underset{a}{CH_3})_3\overset{+}{S}\ I^-$ | 2.93(s) | | |
| $(\underset{a}{CH_3}\underset{b}{CH_2})_3\overset{+}{S}\ Br^-$ | 1.56(t) | 4.73(q) | |
| $(\underset{a}{CH_3})_2\overset{+}{S}\underset{b}{CH_2}\underset{c}{CH_2}\underset{b}{CH_2}I\ I^-$ | 2.96(s) | 3.39(um) | 2.44(m) |
| $(\underset{a}{C_6H_5}\underset{b}{CH_2})_2\overset{+}{S}\underset{c}{CH_3}\ Br^-$ | 7.59(s) | 4.54-4.72(AB)<br>(J=14Hz) | |
| $(\underset{a}{C_6H_5}\underset{b}{CH_2})_3\overset{+}{S}\ HSO_4^-$ | 7.33(s) | 4.89(s) | |
|  $I^-$ | 2.81(s) | 3.47(um) | 2.34(um) |
|  $I^-$ | 2.89(s) | 3.35(um) | 1.81(um) |
|  $BF_4^-$ | 1.5(m) | 3.8(m) | |
|  $O_3SF^-$ | 1.43(bs) | 3.73(s) | 3.21(s) |

|  | a | b | c |
|---|---|---|---|
|  | 7.56(s) | 4.59-5.14(AB)<br>(J=16.6 Hz) | 2.82(s) |
|  | 7.49(s) | 4.69-5.19(AB)<br>(J=16.6 Hz) | 4.65(s) |

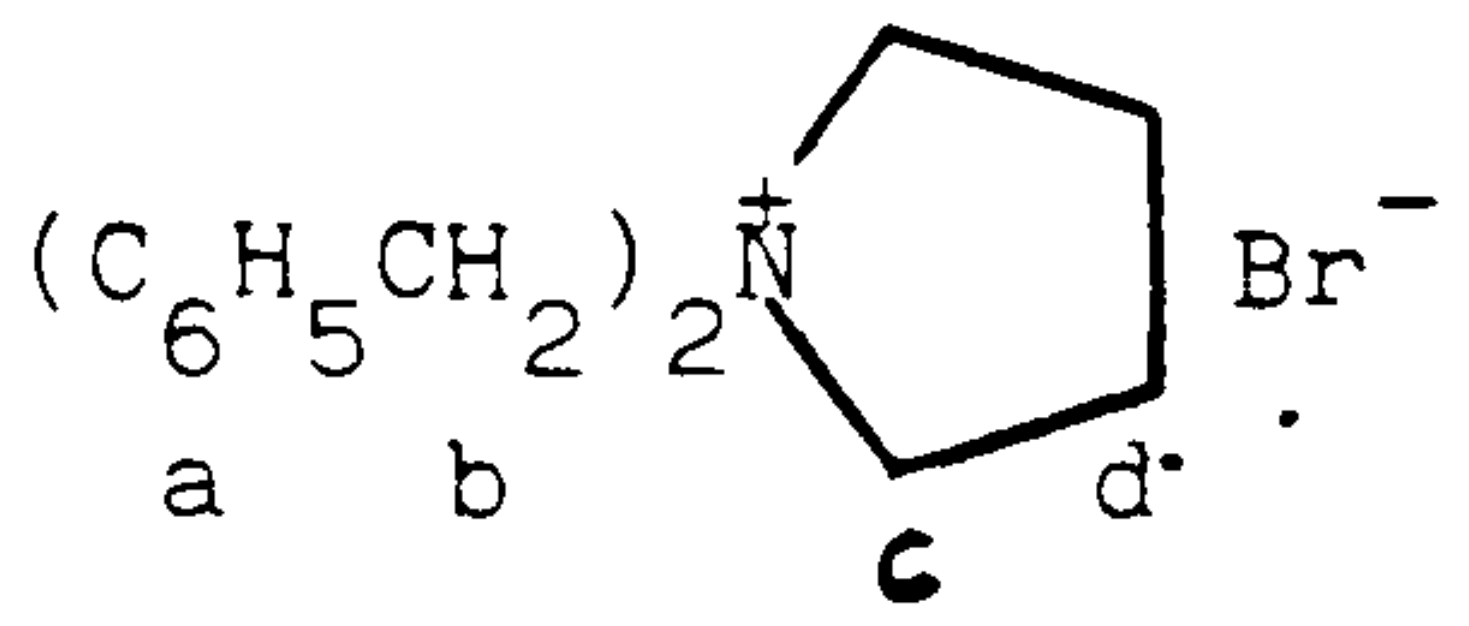
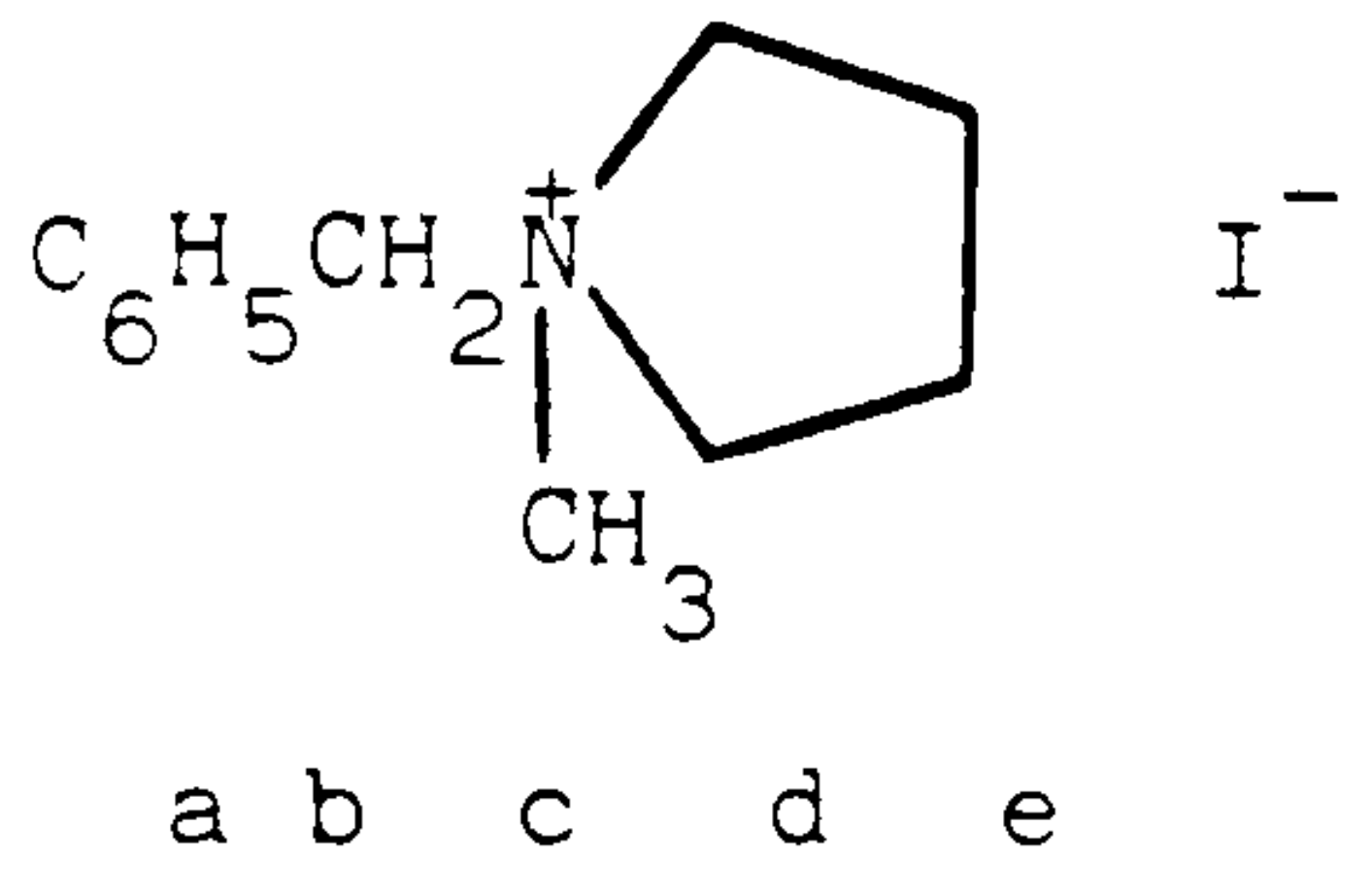
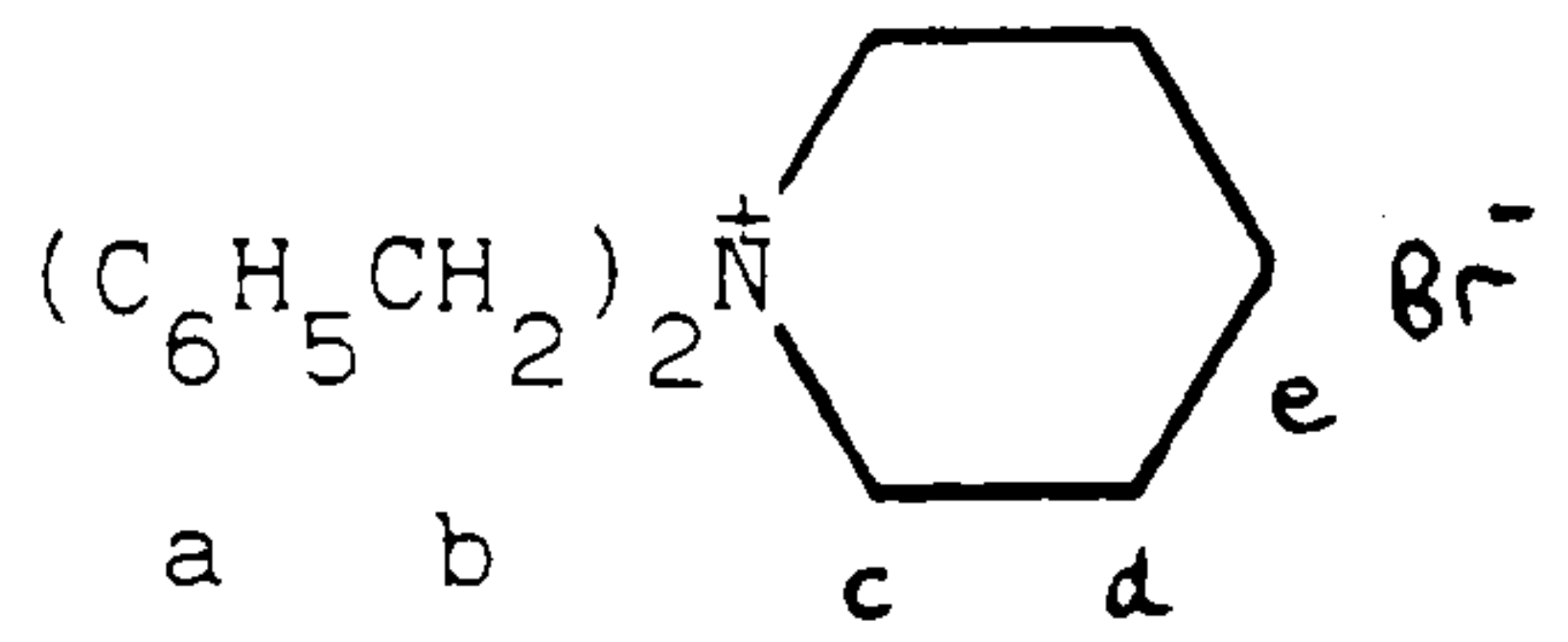
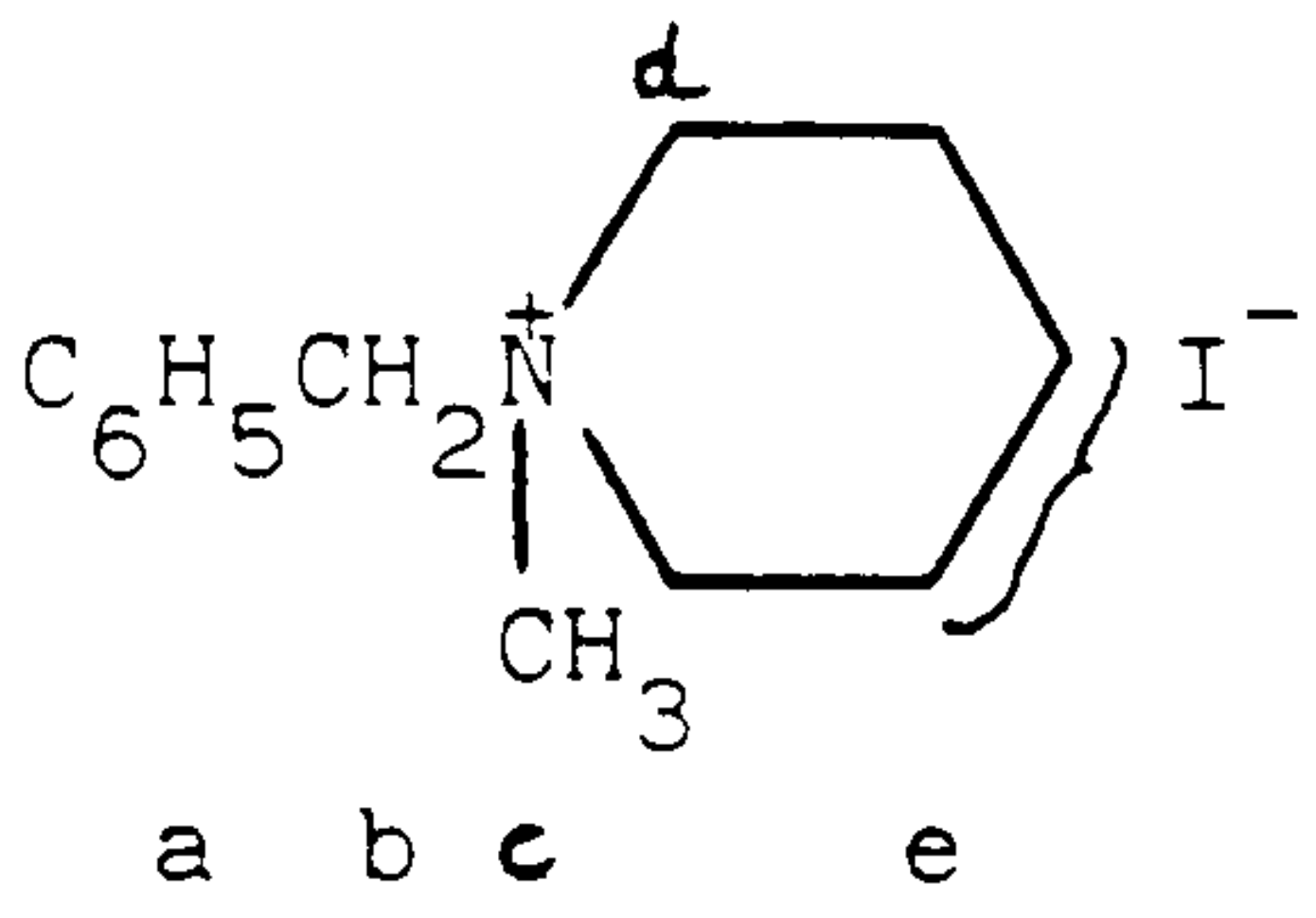
$^1$H nmr shifts of xylylene-bis-sulphonium salts

| | a | b | c | d |
|---|---|---|---|---|
| 2-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ 2Br$^-$<br>c b a b c | 7.86(s) | 5.06(s) | 3.09(s) | |
| 3-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ 2Br$^-$<br>c b a b c | 7.88(s) | 4.83(s) | 2.96(s) | |
| 4-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ 2Br$^-$<br>c b a b c | 7.88(s) | 4.85(s) | 2.97(s) | |
| o-  2Br$^-$ | 7.07(s) | 4.38(s) | 3.60(um) | 2.44(um) |
| m-  2Br$^-$ | 7.72(s) | 4.64(s) | 3.55(um) | 2.34(um) |
| p-  2Br$^-$ | 7.75(s) | 4.63(s) | 3.56(um) | 2.34(um) |

$^1$H nmr shifts of sulphides (δ values ppm)

| | a | b | c | d | e |
|---|---|---|---|---|---|
| $C_6H_5CH_2SCH_2CH_3$<br>a b c d | 7.20(s) | 3.56(s) | 2.21(q) | 1.05(t) | |
| $C_6H_5CH_2SCH_2CH_2CH_3$<br>a b c d e | 7.20(bs) | 3.52(s) | 2.24(t) | 1.43(t/q) | 0.82(t) |
| $C_6H_5CH_2SCH_2CH_2CH_2CH_3$<br>a b c d d e | 7.5-7.7(um) | 3.65(s) | 2.29(t) | 2.0(m) | 0.84(t) |
|  | 7.11(s) | 3.61(s) | 2.34(s) | 1.95(s) | |
|  | 7.07(s) | 3.45(s) | 1.74(s) | | |
|  | 7.11(s) | 4.14(s) | | | |
|  | 1.25(s) | 2.93(s) | | | |

$^1H$ nmr shifts of ammonium salts

| | a | b | c | d | e |
|---|---|---|---|---|---|
| $(\underset{a}{CH_3}\underset{b}{CH_2})_3\overset{+}{N}HBr^-$ | 1.83(t) | 3.77-3.88(q) | | | |
| $(\underset{a}{CH_3})_2\overset{+}{N}H_2Br^-$ | 3.0(t)(J=5.5 Hz) | | | | |
| $(\underset{a}{CH_3})_3\overset{+}{N}\underset{b}{H}\ Br^-$ | 1.83(d) | 3.74(q) | | | |
|  | 7.55(s) | 4.52(s) | 3.48(um) | 2.09(um) | |
|  | 7.59(s) | 4.95(s) | 3.56(um) | 2.96(s) | 2.26(um) |
|  | 7.52(s) | 4.52(s) | 3.29(m) | 2.06(um) | 1.53(um) |
|  | 7.35(s) | 4.38(m) | 3.28(um) | 2.88(s) | 1.78(um) |

$^1$H nmr shifts of xylylene-bis-ammonium salts

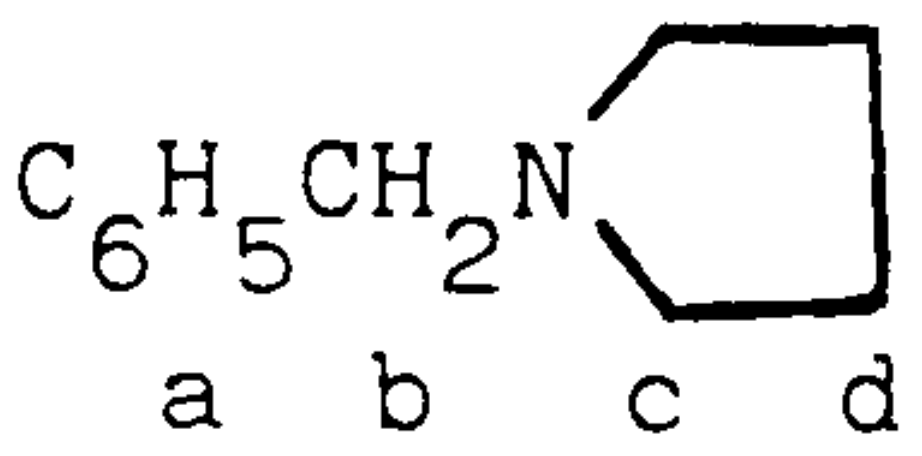
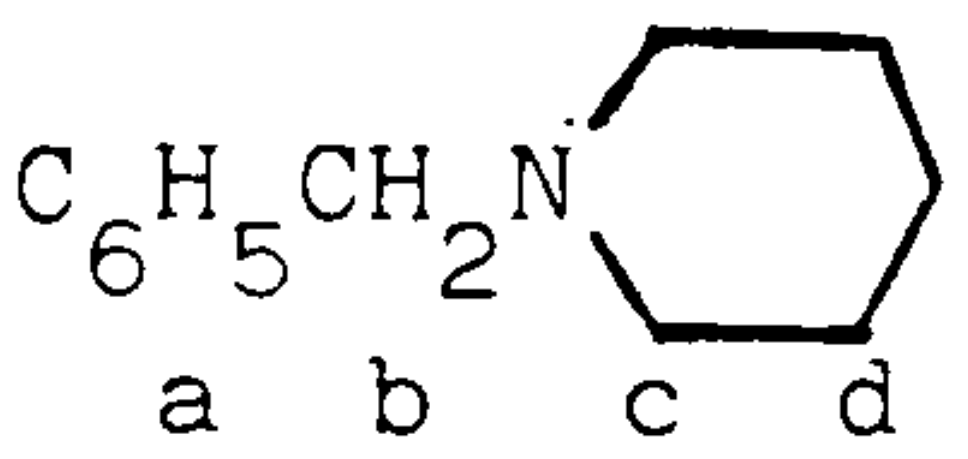
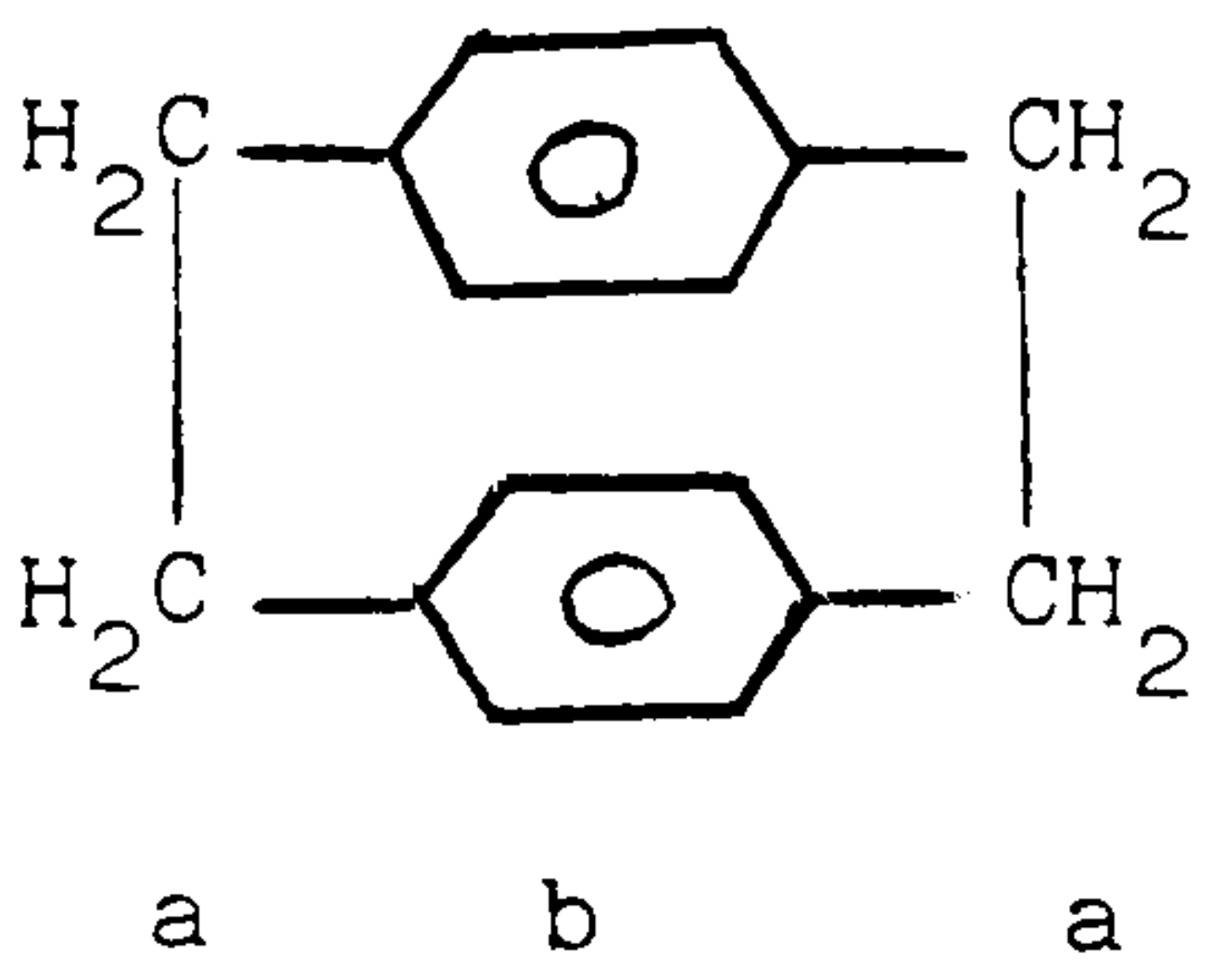
| | a | b | c | d |
|---|---|---|---|---|
| $2\text{-}(\underset{d}{CH_3}\underset{c}{CH_2})_3\overset{+}{N}\underset{b}{CH_2}\underset{a}{C_6H_4}\underset{b}{CH_2}\overset{+}{N}(\underset{c}{CH_2}\underset{d}{CH_3})_3\ 2Br^-$ | 7.76(s) | 4.67(s) | 3.36(q) | 1.37(t) |
| $3\text{-}(\underset{d}{CH_3}\underset{c}{CH_2})_3\overset{+}{N}\underset{b}{CH_2}\underset{a}{C_6H_4}\underset{b}{CH_2}\overset{+}{N}(\underset{c}{CH_2}\underset{d}{CH_3})_3\ 2Br^-$ | 7.72(s) | 4.54(s) | 3.29(q) | 1.45(t) |
| $4\text{-}(\underset{d}{CH_3}\underset{c}{CH_2})_3\overset{+}{N}\underset{b}{CH_2}\underset{a}{C_6H_4}\underset{b}{CH_2}\overset{+}{N}(\underset{c}{CH_2}\underset{d}{CH_3})_3\ 2Br^-$ | 7.69(s) | 4.52(s) | 3.29(q) | 1.44(t) |

## $^1$H nmr shifts of mercury compounds

| | solvent | a(um) | b(s) | $JCH_2$-Hg(Hz)* |
|---|---|---|---|---|
| $C_6H_5CH_2HgCl$<br>a b | $CDCl_3$ | 7.11 | 3.20 | 257 |
| $C_6H_5CH_2HgCl$<br>a b | Py-$d_5$ | 7.15 | 3.24 | 285 |
| $(C_6H_5CH_2)_2Hg$<br>a b | Py-$d_5$ | 7.10 | 2.34 | 140 |
| $(C_6H_5CH_2)_2Hg$<br>a b | $CDCl_3$ | 7.10 | 2.42 | 133 |
| $(p\text{-}CH_3C_6H_4CH_2)_2Hg$<br>a b | Py-$d_5$ | 7.06 | 2.37<br>2.22($CH_3$) | 140 |
| $(p\text{-}ClC_6H_4CH_2)_2Hg$<br>a b | Py-$d_5$ | 7.10 | 2.34 | 145 |
| $(p\text{-}BrC_6H_4CH_2)_2Hg$<br>a b | Py-$d_5$ | 7.05 | 2.31 | 140 |

* $JCH_2$-Hg obtained from Hg satellites

## $^1$H nmr shifts of miscellaneous compounds

| | a | b | c | d |
|---|---|---|---|---|
| $(p\text{-}CH_3C_6H_4CH_2)_2$<br>a b c | 2.31(s) | 7.08(s) | 2.85(s) | |
| $(CH_3CH_2)_3\overset{+}{O}\ BF_4^-$<br>a b | 1.59(t) | 4.73(q) (J=7 Hz) | | |
| $(CH_3)_2C(CH_2O_3SC_6H_5)_2$<br>a b c | 0.92(s) | 3.85(s) | 7.96(s) | |
|  | 6.95(s) | 3.28(s) | 2.30(m) | 1.58(m) |
|  | 6.98(s) | 3.23(s) | 2.23(m) | 1.40(m) |
|  | 6.47(s) | 3.09(s) | | |

## Electrolysis Experiments

### (a) Polarography

Solutions of the sulphonium salts were made in buffers containing gelatine and degassed in a Kalousek cell with nitrogen. The polarograms were recorded automatically on a PO4 Polariter. A manual plot was made for more accurate determination of the half-wave potential ($E_{\frac{1}{2}}$). The polarograms obtained were well defined single waves, all having the same limiting current for a fixed concentration. A typical example is shown in figure 1. Polarograms of the xylylenebis-salts are shown in figures 2, 3 and 4. Table 3 shows the variation of $E_{\frac{1}{2}}$ for substituted sulphonium salts.

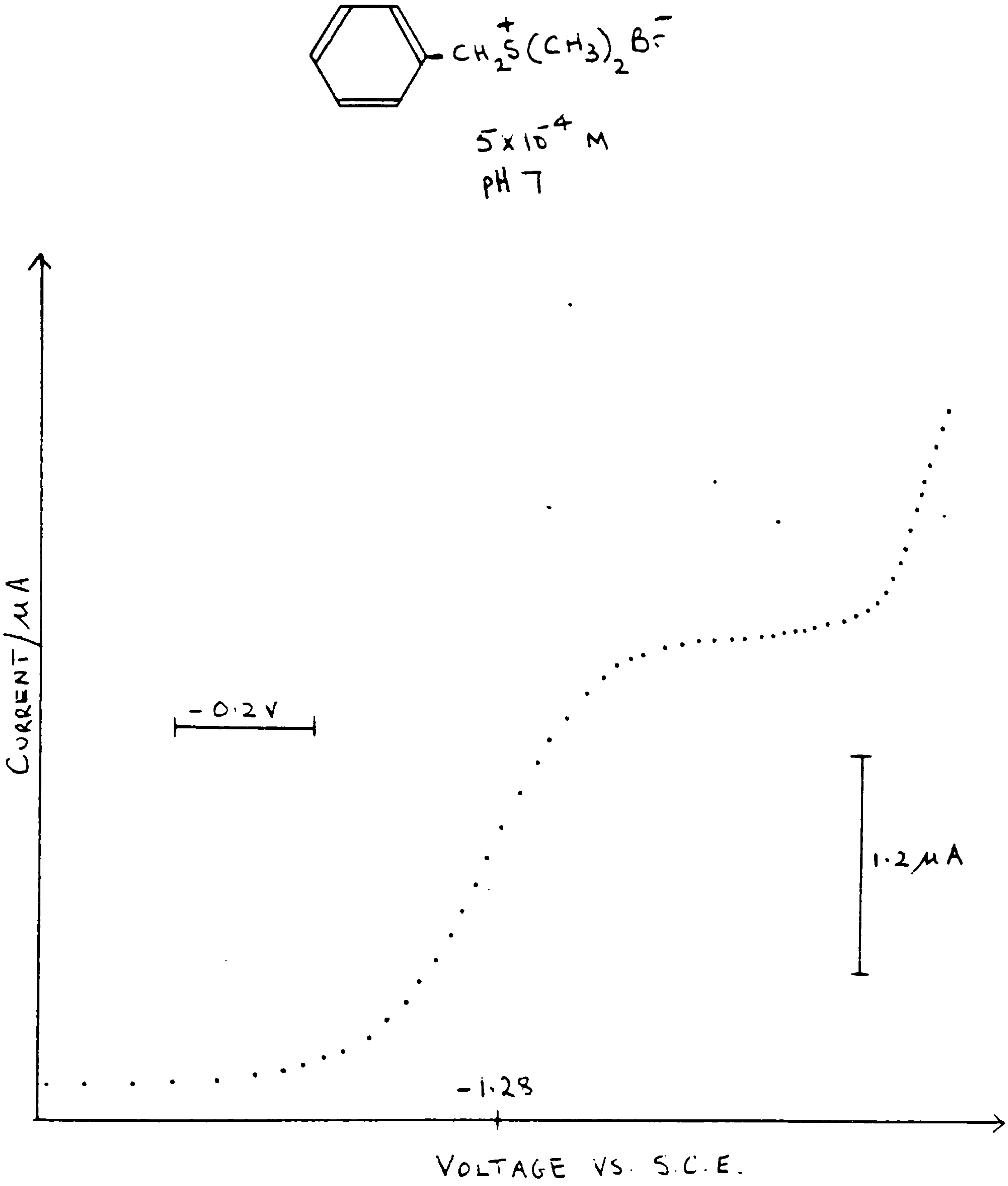

$CH_2\overset{+}{S}(CH_3)_2\ B\bar{F}$
$5 \times 10^{-4}$ M
pH 7
Current/μA
− 0·2 V
1·2 μA
−1·28
Voltage vs. S.C.E.

Fig 1.

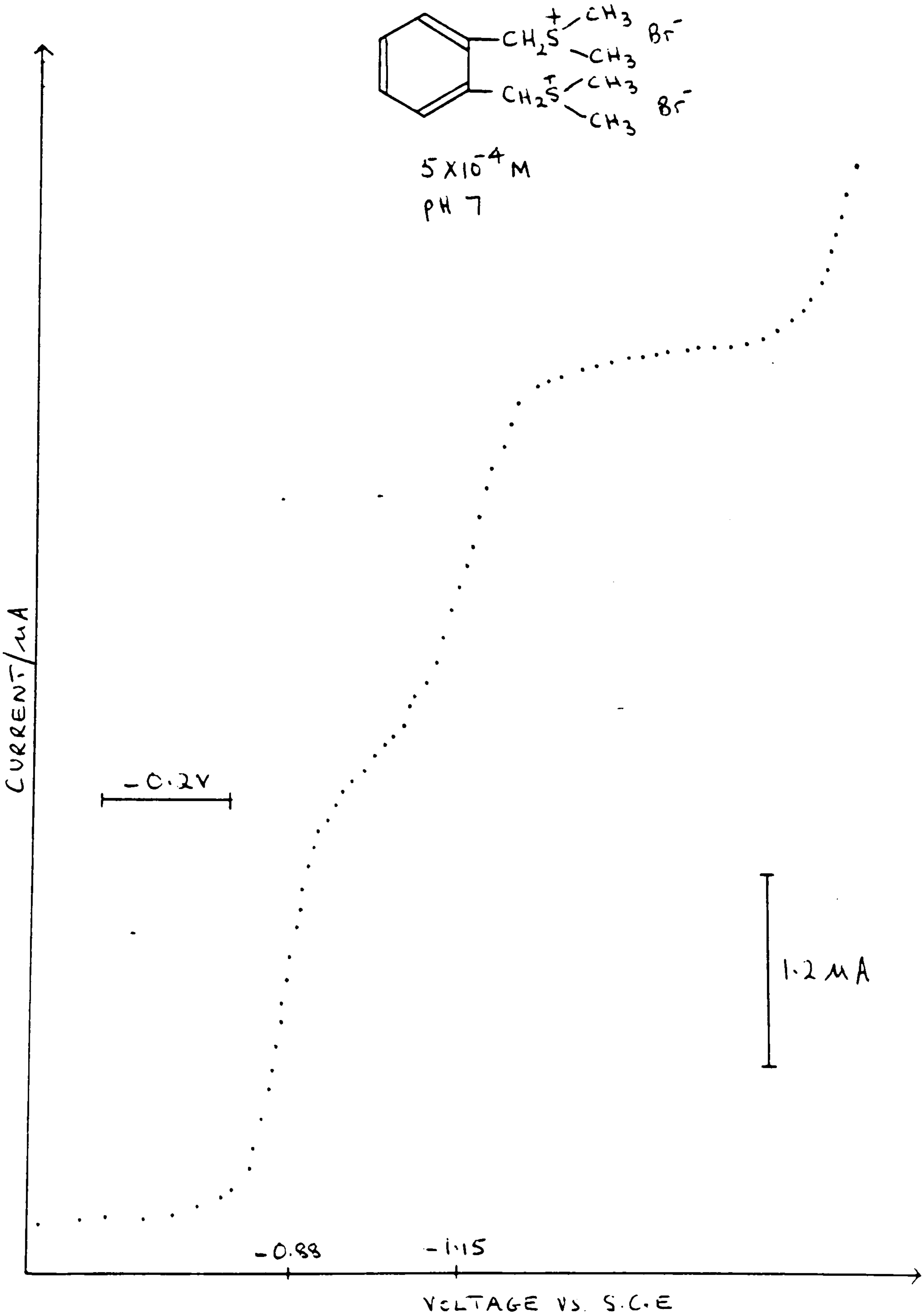

CH2S+ CH3 CH3 Br-
CH2S+ CH3 CH3 Br-
5X10-4 M
pH 7
CURRENT/μA
-0.2V
1.2 μA
-0.88
-1.15
VOLTAGE VS. S.C.E

FIG 2

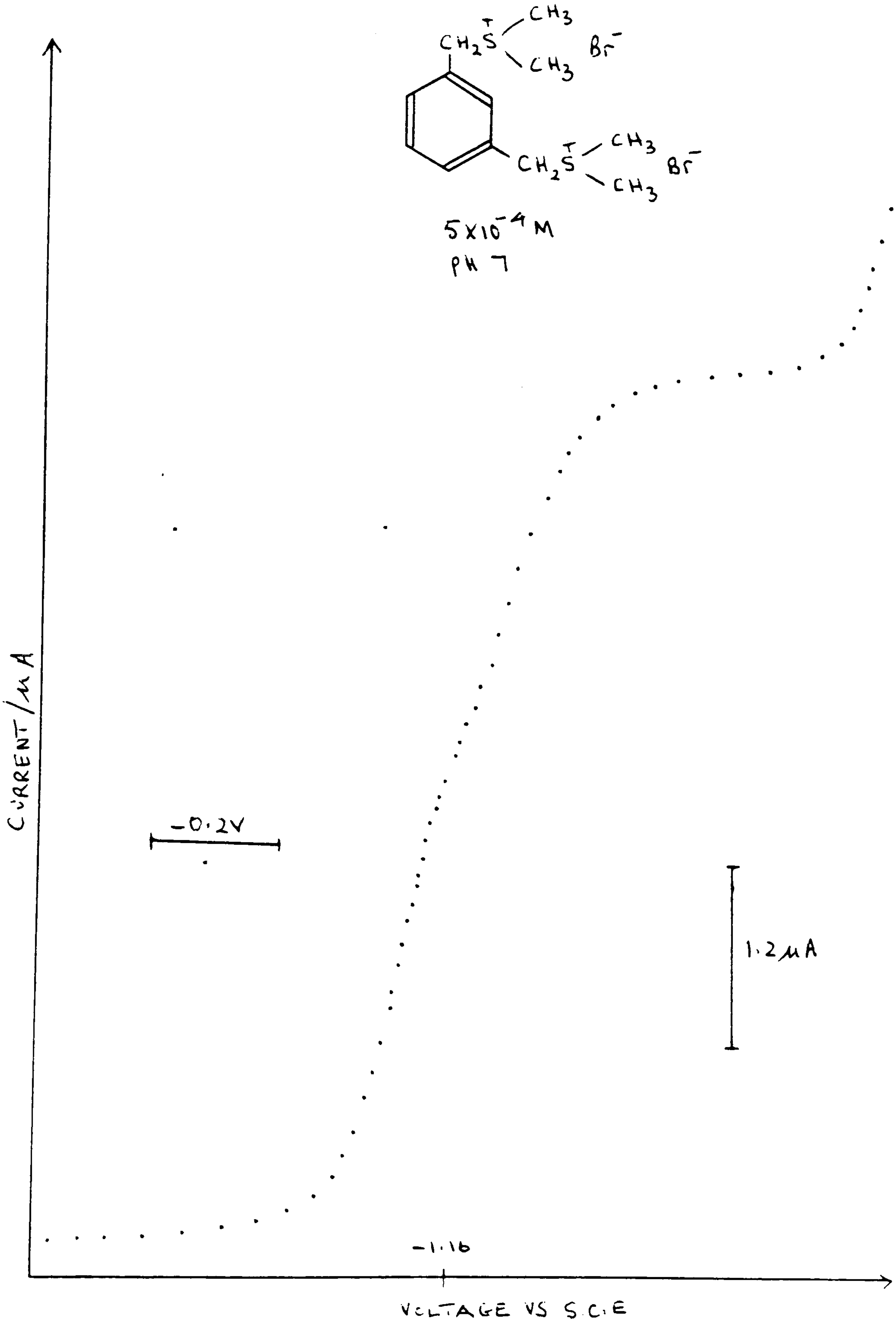

CH$_2\overset{+}{S}$ CH$_3$ CH$_3$ Br$^-$
CH$_2\overset{+}{S}$ CH$_3$ CH$_3$ Br$^-$
5x10$^{-4}$M
pH 7
CURRENT/μA
-0.2V
1.2μA
-1.16
VOLTAGE VS S.C.E

FIG 3

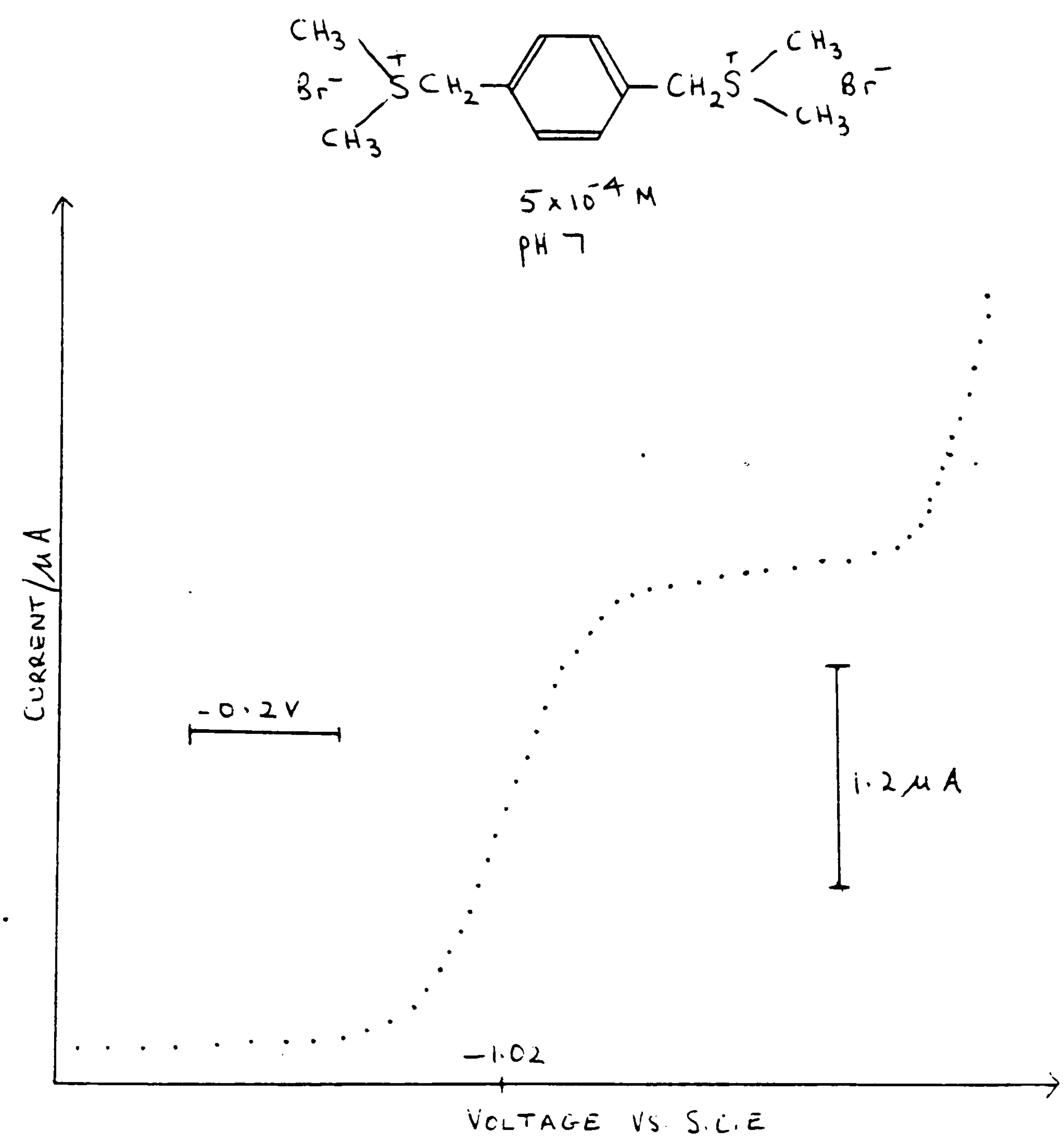
CH3
Br⁻
S⁺
CH2
CH3
CH2
S⁺
CH3
Br⁻
CH3
5 x 10⁻⁴ M
pH 7
CURRENT/μA
-0·2V
1·2 μA
-1·02
VOLTAGE VS S.C.E

FIG 4

TABLE 3

Half-wave potentials of sulphonium salts

$XC_6H_4CH_2\overset{+}{S}R_2Y^-$

| X | R | Y | $E_{1/2}$man(V) | $E_{1/2}$auto(V) |
|---|---|---|---|---|
| H | $CH_3$ | Br | -1.28 | -1.29 |
| 2-$CH_3$ | $CH_3$ | Br | -1.30 | -1.30 |
| 3-$CH_3$ | $CH_3$ | Br | -1.33 | -1.35 |
| 4-$CH_3$ | $CH_3$ | Br | -1.18 | -1.24 |
| 4-Cl | $CH_3$ | Cl | -1.02 | -1.06 |
| 4-Br | $CH_3$ | Br | -1.08 | -1.10 |
| 4-$NO_2$ | $CH_3$ | Br | - | -0.63 |
| H | $(CH_2)_4$ | Br | -1.07 | -1.12 |
| 2-$CH_3$ | $(CH_2)_4$ | Br | -1.02 | -1.04 |
| 3-$CH_3$ | $(CH_2)_4$ | Br | -0.99 | -1.02 |
| 4-$CH_3$ | $(CH_2)_4$ | Br | -1.23 | -1.25 |
| 4-Cl | $(CH_2)_4$ | Cl | -0.89 | -1.00 |
| 4-Br | $(CH_2)_4$ | Br | -0.94 | -0.96 |
| H | $(CH_2)_5$ | Br | -1.22 | -1.26 |
| H | $C_6H_5CH_2$ | $HSO_4$ | -0.66,-1.54 | -0.69,-1.56 |
| H | $C_6H_5CH_2.CH_3$ | I | -0.94,-1.25 | -0.94,1.25 |

TABLE 4

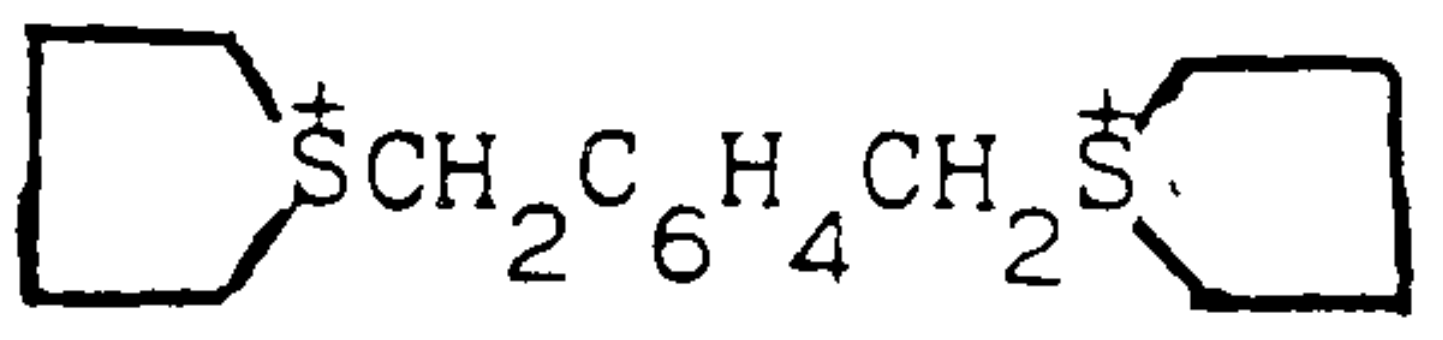
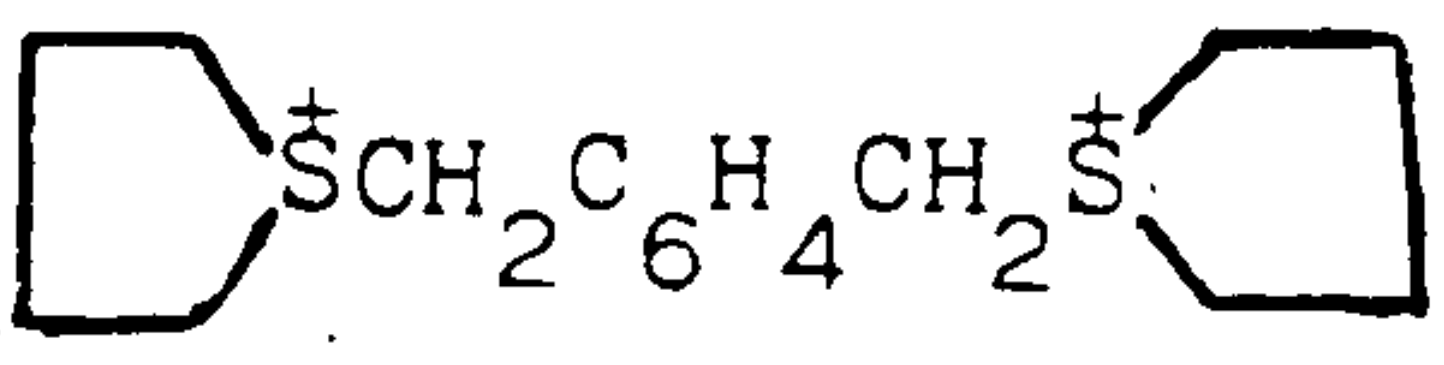
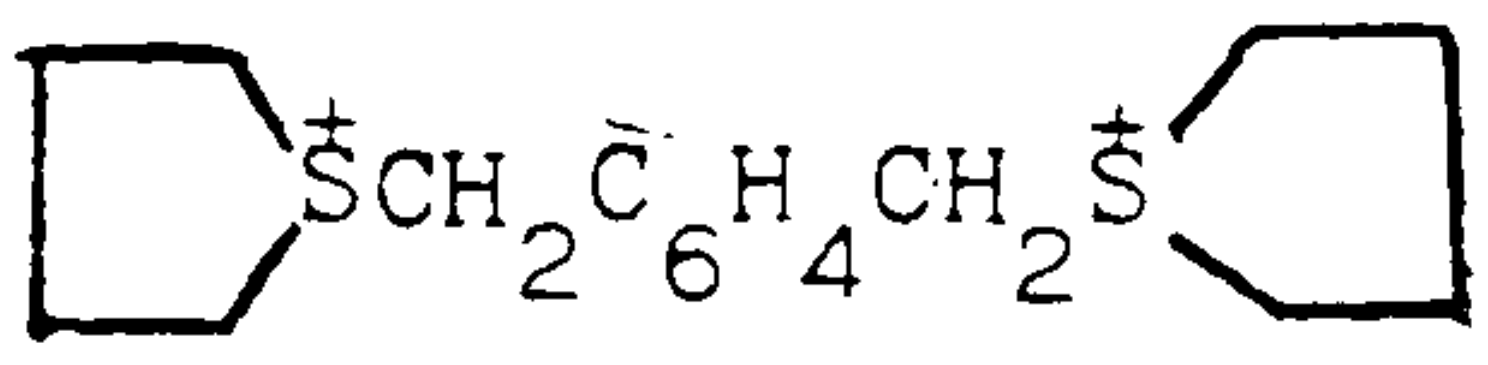
| Xylylene-bis-salts | $E_{\frac{1}{2}}$man (V) | $E_{\frac{1}{2}}$auto (V) |
|---|---|---|
| 2-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ $2Br^-$ | - | -0.88,-1.15 |
| 3-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ $2Br^-$ | - | -1.16 |
| 4-$(CH_3)_2\overset{+}{S}CH_2C_6H_4CH_2\overset{+}{S}(CH_3)_2$ $2Br^-$ | -0.99 | -1.02 |
| o-  $2Br^-$ | -0.83,-1.44 | -0.85,-1.46 |
| m-  $2Br^-$ | -1.05,-1.27 | -1.07,-1.2 |
| p-  $2Br^-$ | -0.96 | -0.97 |

TABLE 5

| Dihalides† | E½(v) | (Lit. values)(29) |
|---|---|---|
| 2-$BrCH_2C_6H_4CH_2Br$ | -0.63,-1.61 | -0.63,-1.58 |
| 3-$BrCH_2C_6H_4CH_2Br$ | -1.40 | -1.32 |
| 4-$BrCH_2C_6H_4CH_2Br$ | -0.82,-1.70 | -0.80,-1.72 |

† Carried out in 0.1 M tetraethylammonium bromide in dimethylformamide solution.

TABLE 6

Ammonium salts $YC_6H_4CH_2\overset{+}{N}R_3X^-$

| Y | R | X |
|---|---|---|
| H | $(CH_2)_5, CH_3$ | I |
| H | $(CH_2)_5, C_6H_5CH_2$ | Br |
| H | $(CH_2)_4, C_6H_5CH_2$ | Br |
| 2-$\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br |
| 3-$\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br |
| 4-$\overset{+}{N}(C_2H_5)_3$ | $C_2H_5$ | 2Br |

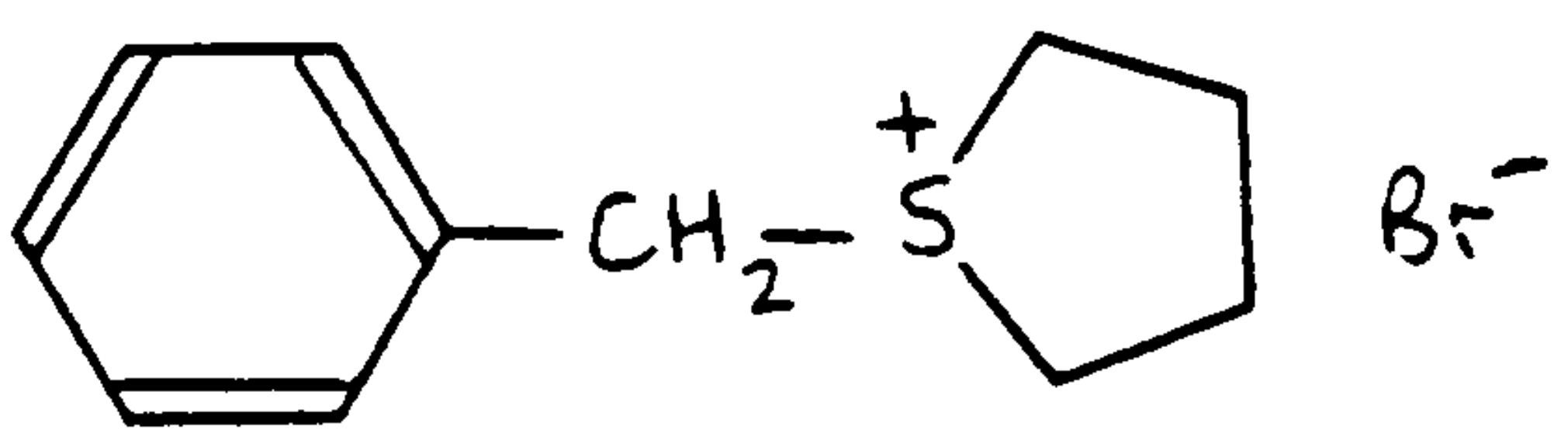
All of these quaternary salts were examined by polarography at the DME as for the sulphonium salts. None of the salts gave a reduction wave before hydrogen discharge ( -2.2v).

An example of semi-log analysis for 1-benzylthioniacyclopentane bromide

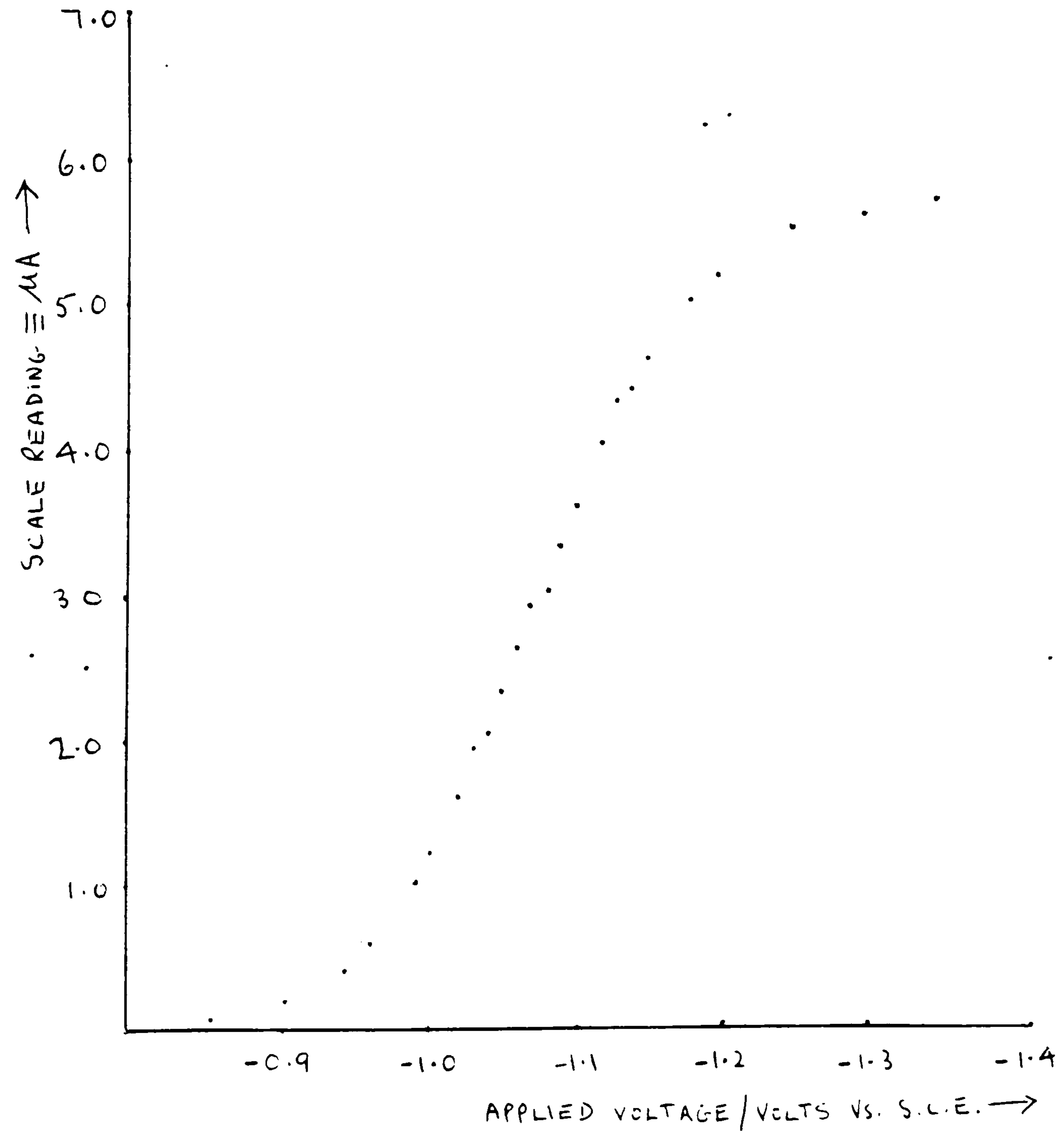
The following results were obtained by manually varying the applied voltage and recording the corresponding deflection on the galvanometer (this is a measure of the current).

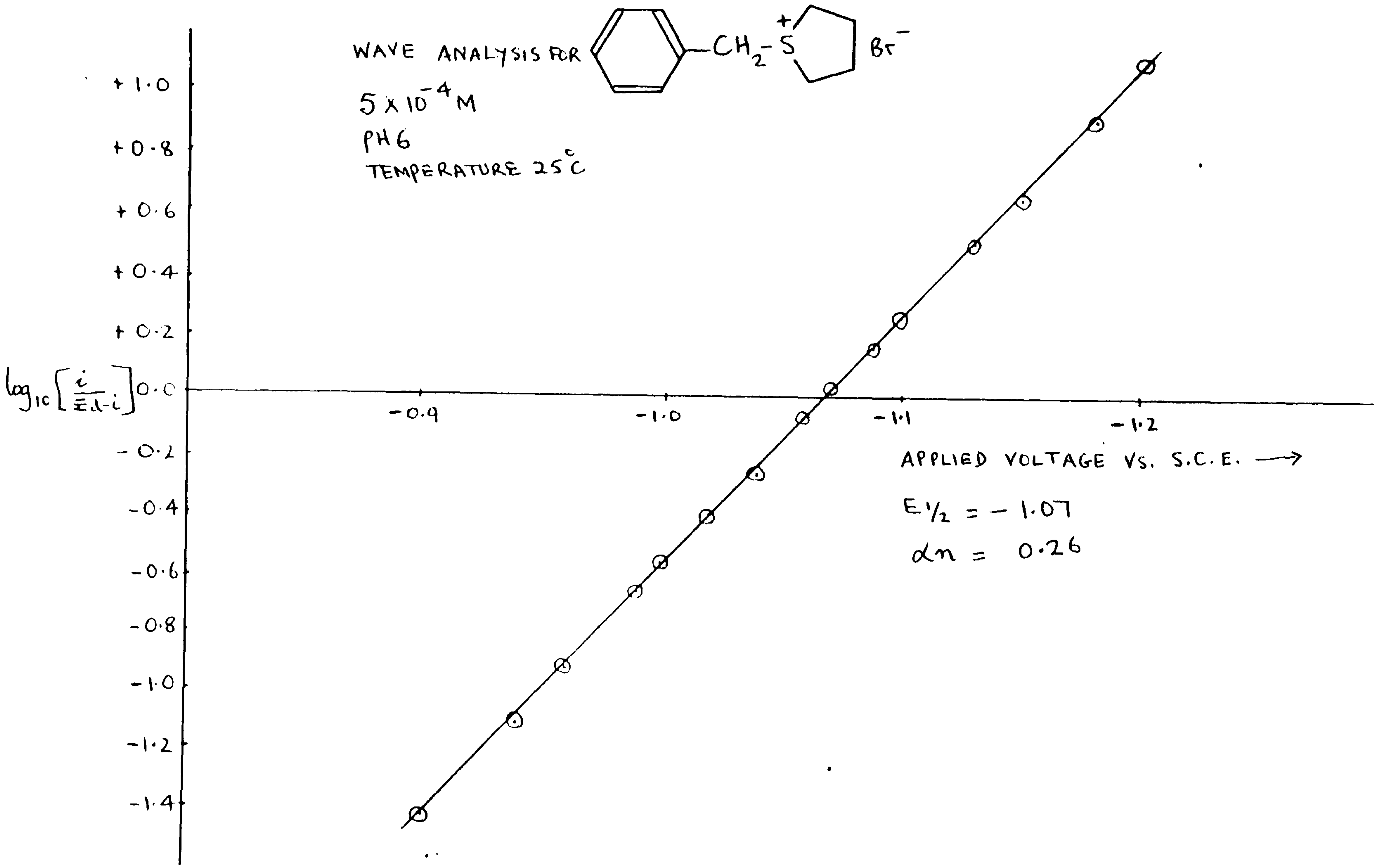
| Applied Voltage (V) | Scale Reading | Id-i | log(i/Id-i) |
|---|---|---|---|
| 0.80 | 0.00 | - | - |
| 0.90 | 0.20 | 5.40 | -1.43 |
| 0.94 | 0.40 | 5.20 | -1.11 |
| 0.96 | 0.60 | 5.00 | -0.92 |
| 0.99 | 1.00 | 4.60 | -0.66 |
| 1.00 | 1.20 | 4.40 | -0.56 |
| 1.02 | 1.60 | 4.00 | -0.40 |
| 1.03 | 1.80 | 3.80 | -0.33 |
| 1.04 | 2.00 | 3.60 | -0.26 |
| 1.05 | 2.30 | 3.30 | -0.16 |
| 1.06 | 2.60 | 3.00 | -0.06 |
| 1.07 | 2.90 | 2.70 | +0.03 |
| 1.08 | 3.00 | 2.60 | +0.12 |
| 1.09 | 3.30 | 2.30 | +0.16 |
| 1.10 | 3.60 | 2.00 | +0.26 |
| 1.12 | 4.00 | 1.60 | +0.40 |
| 1.13 | 4.30 | 1.30 | +0.52 |
| 1.14 | 4.40 | 1.20 | +0.56 |
| 1.15 | 4.60 | 1.00 | +0.66 |
| 1.18 | 5.00 | 0.60 | +0.92 |
| 1.20 | 5.20 | 0.40 | +1.12 |
| 1.25 | 5.50 | 0.10 | +1.74 |
| 1.30 | 5.60 | 0.00 | - |

MANUAL PLOT FOR



AT pH 6, 5 X $10^{-4}$ M, TEMPERATURE 25°C



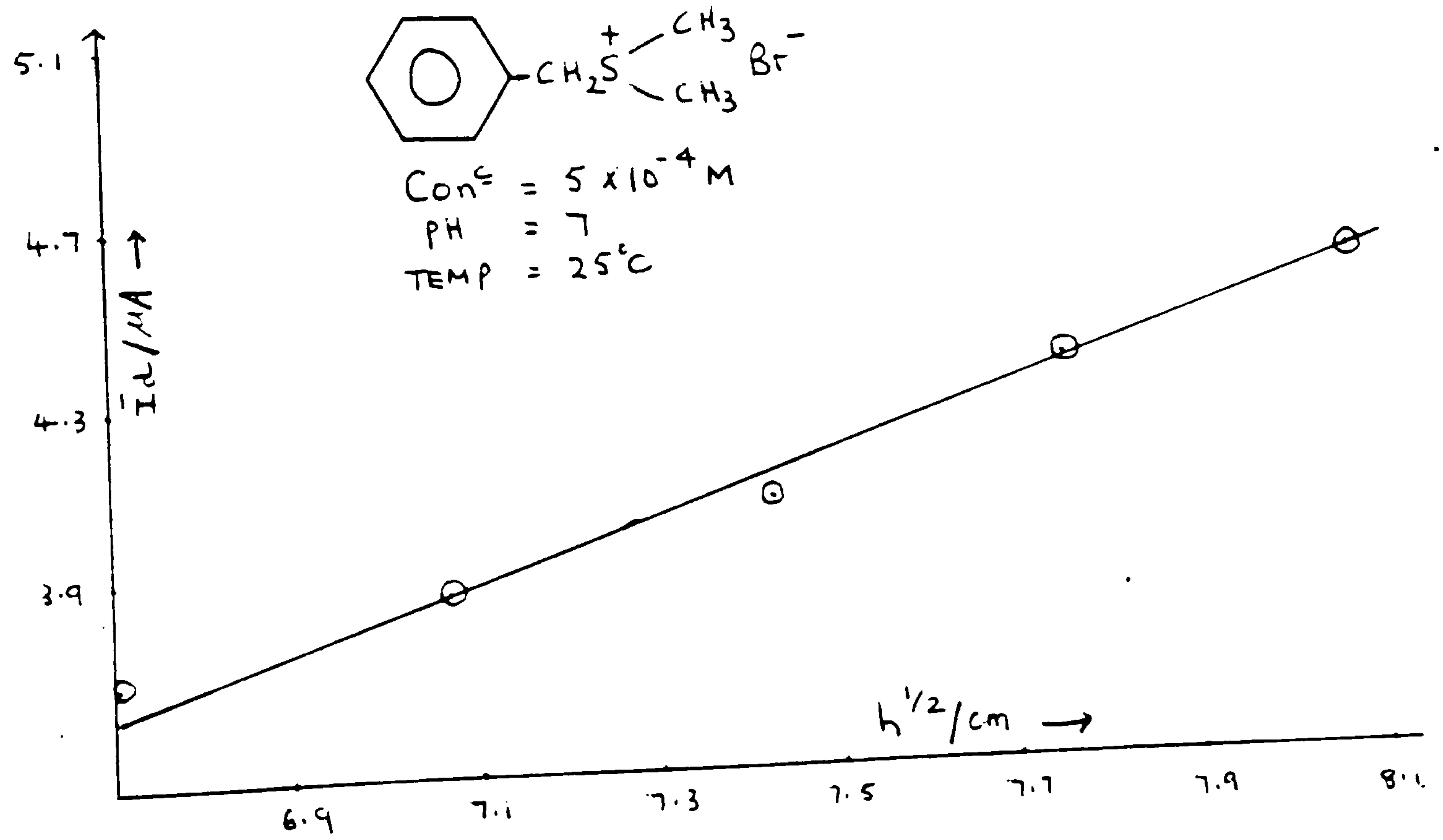

WAVE ANALYSIS FOR
$C_6H_5-CH_2-\overset{+}{S}(CH_2)_4\ Br^-$
$5 \times 10^{-4}$ M
PH 6
TEMPERATURE 25°C
+1.0
+0.8
+0.6
+0.4
+0.2
$\log_{10}\left[\frac{i}{\bar{i}_d - i}\right]$ 0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-0.9
-1.0
-1.1
-1.2
APPLIED VOLTAGE VS. S.C.E. →
$E_{1/2} = -1.07$
$\alpha n = 0.26$

## Effect of mercury column height on limiting current

The polarographic limiting currents ($\bar{I}d$) for benzyldimethylsulphonium bromide at a series of mercury column heights was measured.

| h/cm | $\bar{I}d/\mu A$ | $h^{1/2}/cm$ | $\bar{I}d/h^{1/2}/\mu A cm^{-1}$ |
|---|---|---|---|
| 45 | 3.7 | 6.70 | 0.55 |
| 50 | 3.9 | 7.07 | 0.55 |
| 55 | 4.1 | 7.42 | 0.55 |
| 60 | 4.4 | 7.75 | 0.57 |
| 65 | 4.6 | 8.06 | 0.57 |
| 70 | 4.8 | 8.36 | 0.57 |

The constancy of the term in the last column (slope) shows that the reduction process is diffusion controlled.



Effect of concentration on E½ values

E½ values of benzyldimethylsulphonium bromide in pH 7 buffer solution were determined at various concentrations.

| Concentration x $10^3$/M | E½ (V) |
|---|---|
| 2 | -1.30 |
| 3 | -1.29 |
| 4 | -1.29 |
| 5 | -1.29 |
| 6 | -1.29 |

The concentration invariance of E½ shows that the process is diffusion controlled.

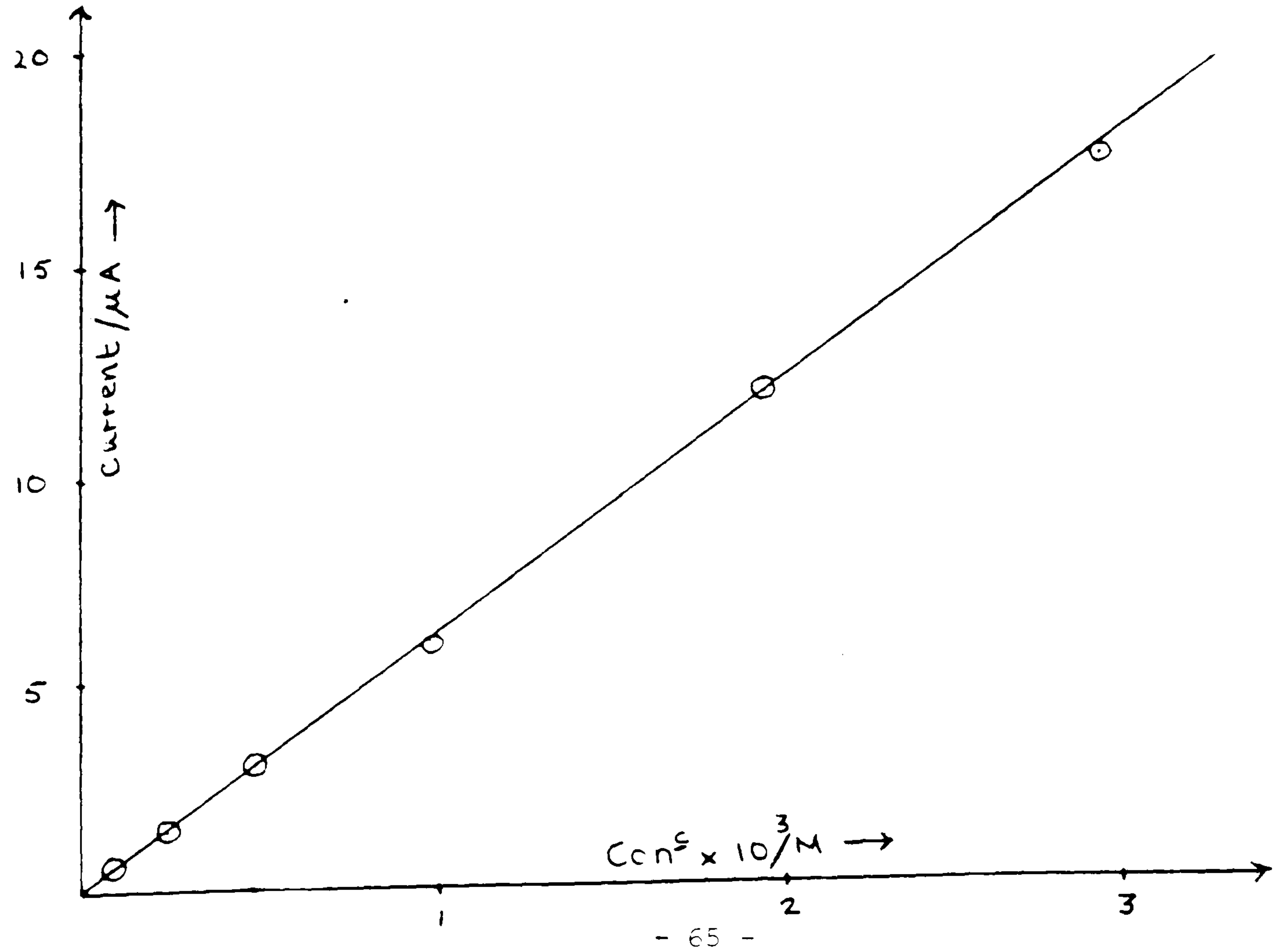
Diffusion current, Īd, as a function of concentration

Polarographic solutions were made in phosphate buffer (pH 7) in the 0.1 to 3.0 x $10^{-3}$ M range and their polarograms recorded; the diffusion currents were measured to test whether the limiting currents were proportional to the depolariser concentration, so that they could be used for the quantitative estimation of the sulphonium salts.

The strict proportionality is also another criterion for showing that the process is diffusion controlled.

1-benzylthioniacyclopentane bromide:

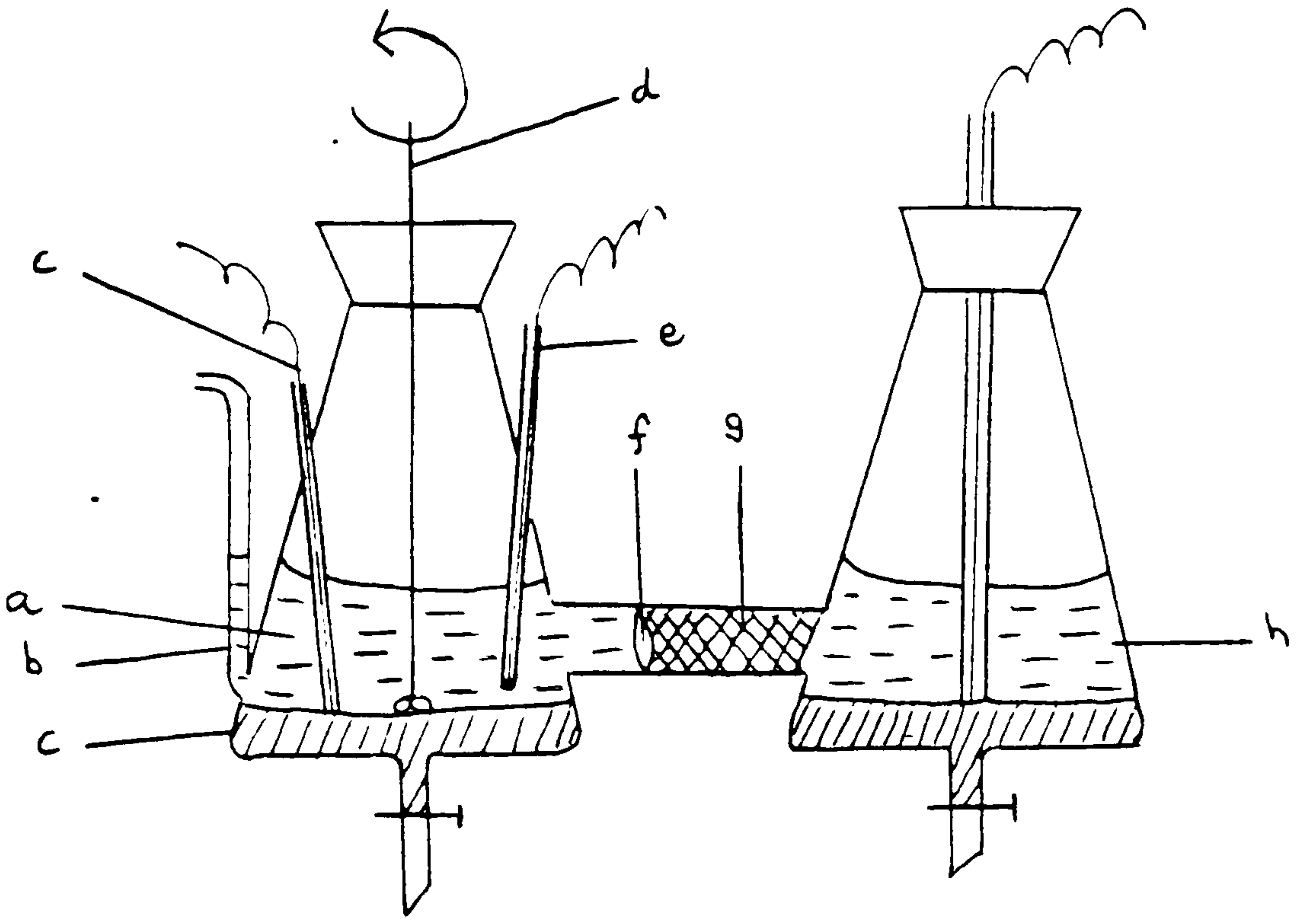
| Concentration x $10^3$/M | Īd/$\mu$A |
|---|---|
| 0.10 | 0.62 |
| 0.25 | 1.50 |
| 0.50 | 3.00 |
| 1.00 | 5.90 |
| 2.00 | 11.80 |
| 3.00 | 17.40 |



### (b) Coulometry

Apparatus:

A diagram of the cell used for the coulometry (and large-scale macroscopic reductions) is shown below:

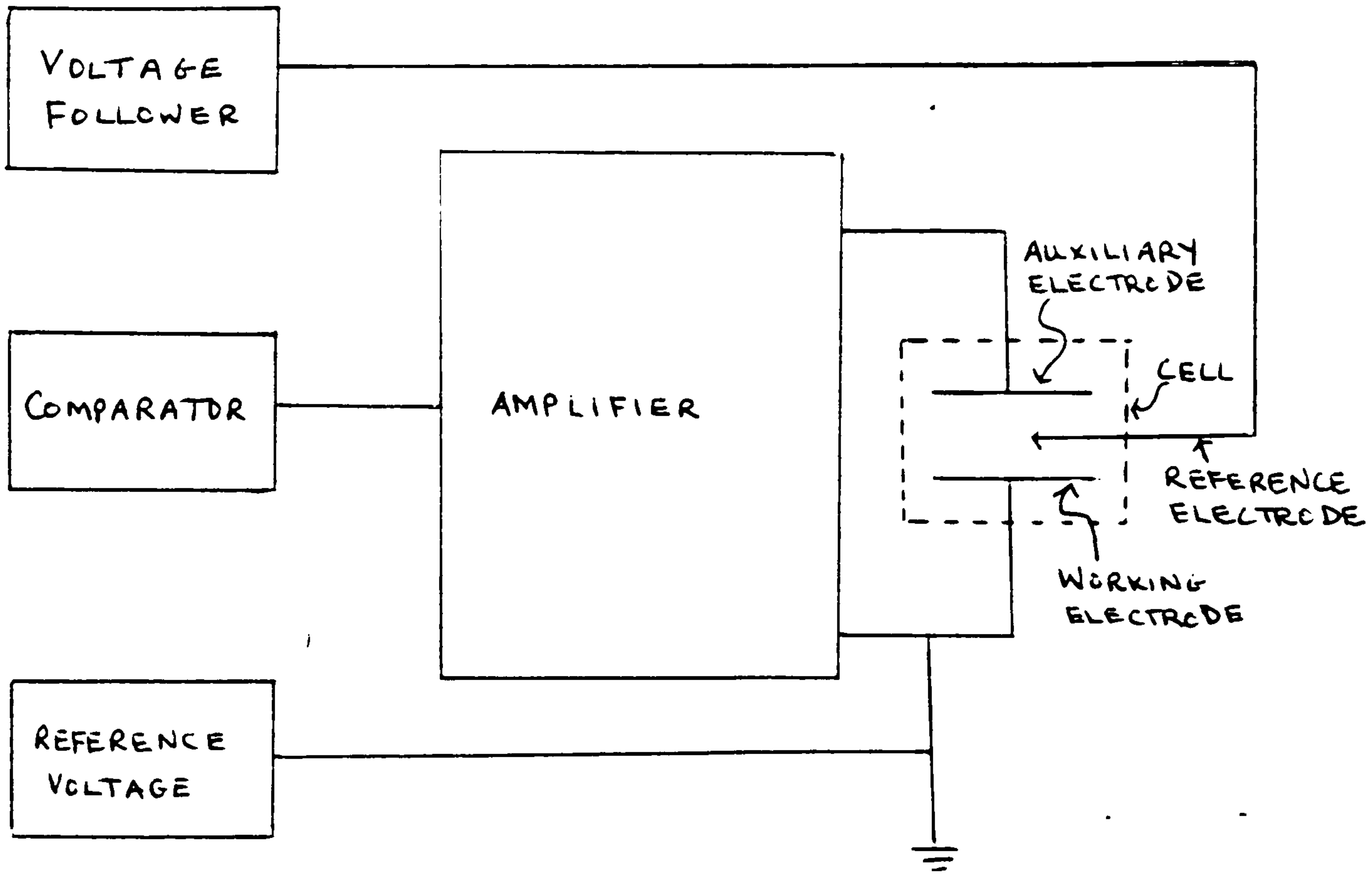


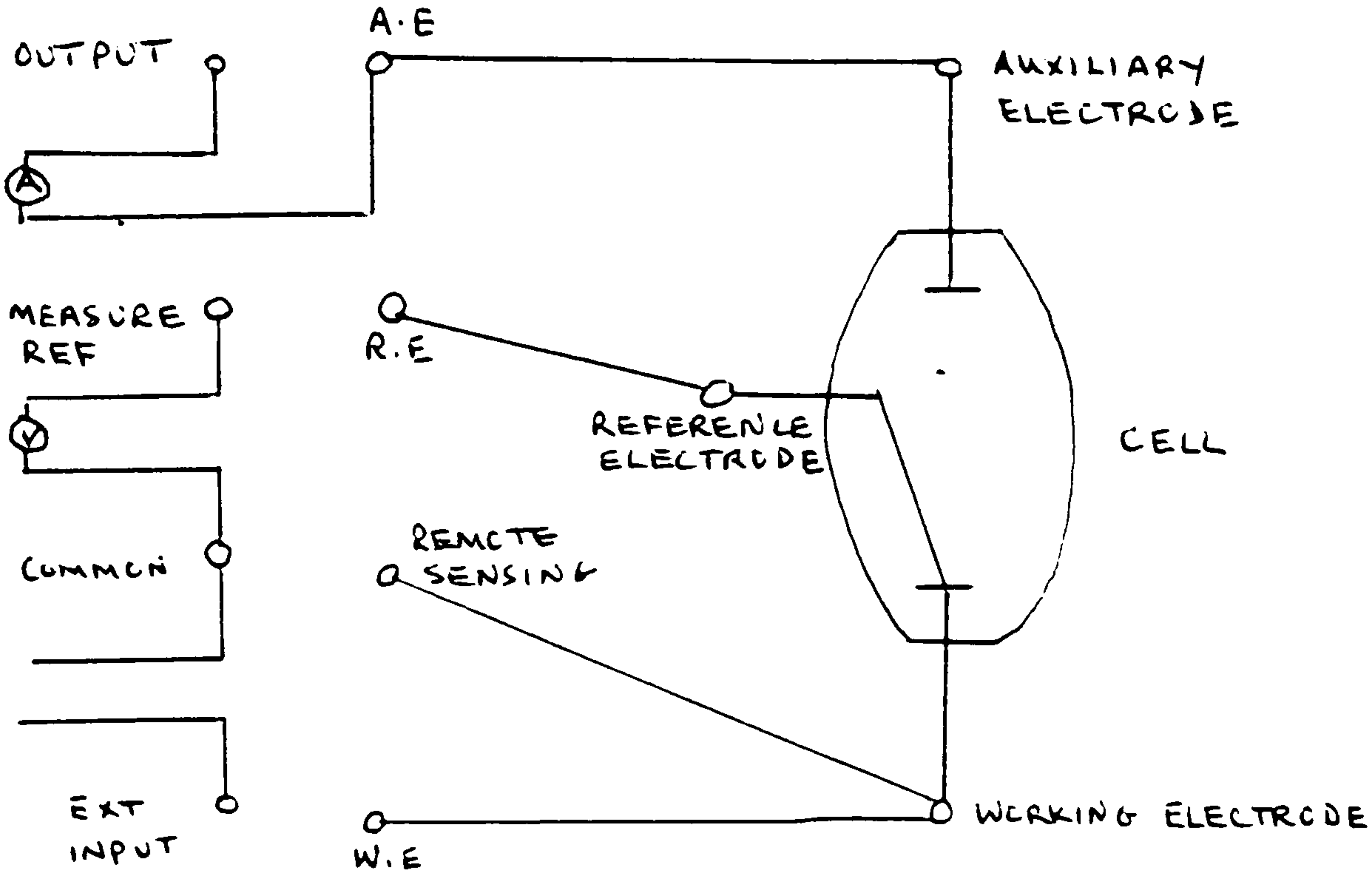
Electrolysis cell for coulometric and macroscopic reductions

a - depolariser
b - gas inlet tube ($N_2$)
c - working cathode
d - mechanical stirrer
e - reference electrode
f - fine glass frit
g - agar/KCl salt bridge
h - auxiliary electrode

The applied working potential was kept constant by a potentiostat (TA251 Ministat) and a Wenking SS170 Coulomb Integrator was used to measure the number of coulombs.

# THE POTENTIOSTAT





CONNECTION DIAGRAM

## General Method of Coulometry

A known amount of sulphonium salt, sufficient to give an approximate M x $10^{-3}$ solution in buffer was electrolysed at a potential corresponding to the polarographic wave plateau until the current fell to a constant small residual current value. A coulometry-time plot was recorded and allowances made for the residual current contribution. The observed coulomb value was compared with those calculated for one or two electron processes. The resulting value of n, or rather, the nearest integer to n, was used for the polarogram, the assumption being that at the same concentration, the polarographic and macro-reduction processes are very likely to be the same. This is not so for macroscopic reductions at much higher concentrations.

The following example illustrates the method:

Salt = p-methylbenzyldimethylsulphonium bromide ($5 \times 10^{-4}$ moles)

Total coulombs used in reduction = 97.4

Residual current = 1.2 mA.

Time of reduction = 22 min.

$$\text{Coulombs consumed by residual current} = \frac{22 \times 60 \times 1.2}{1000} = 1.584$$

Coulombs used in reduction of substrate = 97.4 - 1.584 = 95.816

Theoretical coulomb value for 1 electron reduction

$= 96500 \times 5 \times 10^{-4} = 48.25$

$$n = \frac{95.816}{48.25} = 1.98$$

The results are shown in table 7.

TABLE 7

Coulometry

Substituted sulphonium salts $XC_6H_4CH_2\overset{+}{S}R_2\ Y^-$

| X | (R) | Y | n |
|---|---|---|---|
| H | $C_2H_5$ | Br | 1.98 |
| H | $CH_3$ | Br | 1.99 |
| 2-$CH_3$ | $CH_3$ | Br | 2.03 |
| 3-$CH_3$ | $CH_3$ | Br | 2.02 |
| 4-$CH_3$ | $CH_3$ | Br | 1.98 |
| 4-Cl | $CH_3$ | Br | 1.98 |
| 4-Br | $CH_3$ | Br | 1.98 |
| H | $(CH_2)_4$ | Br | 1.96 |
| 2-$CH_3$ | $(CH_2)_4$ | Br | 1.97 |
| 3-$CH_3$ | $(CH_2)_4$ | Br | 1.93 |
| 4-$CH_3$ | $(CH_2)_4$ | Br | 1.99 |
| 4-Cl | $(CH_2)_4$ | Cl | 1.97 |
| 4-Br | $(CH_2)_4$ | Br | 1.96 |
| 4-$NO_2$ | $CH_3$ | Br | - |
| H | $(CH_2)_5$ | Br | 2.00 |
| H | $(C_6H_5CH_2)$ | $HSO_4$ | - |
| 2-$(CH_3)_2\overset{+}{S}CH_2$ | $CH_3$ | 2Br | 4.00 |
| 3-$(CH_3)_2\overset{+}{S}CH_2$ | $CH_3$ | 2Br | 3.97 |
| 4-$(CH_3)_2\overset{+}{S}CH_2$ | $CH_3$ | 2Br | 1.99 |
| o-$(CH_2)_4\overset{+}{S}CH_2$ | $(CH_2)_4$ | 2Br | 3.98 |
| m-$(CH_2)_4\overset{+}{S}CH_2$ | $(CH_2)_4$ | 2Br | 4.01 |
| p-$(CH_2)_4\overset{+}{S}CH_2$ | $(CH_2)_4$ | 2Br | 1.98 |

## (c) Preparative electrolysis

General method for macroscopic reductions.

These were carried out using the same apparatus as used for coulometry but with larger amounts of the depolariser (approx. $10^{-1}$M). At the end of the electrolysis the products were extracted with ether and analysed. The volatile products ($ArCH_3$ and possible $ArCH_2SR$ and $ArCH_2CH_2Ar$) were detected and estimated by gas liquid chromatography (glc) using a marker as calibrator. The non-volatile products $(ArCH_2)_2Hg$ and/or $ArCH_2CH_2Ar$, were isolated by evaporating the ether extract. Any dibenzylmercury compound was detected visually during the electrolysis because of its insolubility in water. (The coulometry of this process allowed us to monitor relative proportion of concurrent 1 and 2 electron processes.)

The following example is typical of the method.

The macroscopic reduction of benzyldimethylsulphonium bromide: an aqueous solution (50 $cm^3$, 0.1 M potassium chloride) of benzyldimethylsulphonium bromide (1.5 g) was electrolysed at 0°C at a stirred mercury cathode using a working potential of -1.45 volts (polarogram plateau), under an atmosphere of nitrogen, for 70 minutes until almost zero current (1 mA). Total number of coulombs passed were 1204, taking the residual current into account, this was equivalent to 1.93 moles of electrons. At the end of the electrolysis the products were extracted with ether (25 $cm^3$) and 0.1 $cm^3$ of marker (p-xylene) was added and the mixture analysed by glc using an OV1 column at a working temperature of 90°C. Toluene (97%) was the only product. Evaporation of the ether extract gave no solid residue.

## Effect of temperature on product distribution

### (i) Reduction of benzyldimethylsulphonium bromide

A solution of the salt (50 $cm^3$) was degassed with nitrogen prior to electrolysis and a very slow flow maintained to exclude air during the electrolysis.

Salt concentration = $10^{-1}$ M

Supporting electrolyte = B.D.H. buffer, pH7

Working potential -1.4 v

| Temperature/°C | $C_6H_5CH_3$%* | $(C_6H_5CH_2)_2Hg$% | n |
|---|---|---|---|
| 0 | 97 | 0 | 1.93 |
| 25 | 84 | 0 | 1.85 |
| 45 | 80 | 0 | 1.83 |
| 50 | 68 | 0 | 1.82 |
| 60 | 62 | 0 | 1.79 |
| 80 | a | 16 | 1.62 |

a-not determined

### (ii) Reduction of 1-benzylthioniacyclopentane bromide

Method as above.

Concentration = $10^{-1}$ M

Supporting electrolyte potassium chloride (0.1 Molar)

Working potential -1.4 v

| Temperature/°C | $C_6H_5CH_3$ %* | $(C_6H_5CH_2)_2Hg$% | n |
|---|---|---|---|
| 2 | 84 | 9 | 1.84 |
| 25 | 58 | 19 | 1.43 |
| 35 | 32 | 45 | 1.21 |
| 60 | - | 89 | 1.16 |

* Analysed by glc using an OV1 column at 90°C.

### (iii) Reduction of p-methylbenzylsulphonium bromide

Method as above.

Concentration 0.12 M

Supporting electrolyte potassium chloride (0.1 Molar)

Working potential = 1.4 v

| Temperature | p-xylene %* | $(p\text{-}CH_3C_6H_4CH_2)_2Hg$ % | n |
|---|---|---|---|
| 0 | 89 | 8 | 1.93 |
| 10 | 86 | 10 | 1.86 |
| 25 | 79.7 | 14.4 | 1.80 |
| 30 | 74.0 | 17.2 | 1.71 |
| 47 | 46.9 | 36 | 1.50 |
| 60 | 18.8 | 60 | 1.42 |
| 80 | - | 82.4 | 1.15 |

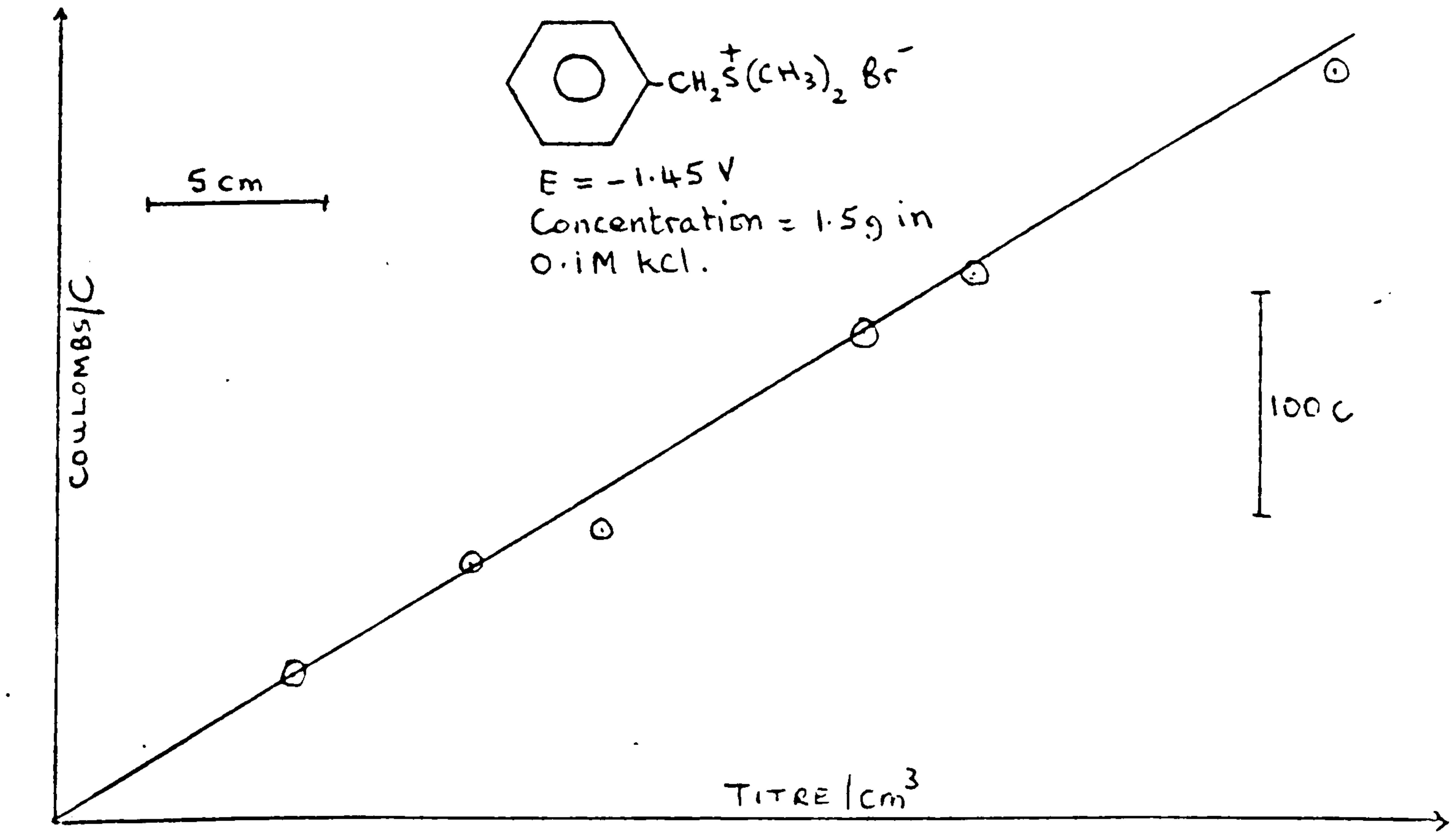
* Analysed by glc using a Silar 5 cp column at 150°C.

Procedure for the accurate determination of toluene

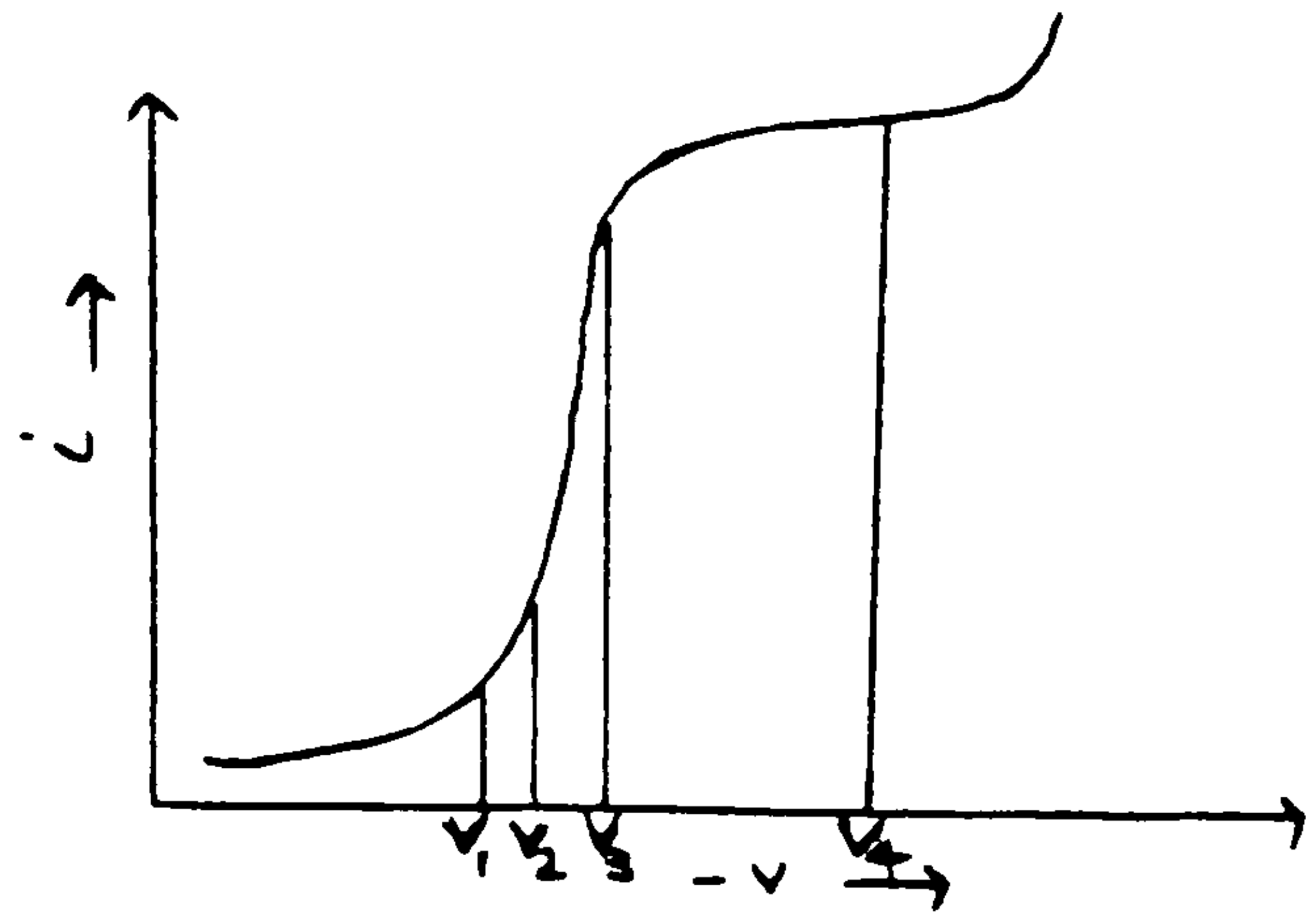
The volatility of toluene makes the quantitative determination of this product less accurate at elevated temperatures, so the following method was devised for the indirect determination of toluene. It is based on the scheme:

$$\begin{tikzcd}
R_2\overset{+}{S}CH_2C_6H_5 + 2e \arrow[r] & R_2S + C_6H_5CH_2^- \arrow[d, "H_2O"] \\
 & OH^- + C_6H_5CH_3
\end{tikzcd}$$

The assumption in this method is that the toluene arises solely by proton transfer to the benzyl anion (or a complexed benzyl anion). The method was tested by electrolysing a solution of benzyldimethylsulphonium bromide and titrating with standardised acid at known coulometric values. The hydroxyl ion concentration can be determined with standard acid. The coulomb/acid titre graph gave a straight line. This method was devised too late in the investigation to be used in this work.



Effect of applied working potential



Both coulometric ($5 \times 10^{-4}$ M) and macroscopic ($10^{-1}$ M) electrolysis were carried out at different applied working potentials, $V_1 - V_4$, at constant temperature until almost zero current. A gradual change in n value was observed.

Benzyldimethylsulphonium bromide

| Applied voltage/v | n |
|---|---|
| -1.4 | 1.89 |
| -1.3 | 1.77 |
| -1.2 | 1.11 |
| -1.1 | 1.06 |

This variance in n values was reflected in the final product distribution: a change from an almost two electron process, resulting in toluene formation, to a one electron process giving dibenzylmercury.

Benzyldimethylsulphonium bromide

| Applied potential/v | $C_6H_5CH_3$% | $(C_6H_5CH_2)_2Hg$% |
|---|---|---|
| -1.4 | 97 | - |
| -1.3 | 80 | 16 |
| -1.2 | 14 | 83 |
| -1.1 | 6 | 91 |

## Electrolysis of p-nitrobenzyldimethylsulphonium bromide

The sulphonium salt (50 $cm^3$ of $10^{-1}$ M solution) in BDH phosphate buffer pH 7, was placed in the cathode chamber and the reduction allowed to proceed at a constant working plateau potential (E = -0.8V). In approximately 30 minutes the current between the working electrode fell from 450 mA to 0.8 mA. When this steady current was reached the electrolysis was stopped, and the catholyte worked up.

The solid product was filtered off and the filtrate was extracted with ether which was dried over calcium chloride. Removing the ether in vacuo afforded more of the solid.

The total weight of the product = 0.67 g (98%).

mp 183°C (lit 180-185°C) (12).

Number of coulombs used in the reduction = 498·4 this is equivalent to 1.03 electrons.

Total coulombs used in reduction = 498.4

Residual current = 0.8 mA.

Time of reduction = 30 min.

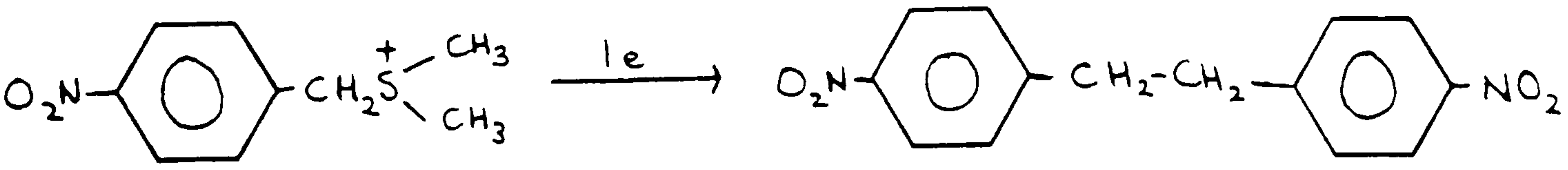
$\therefore$ coulombs consumed by residual current = $\frac{30 \times 60 \times 0.8}{1000}$ = 1.44

$\therefore$ coulombs used in reduction of substrate = 498.4 - 1.4 = 497

Theoretical coulomb value for 1 electron reduction = $96500 \times \frac{1}{200}$ = 482.5

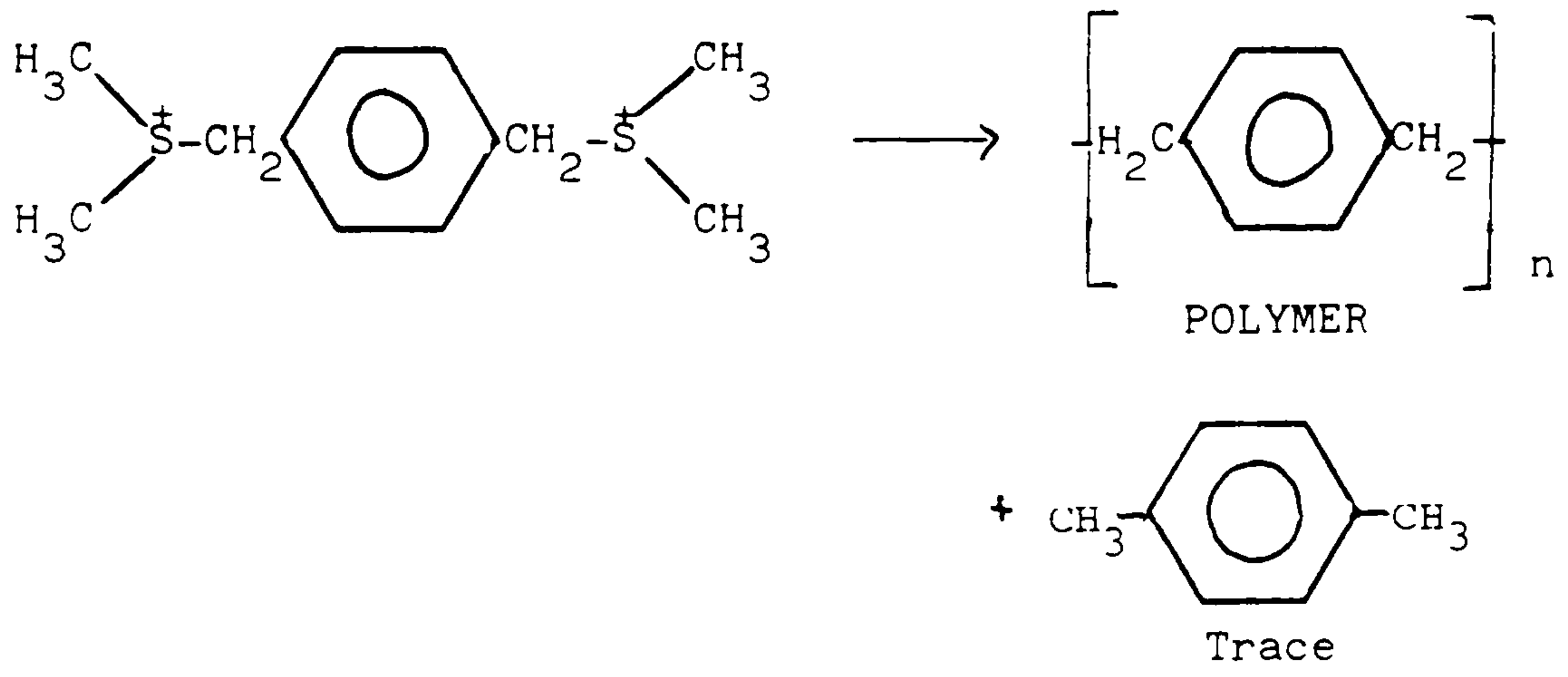
$\therefore$ n value = $\frac{497}{482.5}$ = 1.03

The $^1H$ nmr spectrum of the product was consistent with the structure for 4,4'-dinitrobibenzyl.



## Electrolysis of p-xylylenebis(dimethylsulphonium bromide)

An aqueous solution (50 $cm^3$; buffer pH 7) of the salt (1.5 g) was electrolysed at a working potential of -1.2 volts (polarogram plateau), for two hours, at a stirred mercury cathode under an atmosphere of nitrogen until almost zero current. The resulting product was filtered off and dried in a vacuum and was identified by its mass spectrum as being poly-p-xylylene. Yield 0.39 g (97%), mp. >300°C. Coulometry equivalent to $n = 2$ electrons. The aqueous fraction was extracted with ether and chromatographed; only a trace of p-xylene was detected.



No p-cyclophane was detected.

## Identification of polymeric product

The polymeric material was identified by elemental analysis, infra-red and mass spectra.

Analysis: calculated: C, 92.13%; H, 7.69%

found: C, 92.28%; H, 7.52%

The infra-red spectrum (film) of the polymer gave a band (820 $cm^{-1}$) corresponding to a p-substituted benzene system.

The mass spectrum shows a regular repeat unit degradation of the polymer, resulting in groups of peaks centred at: 726, 624, 520, 415, 311, 207, 105. This is indicative of the p-xylylene unit being present in the polymer. (See page 146).

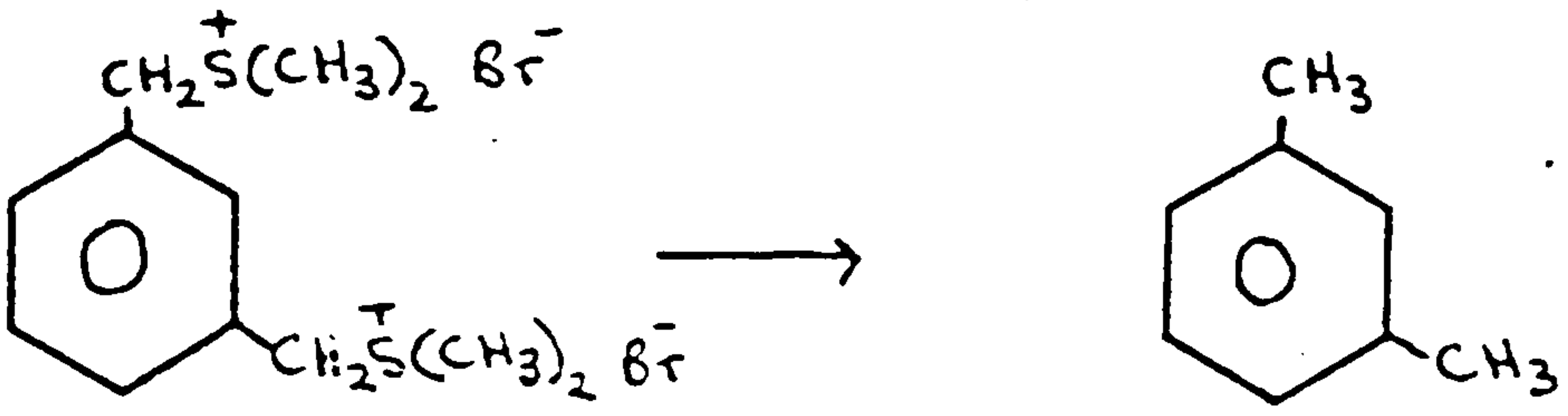
## Electrolysis of m-xylylenebis(dimethylsulphonium bromide)

The same method as for the para- salt using the conditions below:

| | |
|---|---|
| sulphonium salt | 1.5 g |
| supporting electrolyte | BDH phosphate buffer (pH 7) |
| applied potential* | -1.4 volts |
| current range | 550 to 3 mA (residual current) |
| coulometry | 3.94 electron equivalents |
| yield of product m-xylene | 97%[✱] |

* electrolysis carried out at the plateau of the second polarographic wave.

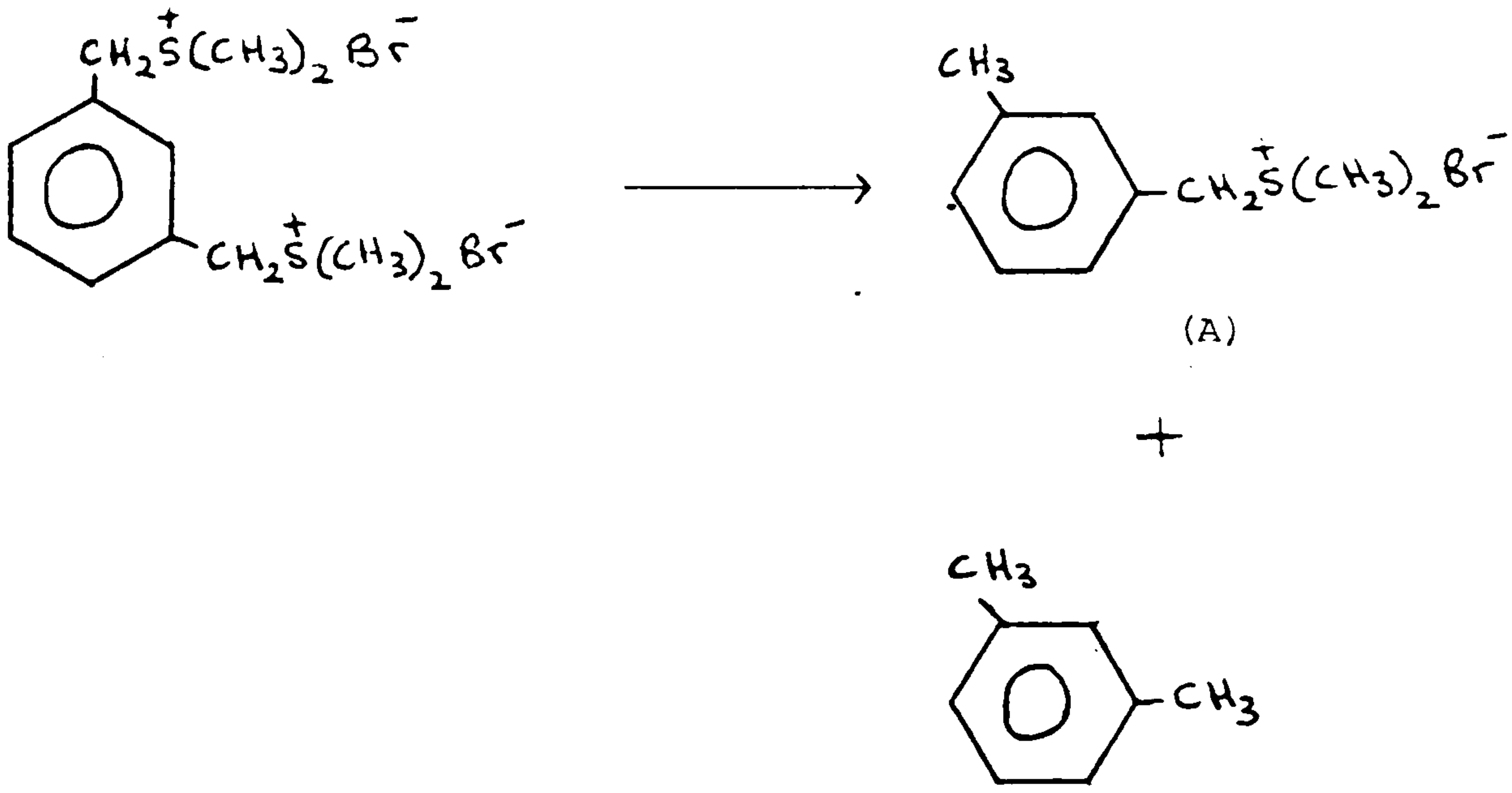
[✱] analysed by glc; conditions: column temperature 168°C, using a Silar 5 cp column.



### (b) Electrolysis at the 'kink' potential of the polarogram

The conditions and results are shown below:

| | |
|---|---|
| sulphonium salt | 1.5 g |
| supporting electrolyte | BDH phosphate buffer (pH 7) |
| applied potential | -1.16 volts |
| current range | 300 to 2 mA. |
| coulometry | 2.0 electron equivalents |
| yield of product (A) | 95% (estimated by polarography)<br>$E_{1/2} = -1.33$ v |



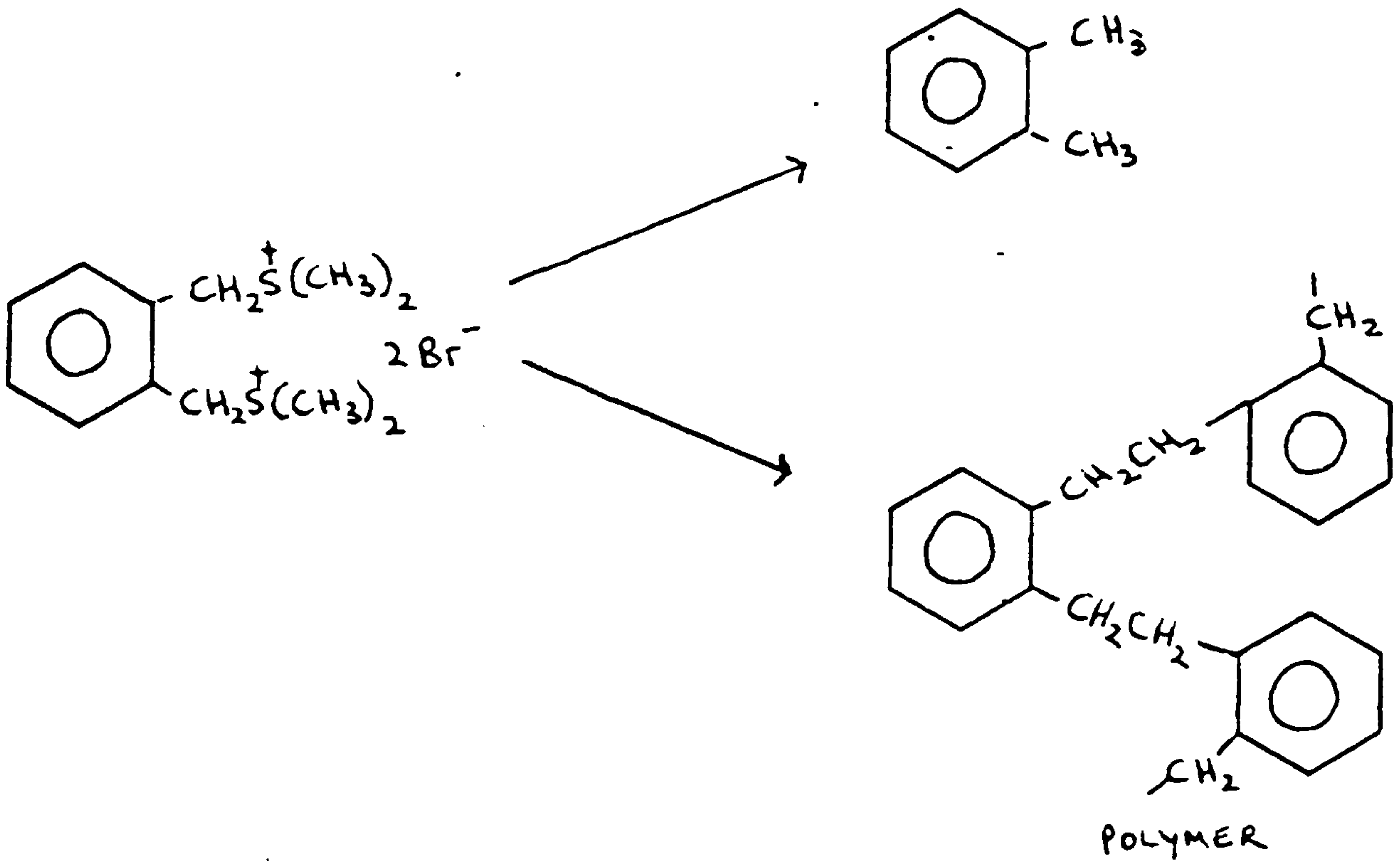
(A)

## Electrolysis of o-xylylenebis(dimethylsulphonium bromide)

The procedure was the same as for the para- salt. The conditions and results are shown below.

(a)

| | |
|---|---|
| sulphonium salt | 1.5 g |
| supporting electrolyte | BDH phosphate buffer (pH 7) |
| applied potential | -1.4 volts |
| current range | 400 to 5 mA (residual current) |
| coulometry | 3.9 electron equivalents |
| yield of polymer | 21% |
| yield of o-xylene | 72%* |



* Analysed by glc, using a Silar 5 cp column at 169°C.

(b) Electrolysis at the plateau of the first polarographic wave:

The conditions and results are shown below:

| | |
|---|---|
| sulphonium salt | 1.5 g |
| supporting electrolyte | BDH phosphate buffer (pH 7) |
| applied potential | -0.95 volts |
| current range | 350 to 8 mA(residual current) |
| coulometry | 2.2 electron equivalents |
| yield of o-xylene | 11%* |
| yield of polymer | 82%, mp > 300°C. |

---

* Analysed by glc, using a Silar 5 cp column at 169°C.

## DISCUSSION

Although the elucidation of the reduction mechanism of reduction draws on both polarography and macroscopic reduction studies, it is convenient to discuss the polarography first.

Nearly all the sulphonium salts gave smooth wave polarograms, independent of pH and of the same diffusion current for the same molar concentrations. All the coulometry values at this concentration corresponded to an overall two electron reduction process, consistent with cleavage of the carbon-sulphur bond to give the corresponding toluene:

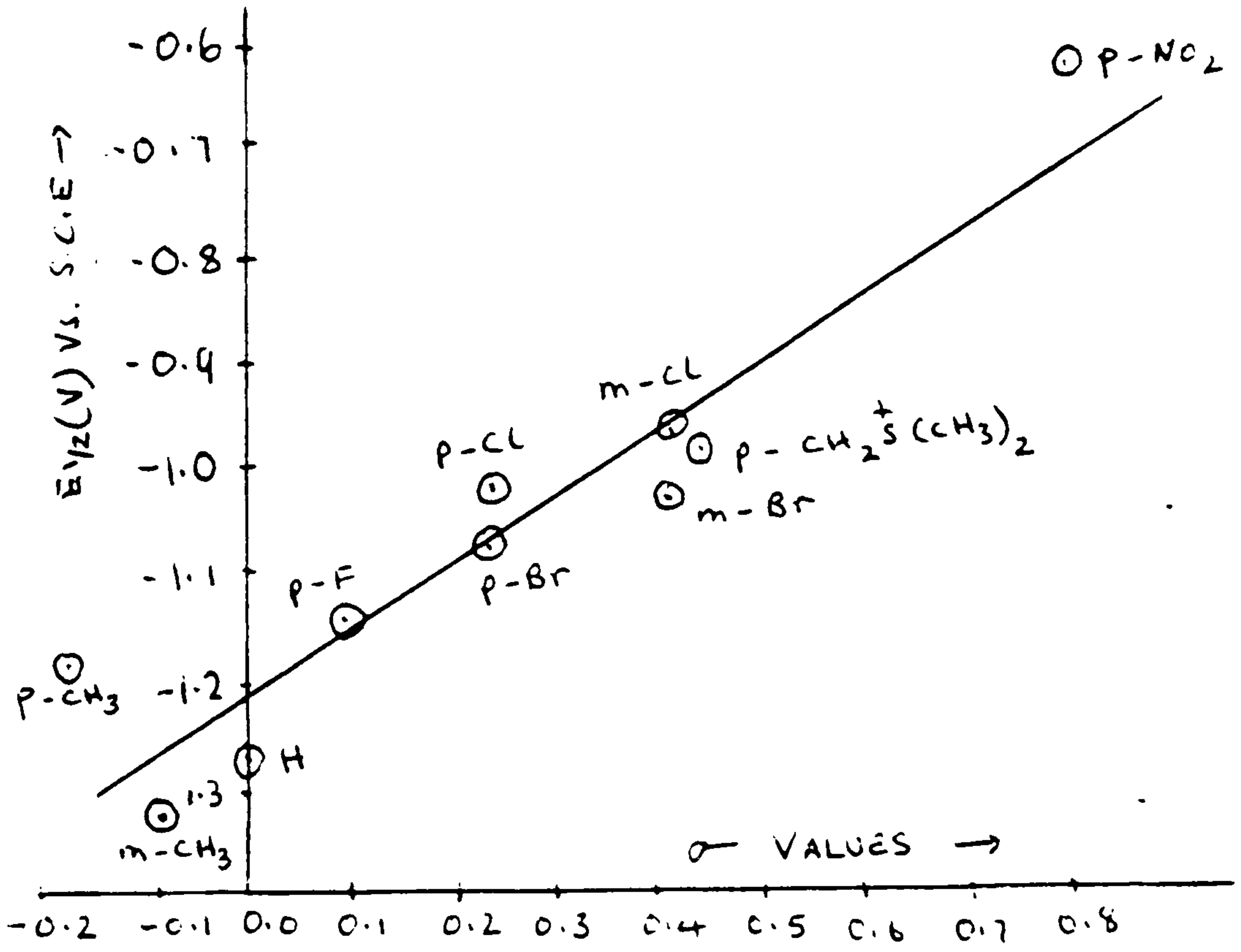
$$\text{p-XC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2\text{Br}^- \xrightarrow{2e/\overset{+}{\text{H}}} \text{p-XC}_6\text{H}_4\text{CH}_3 + \text{S(CH}_3)_2$$

The following series shows the effect of the para substituent on the ease of reduction:

| | E½ (V) |
|---|---|
| $\text{C}_6\text{H}_5\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -1.28 |
| $\text{p-FC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -1.15 |
| $\text{p-ClC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -1.02 |
| $\text{p-BrC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -1.08 |
| $\text{p-CH}_3\text{C}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -1.18 |
| $\text{p-O}_2\text{NC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}(\text{CH}_3)_2$ | -0.63 |

The half-wave potential (E½) show that para-substituents cause a decrease in E½ values relative to the parent compound: i.e. para-substituents increase the ease of reduction.

The half-wave potentials of para-substituted benzylsulphonium salts in pH 7 buffer are plotted against Hammett $\sigma$ Values in the diagram. Some meta-substituted salts values are also included in the diagram.



A best straight line has been drawn but it is obvious that there is appreciable scatter about the line and the plot shows a poor free energy relationship.

Increased ease of reduction is not unexpected for electronegative substituents and is consistent with a two electron reduction to give the anion. However, the para-methyl group also enhances the reduction. This is inexplicable with the single step transfer of two electrons to give the anion, as the methyl group should destabilise this, but it is consistent with a one electron transfer to give a radical, since all substituents tend to stabilise radicals.

Similar effects were observed by Grimshaw et al( 36 ) in the polarographic reduction of benzyl bromides:

| $p\text{-}XC_6H_4CH_2Br$ | X | E½ (Volts)* |
|---|---|---|
| | H | -1.13 |
| | Cl | -1.05 |
| | $CH_3$ | -1.08 |
| | $CH_3O$ | -1.19 |
| | $NO_2$ | -0.40 |

* E½ values for methanol solution; lithium chloride as the supporting electrolyte.

In macroscopic reductions Grimshaw and Ramsey reported that para- substituted benzyl bromides having negative or small positive $\sigma$ values, e.g. alkyl, tended to favour formation of the organomercury product, whereas substituents with a large positive $\sigma$ value e.g. the nitro group gave only the dimer( 37 ). Substituents with intermediate $\sigma$ values gave a mixture of organomercury compound and dimer. A similar trend was observed in our work e.g. p-methylbenzyldimethylsulphonium bromide reduced more readily than the unsubstituted salt and it is interesting to note that whereas the ortho- and para-methyl salts gave the organomercury compound, the meta- methyl salt did not. The para- nitro salt gave only dimer product: it would appear that the nitro group destabilises the sulphonium radical $p\text{-}NO_2C_6H_4CH_2\dot{S}(CH_3)_2$, to give a highly stabilised radical $p\text{-}NO_2C_6H_4\dot{C}H_2$ which dimerises. It is noteworthy that, unlike the workers with benzyl halides, we never observed the simultaneous formation of coupled and organomercury products.

A Hammett treatment of substituted benzyl bromides E½ values gave a similar unsatisfactory relationship, with significant scatter about the best straight line. Streitwieser and Perrin(38) found a similar poor Hammett relationship for the polarographic reduction of benzyl chlorides ($\rho$ = 0.39 v) and concluded that the poor correlation of half wave potentials with $\sigma$ was due to "the special requirement of a transition state which strikes a balance between radical and anion character". The slopes indicate that the sulphonium salts ($\rho$ = 0.5 v) are more sensitive to substituents than the benzyl halide. However it should be noted that the solvents were different.

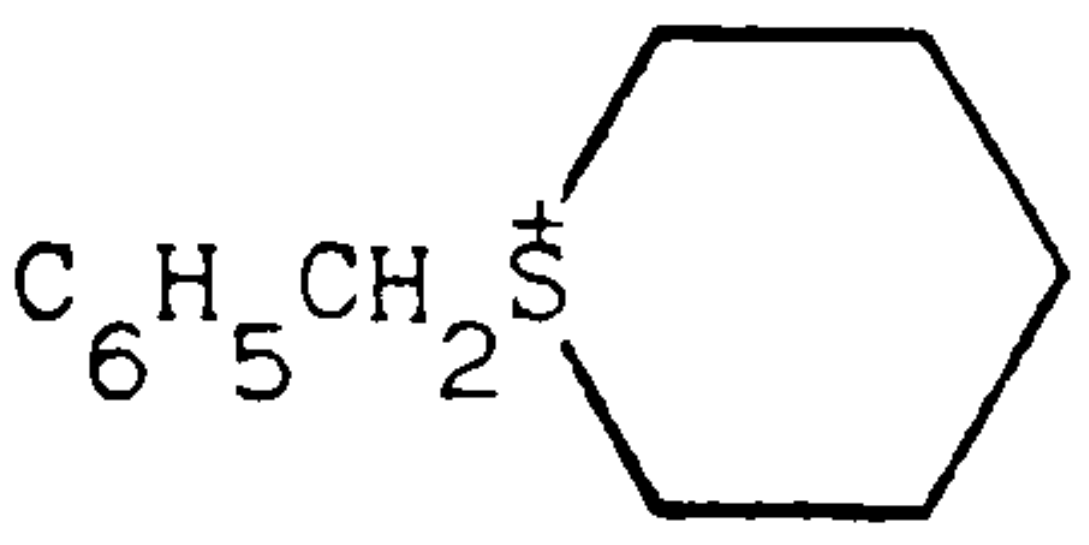
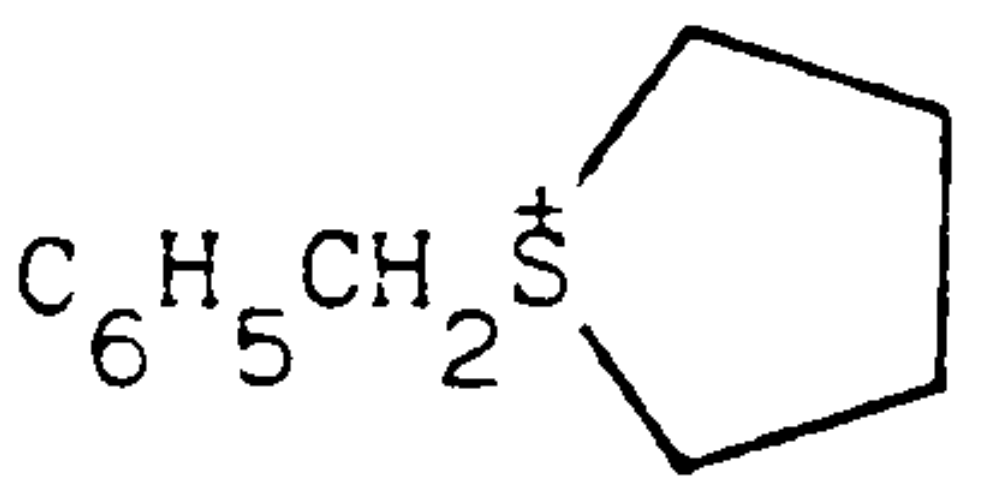
## The Effect of Chain Length of R Groups on E½ Values:

| $C_6H_5CH_2\overset{+}{S}(CH_3)_2$ | $C_6H_5CH_2\overset{+}{S}(C_2H_5)_2$ | $C_6H_5CH_2\overset{+}{S}(C_3H_7)_2$ | $C_6H_5CH_2\overset{+}{S}(C_4H_9)_2$ |
|---|---|---|---|
| E½ (V) = -1.28 | -1.30 | -1.20 | -1.08 |

The polarogram slopes and diffusion current are all very similar and suggest the same reduction process in each case. The similar E½ values for the dimethyl and diethyl salts suggested that the size of the open chain ligand does not have a significant effect on the reduction, however, later work on salts with larger ligands (n-propyl and n-butyl), produced marked reduction in E½ values, and this was unexpected. It is not easy to find a convincing interpretation for this difference; it is difficult to see how polar or steric effects can account for it. Perhaps differential solvation effects are involved; the smaller group salts will be more solvated than the salts with larger and more hydrophobic groups, and if some desolvation is necessary for reaction at the electrode then this might be important. It is interesting that the thiacyclohexa salt (page 86) has almost the same value as the di-n-propyl compound. Benzylmethyl-n-dodecylsulphonium chloride also has a low E½ value (-1.11 v)(39). While this also fits with the trend discussed above, it must be remembered that the large R group makes this a 'detergent' type substrate and surface effects and/or micelle formation might be affecting the reduction process.

## The Effect of Cyclic R Groups on E½ Values

This part of the investigation was to determine the effect of ring size on the ease of reduction.

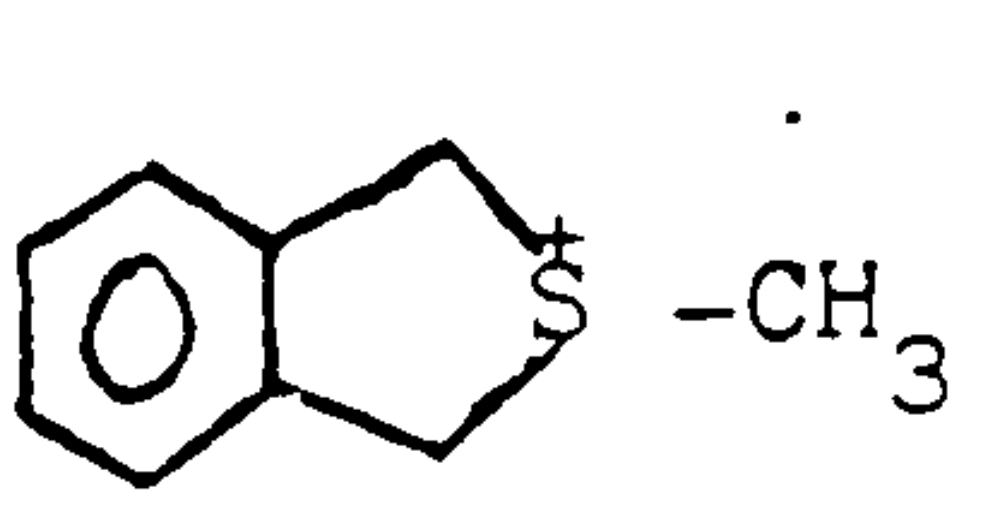
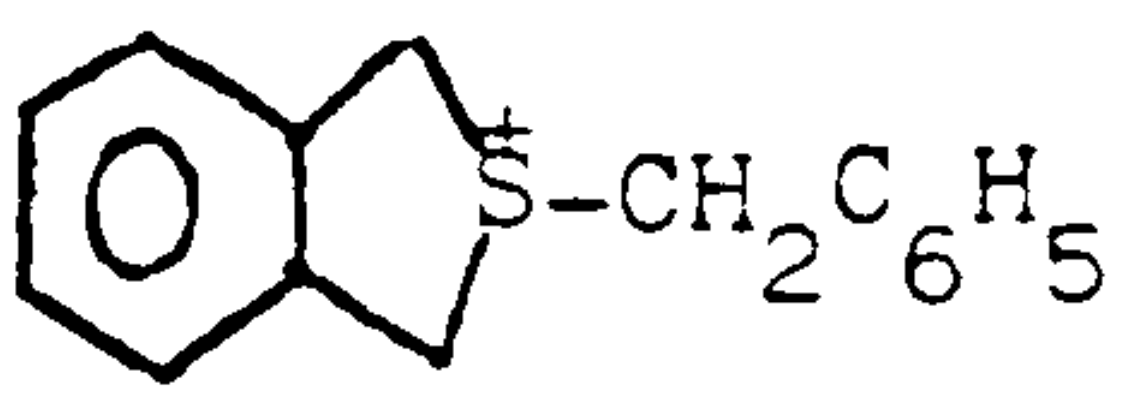
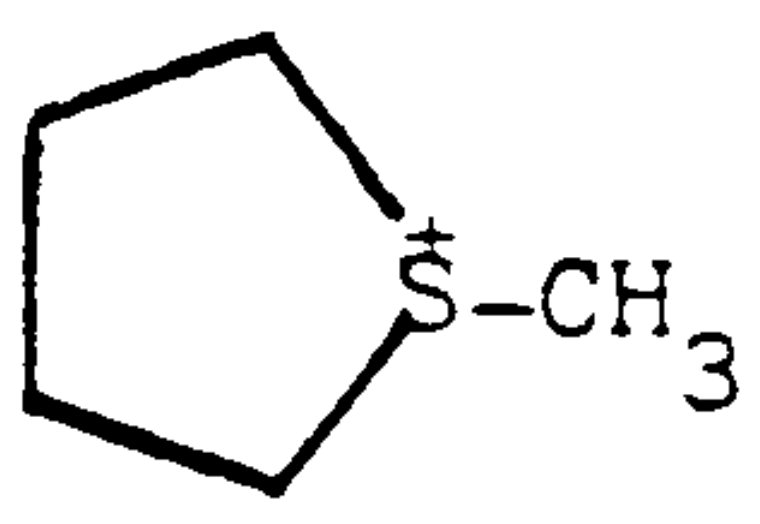
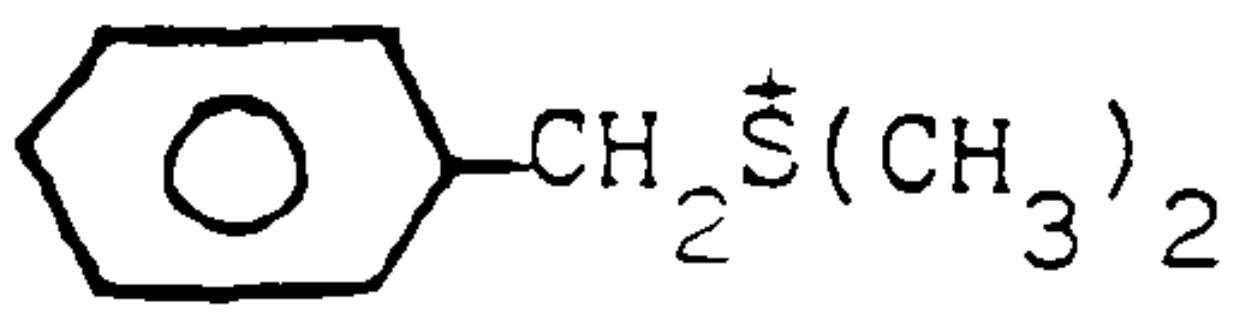
| | | | |
|---|---|---|---|
| $C_6H_5CH_2\overset{+}{S}(CH_3)_2$ | $C_6H_5CH_2\overset{+}{S}(C_2H_5)_2$ |  |  |
| E½(V) = -1.28 | -1.30 | -1.22 | -1.07 |

We had hoped to examine ring sizes 3-6 but encountered such difficulties with the syntheses of the small ring compounds that our results are mainly confined to the five- and six-membered rings.

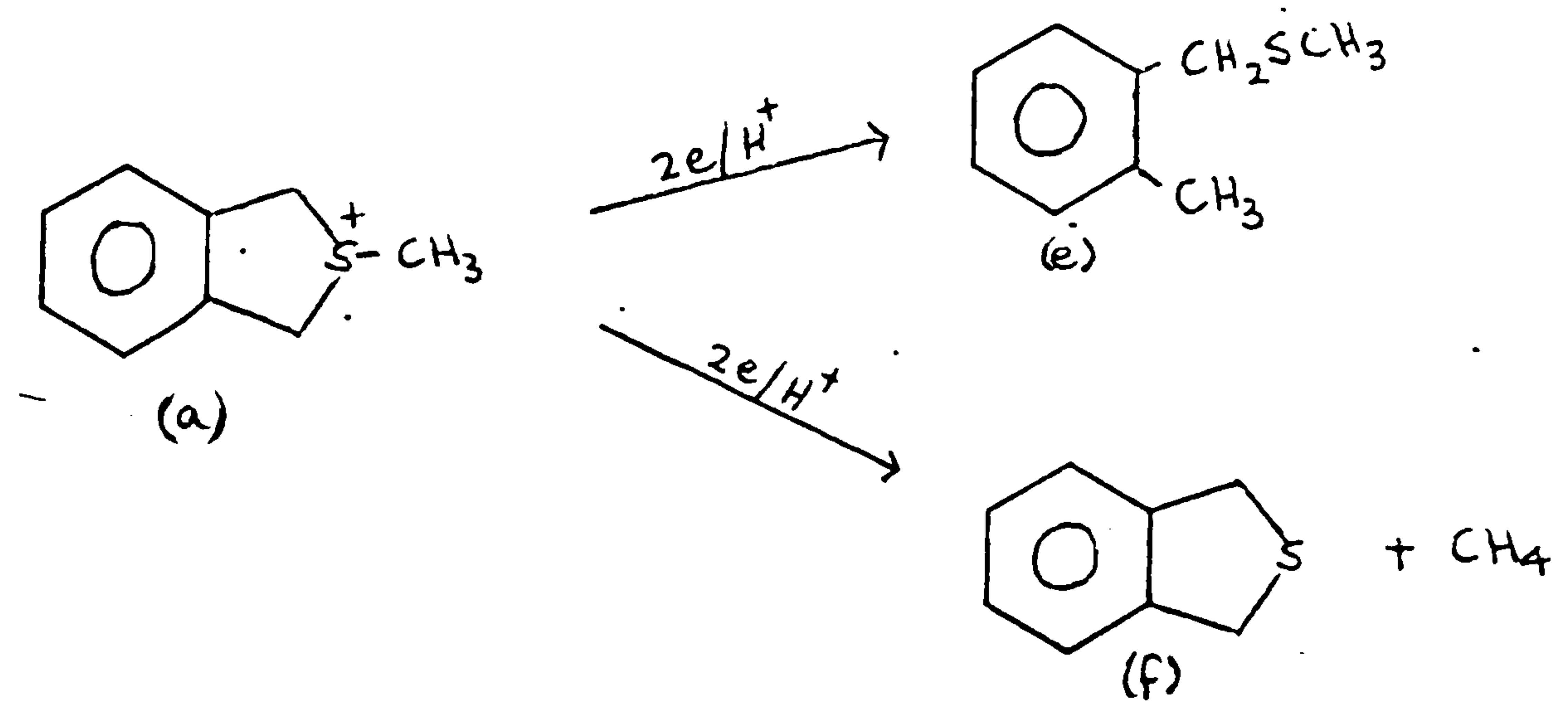
Compared with the analogous open chain salts, the puckered six-membered ring sulphur salt is very similar in ease of reduction but the five-membered ring salt is much more readily reduced. The higher reactivity of the five-membered ring is typical of the higher reactivity of the cyclopentyl group in carbon compounds and is probably related to the relief of eclipsing conformation compressions in the initial salt on cleavage of the C-$\overset{+}{S}$ bond. This easier reduction of the thiacyclopentane salt also applies to the p-chlorobenzyl and p-bromobenzyl salts as well (see page 57) although it is not so marked. This is as expected; the more stabilised the resulting benzyl group, the smaller the effect of the R group should be.

The substituents affect not only the E½ values but also the products in macroscopic electrochemical reductions: the thiacyclopentane salt formed dibenzylmercury more easily than the dimethyl salt and this finding could be of value in preparative chemistry. (See later section.)

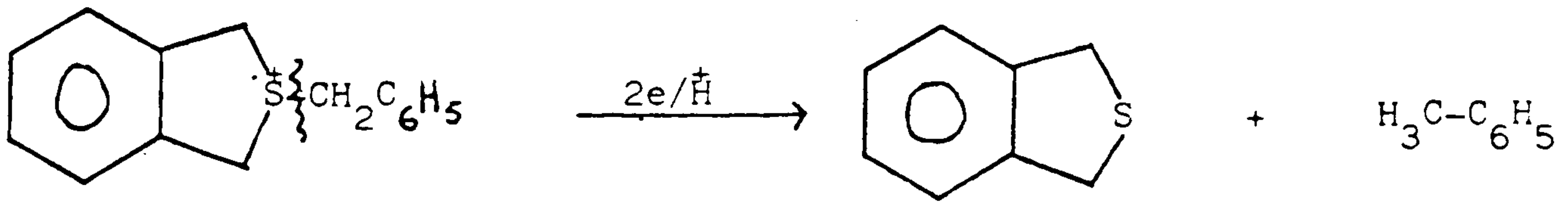
The benzthioniacyclopentane salts (a) and (b) were also investigated.

| | | | |
|---|---|---|---|
|  |  |  |  |
| (a) | (b) | (c) | (d) |
| E½(V) = -1.45 | -0.84 | $\geqslant$ -2.2 | -1.28 |

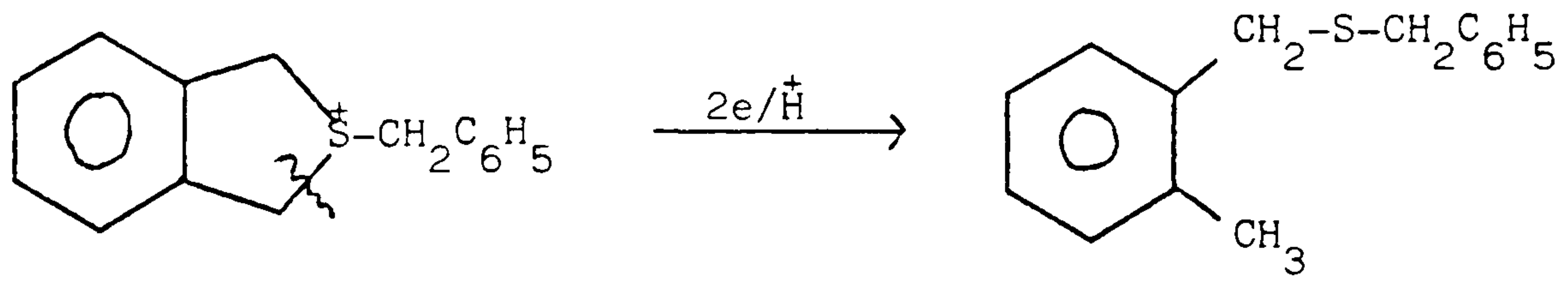
Structure (a) can be regarded not only as a thiocyclopentane derivative but also as a special kind of bis-benzyl sulphonium salt. Comparing (a) with the saturated parent thiacyclopentane salt (c) there is a large decrease in E½ value. However, comparing it with the open chain benzyldimethylsulphonium salt (d) the E½ value is higher. Controlled potential macroelectrolysis of compound (a) at a value corresponding to the plateau (V = -1.65) and isolation of the products showed that cleavage of the five-membered ring had occurred to give compound (e) instead of the product of $\overset{+}{S}-CH_3$ bond breakage (f).



The high value of E½ indicates that breaking of the ring C-S bond in (a) is more difficult than breaking of the benzylic C-S bond in (d) and presumably has some relationship to the stability of the five-membered ring. The benzyl salt (b) is much more readily reduced than the acyclic salt (d) and must have involved the cleavage shown.



This scheme was confirmed by microelectrolysis at the dropping mercury electrode using a plateau potential of -1.0 volts. After seven hours of electrolysis, isolation of products followed by glc analysis, showed the presence of toluene and the benzthiacyclopentane. These products were confirmed by 'spiking' the glc injections with authentic samples of these substances. The alternative cleavage to give (g)

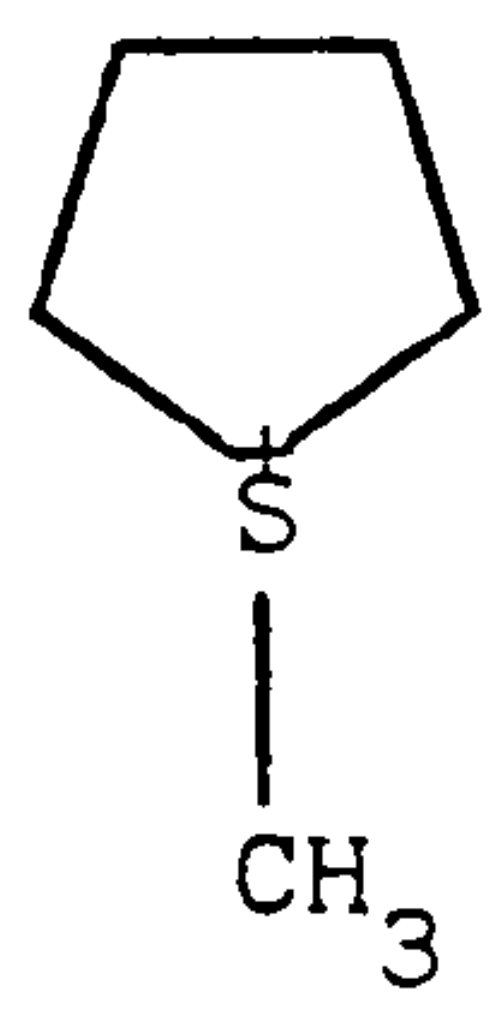
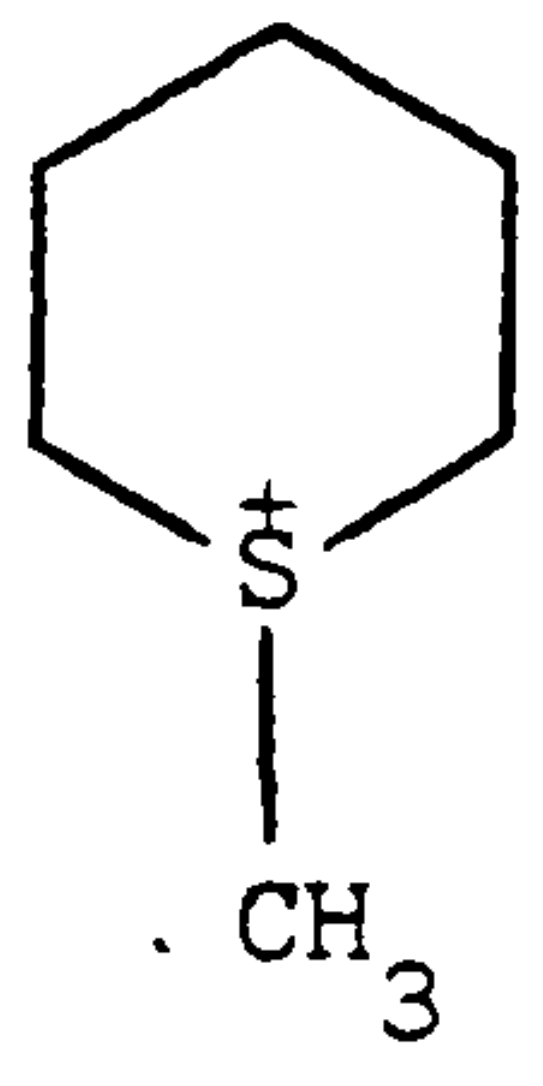


(g)

would have a E½ value very similar to (a). The very low value of E½ for (b) indicates that the benzthiacyclopentane group is a much better 'leaving group' in this electrolysis than the dimethylsulphide and thiacyclopentane groups.

Other cyclic sulphonium salts

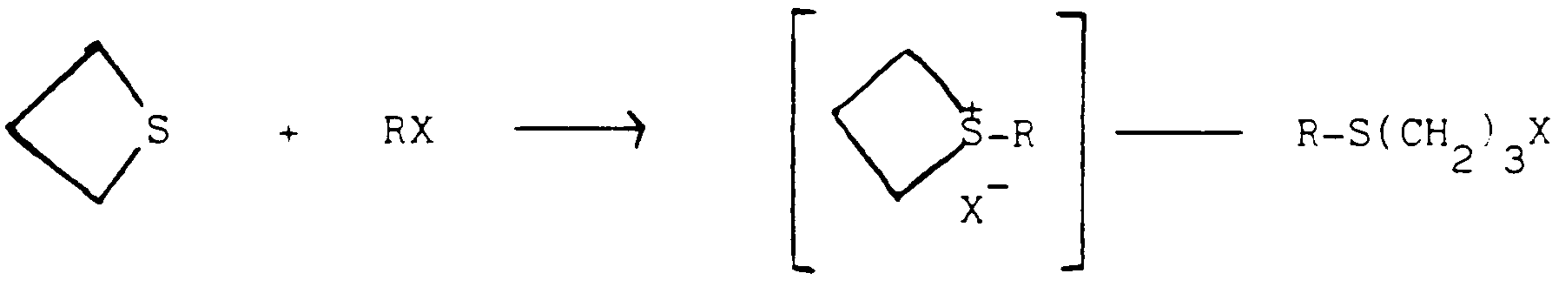
In connection with the attempted synthesis and examination of thietane sulphonium salts (see section 3), the methyl sulphonium salts of the five- and six-membered ring compounds were made for comparison. Neither of these salts gave a polarographic wave, indicating that the E½ values must be at least greater than -2.2 volts. To complete the comparison we prepared the diethylmethylsulphonium salt.

| | | | | | |
|---|---|---|---|---|---|
| |  |  | $\overset{+}{S}(C_2H_5)_3$ | $\overset{+}{S}(CH_3)_3$ | $H_3C-\overset{+}{S}(C_2H_5)_2$ |
| E½(V) | $\geqslant$ -2.2 | $\geqslant$ -2.2 | -1.86 | -1.88 | -1.82 |

These results are somethat unexpected because in the reduction of benzyl salts the five- and six-membered rings are better leaving groups than dimethyl sulphide and diethyl sulphide. We are unable to give a convincing explanation for these results.

## Thietane sulphonium salts

We wished to extend the sulphonium salt series to the four-membered thietanium salt; however, treatment of thietane with the 'normal' alkylating agents led to ring opened products, presumably by way of the intermediate thietanium ion.



This inaccessibility of the four-membered ring salt is probably due to the enhanced lability caused by ring strain: the ring opening reaction can occur by nucleophilic substitution at the α-carbon position.

We confirmed a literature report(40) that methyl iodide reacted with thietane to give the ring opened product, $(CH_3)_2\overset{+}{S}(CH_2)_2CH_2I\ I^-$, and showed that the $^1H$ nmr spectrum is consistent with this structure. Attempts to alkylate thietane using benzyl bromide with and without silver fluoroborate gave only the open chain products.

The purpose of adding silver tetrafluoroborate to the thietane and bromide mixture was to remove any bromide ion arising from the initial formation of the sulphonium salt and hence reduce the likelihood of ring opening of the sulphonium ring compound by replacing the highly nucleophilic bromide ion by the much less nucleophilic fluoroborate ion. It was recognised that silver tetrafluoroborate might also catalyse the reaction by formation of benzyl cation.

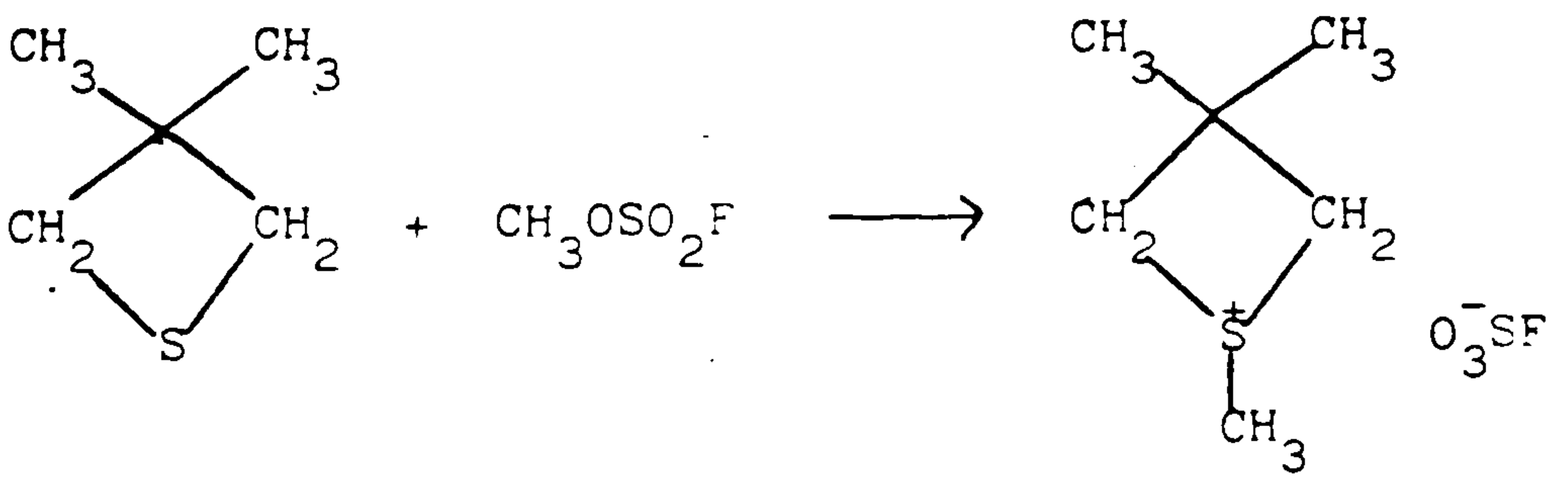
$$C_6H_5CH_2Br + AgBF_4 \longrightarrow C_6H_5\overset{+}{C}H_2BF_4^- + AgBr$$

However, a later experiment showing a vigorous reaction between thietane and silver tetrafluoroborate vitiated our attempts to prepare the sulphonium salt by the above method. The product from the thietane/silver tetrafluoroborate reaction was probably a polymer. There are literature reports on the polymerisation of thietane by Lewis acids.(41) It is difficult to conceive of a ring opening process under these conditions except one going via the initial formation of a sulphonium salt which then ring opens by a nucleophilic substitution reaction (either $S_N1$ or $S_N2$). We therefore prepared 3,3-dimethylthietane: sulphonium salts of this should be more stable to ring opening than the unsubstituted thietane salts because (a) the gem-dimethyl group should stabilise the four-membered ring (cf. the effect of a gem-dimethyl group in cyclopropanes and cyclobutanes) and hence reduce the tendency to unimolecular heterolysis of a ring C-$\overset{+}{S}$ bond.

(b) Any $S_N2$ ring opening process by attack of a nucleophile at the ring position would be very hindered by the gem-dimethyl group (cf. the steric hindrance of neopentyl compounds in nucleophilic substitutions). However, even this compound reacted with benzyl bromide to give the ring opened product, $C_6H_5CH_2SCH_2C(CH_3)_2CH_2Br$, and no sulphonium salt was isolated or detected, even when the reaction was monitored in the nmr spectrometer. The reaction with methyl iodide gave the acyclic sulphonium salt,

$$(CH_3)_2\overset{+}{S}CH_2C(CH_3)_2CH_2I\ I^-$$

One of the factors influencing ring opening is the nucleophilicity of the resulting anion of the alkylating agent. We therefore treated 3,3-dimethylthietane with methyl fluorosulphonate at 0°C.



The $^1H$ nmr spectrum is identical with that reported for the sulphonium ion in the literature( 28 ). It is, however a simpler spectrum than predicted for this structure: because of the non-planar sulphonium group, the two methyl groups are non-equivalent and the gem-methylene hydrogens will also be non-equivalent. The singlet assigned to the methyl groups is broad and may consist of two overlapping singlets. However the ring methylene groups give a sharp singlet and do not show different signals for the cis and trans hydrogens. While it is possible for the structure to be as shown, with the spacially different groups accidently having the same chemical shifts, it is preferable at present to regard the salt structure as provisional.

Polarography

The polarogram of this salt consisted of two waves of equal height, each equivalent to the transfer of one electron per step. The first wave ($E\frac{1}{2}$ = -1.08V) also exhibited some adsorption phenomena. The second wave ($E\frac{1}{2}$ = -1.43V) is also considerably lower than the value for the corresponding five- and six-membered ring sulphonium salts ($E\frac{1}{2} > 2.2V$). The lability of the thietane system to ring opening reactions suggests that cleavage of a C-S ring bond is occurring, rather than S-$CH_3$ cleavage. However, without further investigation, it is not possible to state what reactions are occurring in these reduction steps and because of the uncertainty of the structure of the salt the polarographic results were regarded as provisional.

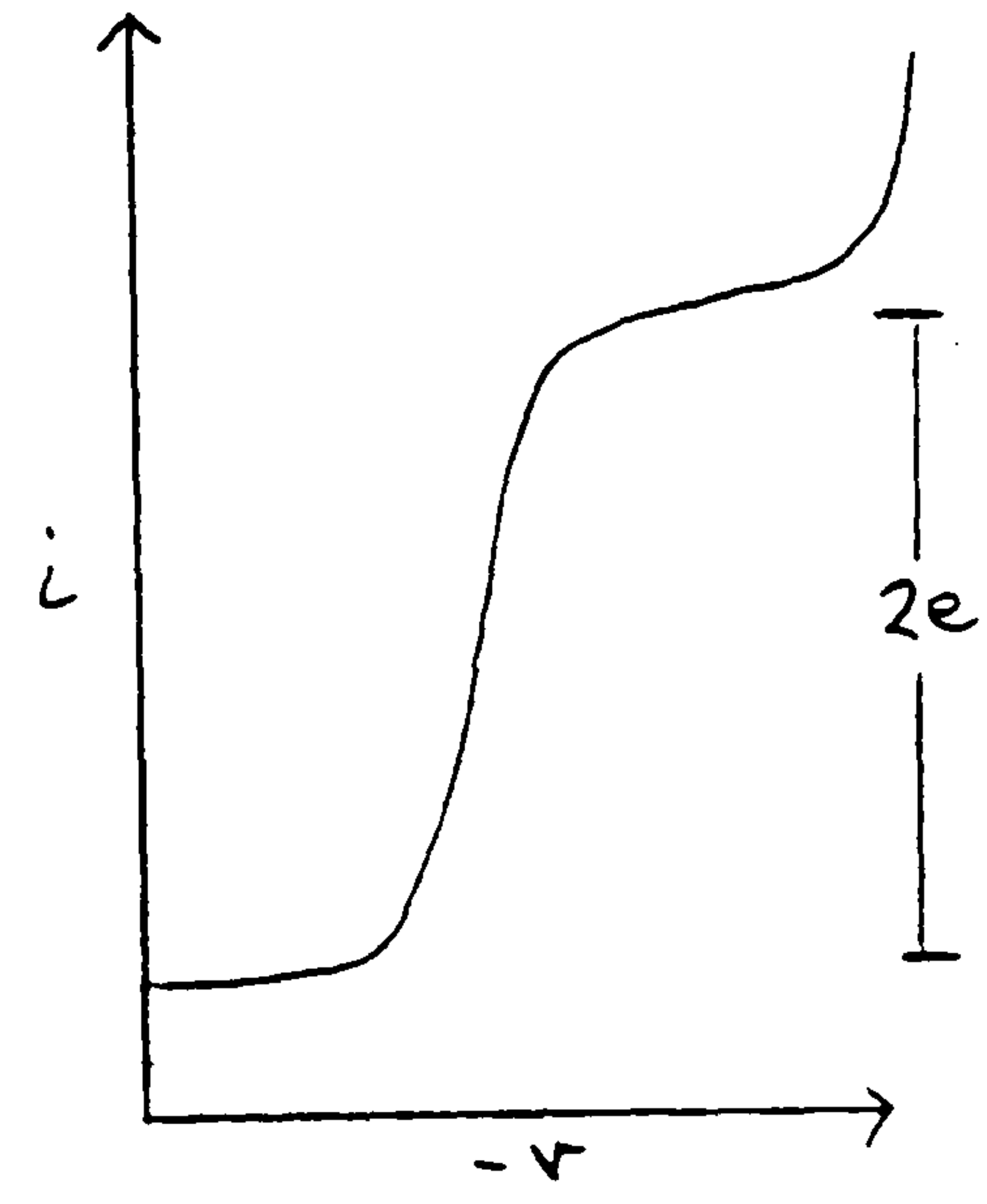
The corresponding ethylsulphonium tetrafluoroborate was prepared; the polarogram however was ill-defined and no useful conclusions could be drawn from it.

### Dibenzyl- and tribenzylsulphonium salts:

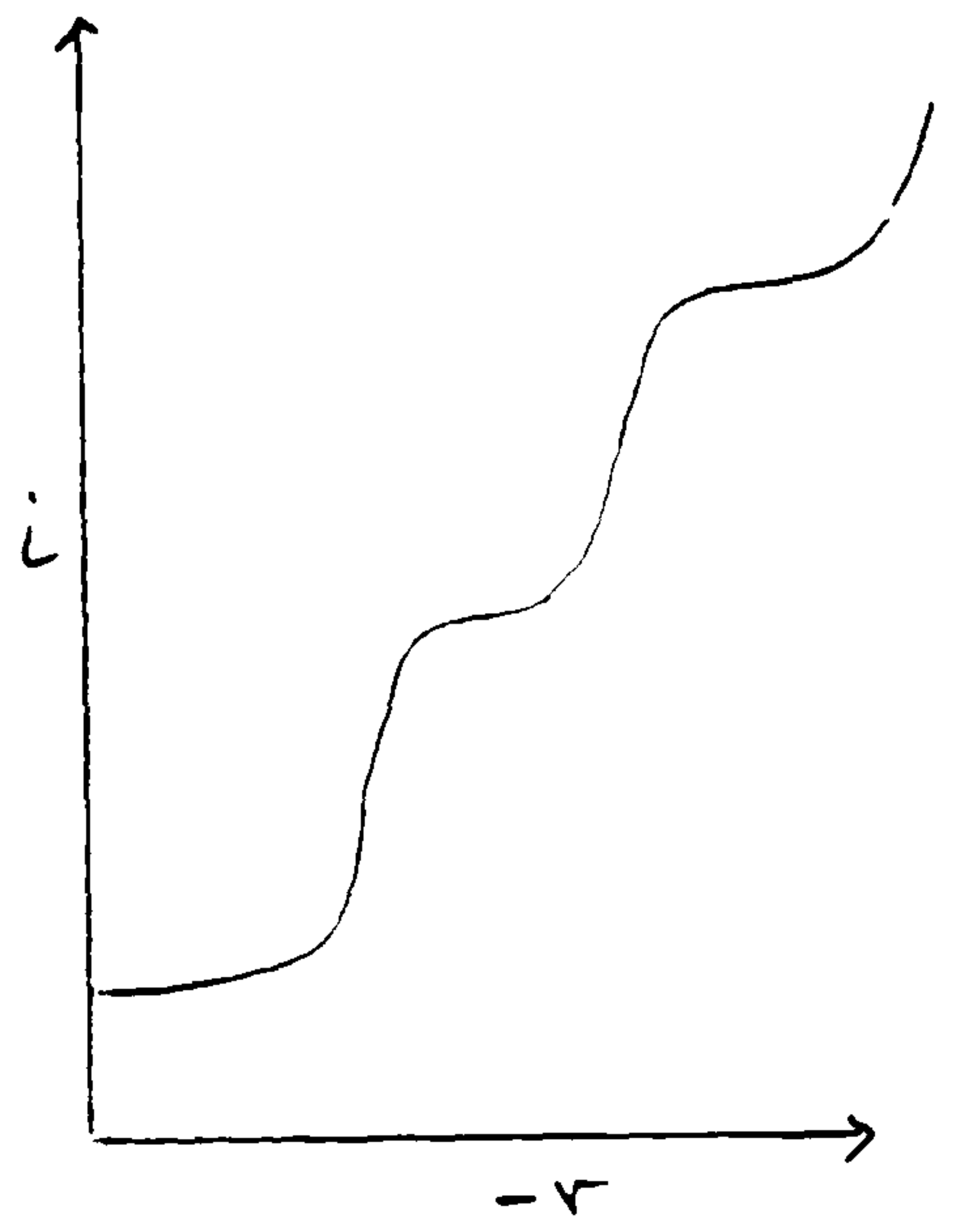
Benzyl substituents are particularly effective in lowering the half-wave potentials of sulphonium salts; this is illustrated by the successive replacement of the methyl groups in trimethylsulphonium bromide:

| $(CH_3)_3\overset{+}{S}$ | $C_6H_5CH_2\overset{+}{S}(CH_3)_2$ | $(C_6H_5CH_2)_2\overset{+}{S}CH_3$ | $(C_6H_5CH_2)_3\overset{+}{S}$ |
|---|---|---|---|
| $E_{1/2}(V) = -1.88$ | $-1.28$ | $-0.94$, $-1.25$ | $-0.66$, $-1.54$ |

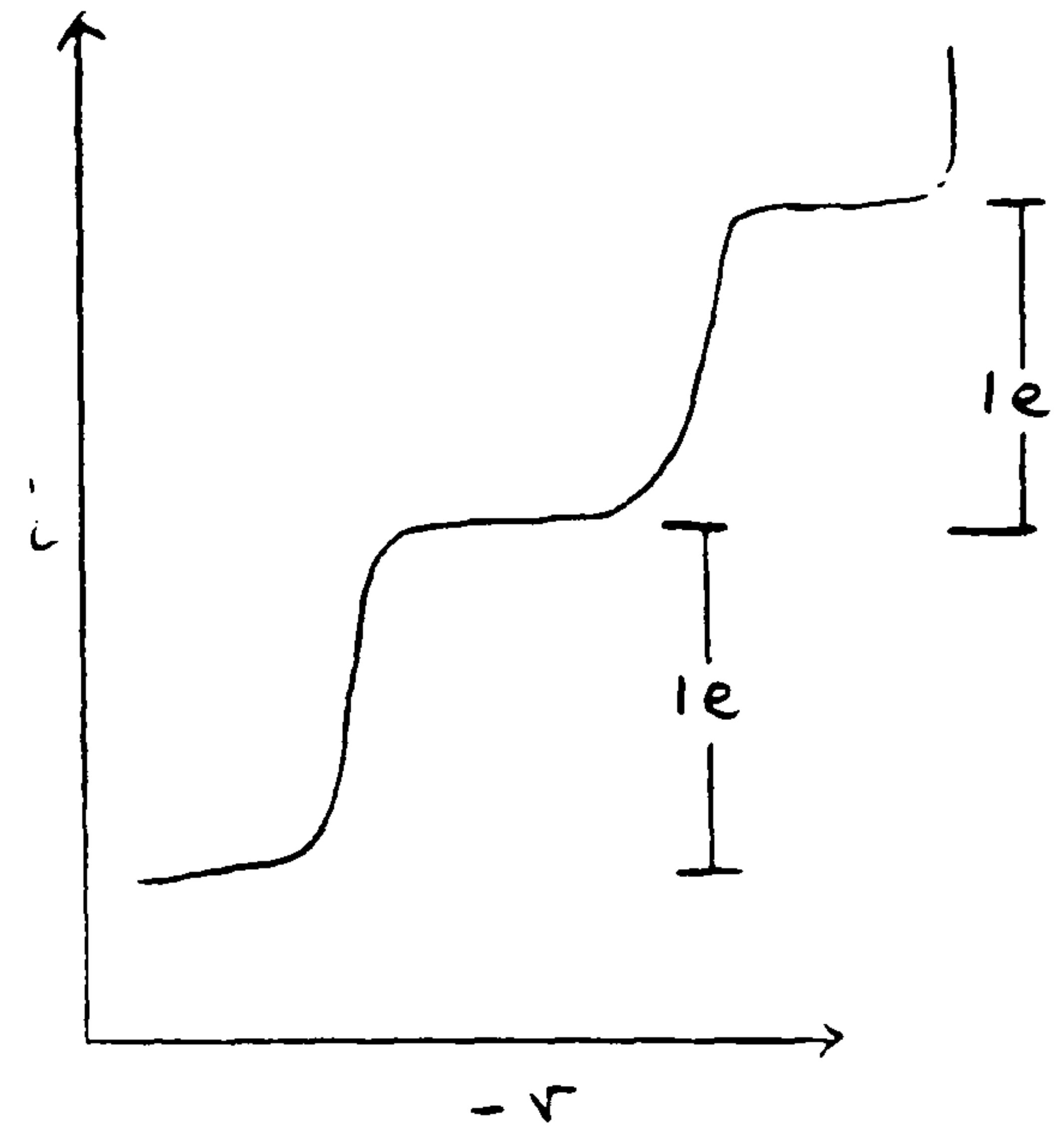
Both the trimethyl and benzyldimethyl salts exhibit smooth single 2-electron polarograms (see earlier). However, the dibenzyl and tribenzyl salts showed two discrete waves of the same limiting current corresponding to an overall one-plus-one electron reduction. For both the dibenzyl-and tribenzylsulphonium salts, only the second wave is pH dependent (56 mV/pH). This indicates that protons are involved in the process occurring at the second reduction wave but not in the first process. The following waves were observed:



pH 4.2



pH 7.0



pH 9.2

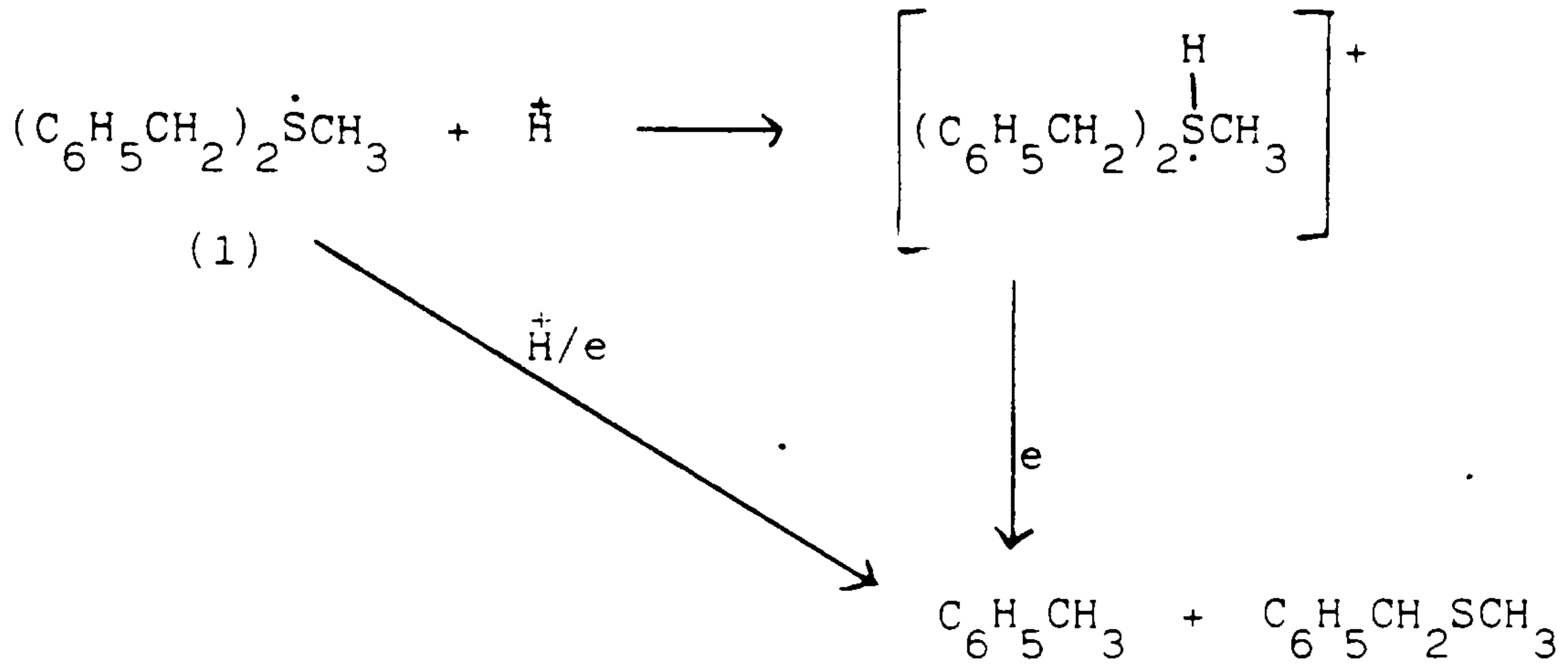
The following scheme is consistent with the polarography:

Step 1

$$(C_6H_5CH_2)_2\overset{+}{S}CH_3 \xrightarrow{e} \underset{(1)}{(C_6H_5CH_2)_2\dot{S}CH_3}$$

Step 2

The second wave is pH dependent and requires that a proton is involved either before or during the reduction step.

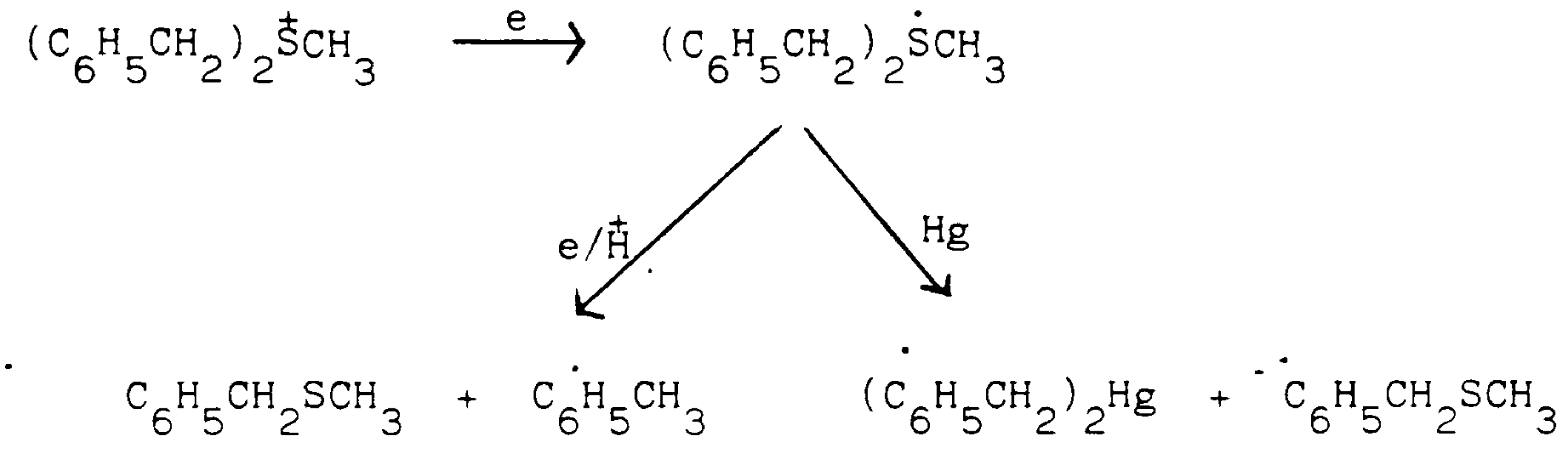


The single wave at pH 4.2 can be accounted for if at this pH the hydrogen ion concentration is sufficient to ensure formation of the complex at the moment of formation of the first radical. The main reservation we have about this interpretation is that it is difficult to see why the radical species (1) should be basic.

Macroscopic reductions also gave results in accord with the scheme. At pH 4.2, reduction at a potential corresponding to the polarogram plateau of the two electron wave ($E = -1.25V$; $n = 1.93$) afforded toluene (95%), benzyl methyl sulphide and only a trace of dibenzylmercury.

$$(C_6H_5CH_2)_2\overset{+}{S}CH_3 \xrightarrow{2e/\overset{+}{H}} C_6H_5CH_3 + C_6H_5CH_2SCH_3$$

Similar results were obtained at pH 9.2 when the reduction was effected at the plateau of the second wave (E = -1.95V). Coulometry indicated an overall two electron reduction and the products were toluene (97%) and benzyl methyl sulphide. When the reduction at pH 9.2 was performed at a working potential corresponding to the first wave plateau of the polarogram (E = -1.1V), the coulometry showed a one electron reduction and dibenzylmercury was isolated; only a trace of toluene was detected.



Bär(8) reported similar results for the tribenzylsulphonium salt. During the course of this work we prepared the tribenzylsulphonium salt and found the same polarographic behaviour as reported by Bär. The present work shows that the change in polarography from a single two step wave to a two one electron waves occurs at the dibenzyl salt stage rather than the tribenzyl stage.

## Macroscopic scale reductions

These reductions were carried out on a sufficiently large scale to permit the isolation and identification of the products. At the same time, by measuring the coulometry, information was obtained about the number of electrons (n value) involved in the reduction. The reductions were effected at fixed potentials, using a potentiostat, and these potentials were chosen by reference to the polarograms. However, when attempting to correlate these results with those from polarography, it must be recognised that the experimental conditions in the two techniques are very different. In polarography the ideal conditions are a very dilute solution of substrate in a large excess of supporting electrolyte, and a quiescent solution to ensure that only diffusion controlled processes are occuring and the current seldom exceeds a few microamps. In macroscopic reductions the sulphonium salt concentration is relatively high and the solution is stirred vigorously in order to remove the insoluble products from the mercury cathode surface. The absence of stirring leads to a rapid fall in current, making the process inoperable. The current is also quite high, initially of the order of amperes, which leads to heating, even when the reduction cell is immersed in a thermostat. Despite these differences, the two techniques are complementary and give information on the mechanism of the reduction and the optimum conditions for electrochemistry. Reference has already been made to the use of these complementary studies in the investigation of the reduction of benzthioniacyclopentane salts (page 87 ) and dibenzylmethylsulphonium bromide (page 92 ).

Investigation of the effect of temperature on distribution of the products of macroscopic reduction led us to examine more closely the effect of potential and hence to a more detailed description of the reaction mechanism.

## Effect of temperature

Reduction of benzyldimethylsulphonium bromide in pH 7 buffer at a plateau potential (E = -1.4V) at room temperature gave only the expected product, toluene (apart from the concomitant volatile dimethyl sulphide, which we shall not record as a product in this discussion). The coulometry ($n \simeq 2$ electrons) corresponded with the product. Similar results were obtained for benzyldiethylsulphonium bromide. Settineri et al. in patent literature(11) reported that at higher temperatures the formation of dibenzylmercury was favoured. We examined the effect of temperature on the reduction of benzyldimethylsulphonium bromide.

| Temp (°C) | $C_6H_5CH_3$ (%) | $(C_6H_5CH_2)_2Hg$ (%) | n |
|---|---|---|---|
| 0 | 97 | 0 | 1.93 |
| 25 | 84 | 0 | 1.85 |
| 45 | 79.7 | 0 | 1.83 |
| 50 | 68 | 0 | 1.82 |
| 60 | 62 | 0 | 1.79 |
| 80 | - | 16 | 1.62 |

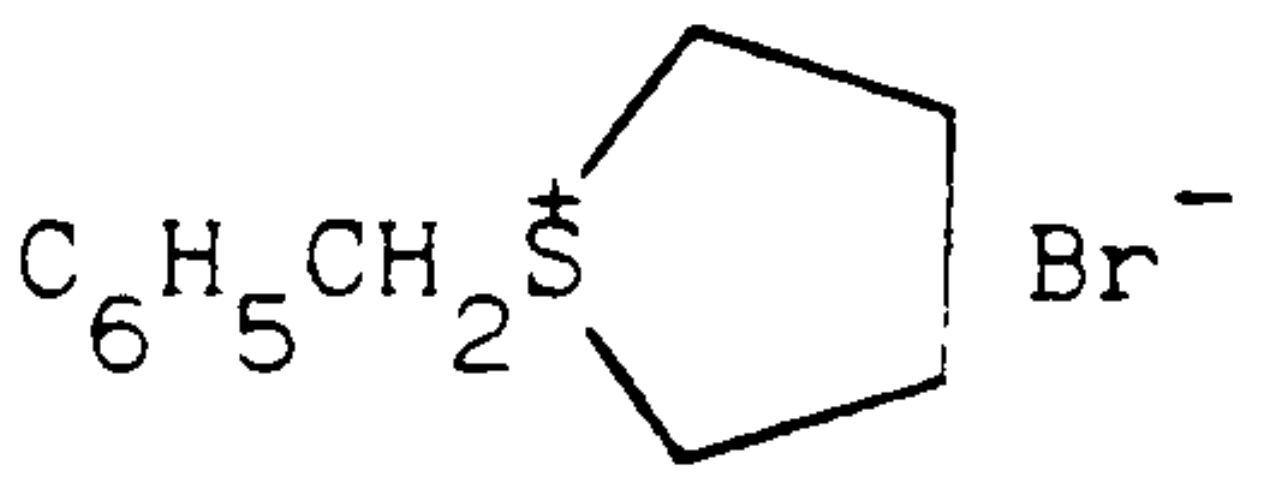
Only toluene and dibenzylmercury were formed: no bibenzyl or benzyl methyl sulphide was detected. The absence of the last compound is in contrast to a reduction of the sulphonium salt with sodium borohydride, when a small amount of benzyl methyl sulphide (7%) was observed.(17) Reduction at the mercury cathode must be more selective than borohydride.

There is a marked difference between the observed and calculated n values and the quantitative analysis shows appreciable loss of product (presumably the more volatile toluene), particularly at the higher temperatures. However, the change in product ratio and the n values have the same trend and show clearly that high temperature is conducive to the formation of the organomercury compound. Examination of the effect of heat alone, without electrolysis showed that the difference was not due to chemical change in the substrate prior to electrolysis.

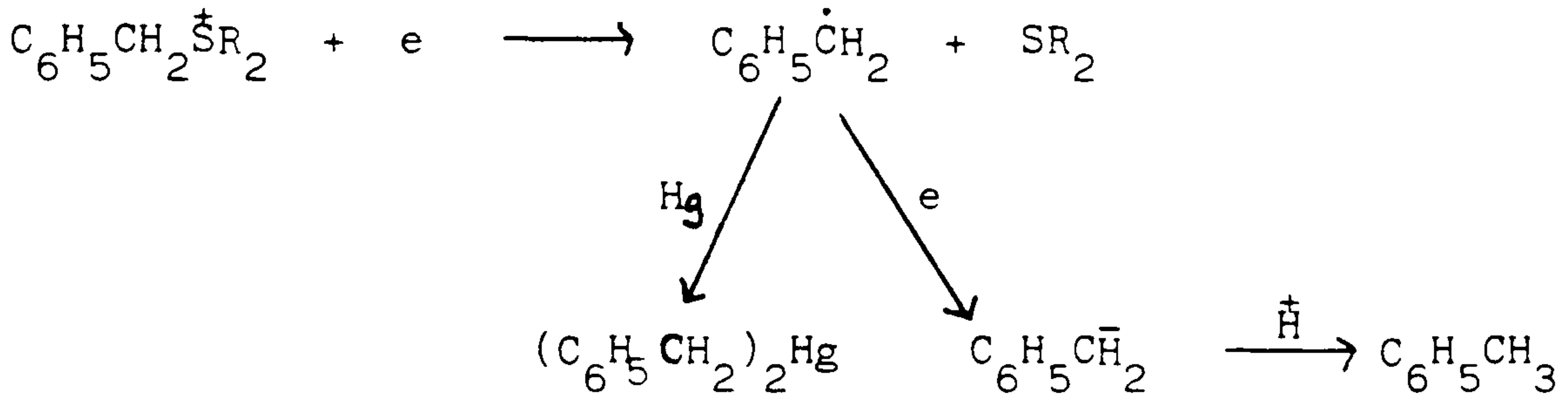
Similar results were obtained for benzyldiethylsulphonium bromide except that the yield of dibenzylmercury at 80° was considerably higher (61%) than from the dimethyl salt (16%).

Much more complete sets of results were obtained for 1-benzylthioniacyclopentane bromide (page 71) and p-methylbenzyldimethylsulphonium bromide (page 72).

When comparing the results from $C_6H_5CH_2\overset{+}{S}(CH_3)_2$ and $C_6H_5CH_2\overset{+}{S}(C_4H_8)$ salts it was noted that the latter salt gave some dibenzylmercury (19%) even at room temperature electrolysis and we initially ascribed this difference in product ratio to the different R groups. Because of the differences in E½ values electrolyses had been carried out at different potentials; when electrolyses were carried out at the same potential (-1.2v) at 25°, the following results were obtained:

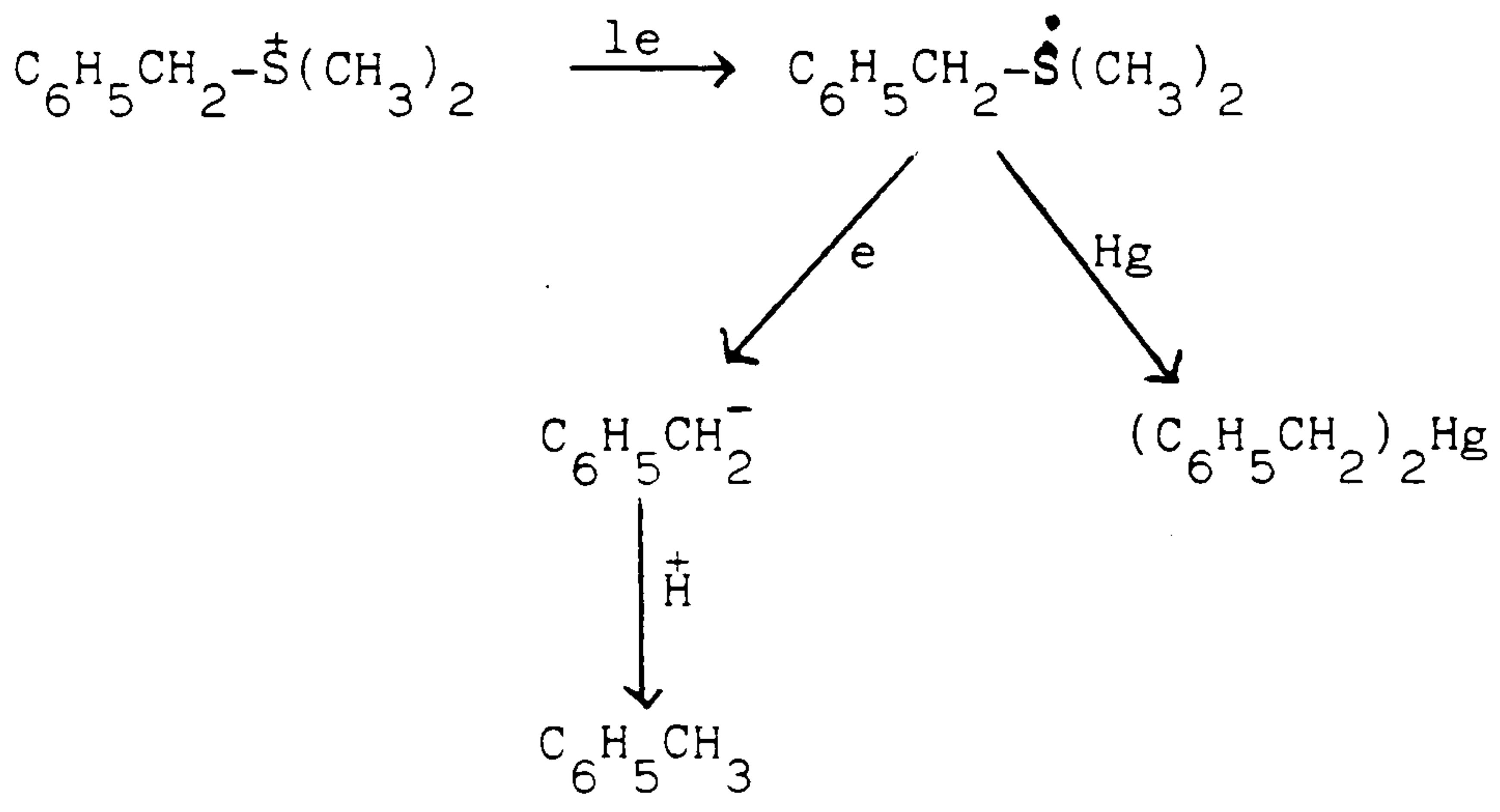
| | | |
|---|---|---|
| $C_6H_5CH_2\overset{+}{S}(CH_3)_2\ Br^-$ | 79.4% | dibenzylmercury |
| $C_6H_5CH_2\overset{+}{S}(C_2H_5)_2\ Br^-$ | 73.0% | " |
|  | 19.0% | " |

This variation in the distribution of products at a fixed potential from salts with different ligands gives further information on the reaction mechanism. If the initial radical species formed was the benzyl radical, the product ratio should be independent of the R ligands.



Since this is not so, another radical species, dependent on the ligands, must be formed initially. The most likely is $C_6H_5CH_2\dot{S}R_2$, which can either react with the mercury to form dibenzylmercury or accept another electron from the cathode to form the benzyl anion, which reacts with a proton donor (water) to give toluene. The absence of bibenzyl in the products is also support for the formation of the benzyldialkylsulphur radical rather than the benzyl radical; if the benzyl radical was formed it is very likely, though not essential, that some bibenzyl would result from coupling.

The following reaction scheme accounts for the results:



This is essentially the mechanism put forward by Luttringhaus and Machatzke(6), but with little evidence to support it. Our work provides strong support for the structure of the initial radical intermediate.

Since the polarogram shows a single two electron wave, if the above mechanism holds the transfer of the second electron at the mercury drop must be very easy and rapid to account for the single waveform. The more negative the cathode, the more likely is a radical adsorbed on the mercury surface to accept another electron (the greater the "electron pressure" of the cathode) and form a carbanion leading to the hydrocarbon product. Conversely, lower cathode potentials should not favour the second electron transfer so much and hence favour the formation of the organomercury compound. This finding that the process can be changed from an essentially one electron process to a two electron process by merely varying the cathode potential is of practical significance and Settineri and Wessling report examples in a patent(12). These results give a note of caution against extrapolating too completely the results of polarography to macroscopic reduction processes. It is also noteworthy that even using an unstirred mercury pool cathode, the plot of the current-voltage values gave a smooth curve with no sign of two close successive waves. This dichotomy of behaviour of the sulphonium salts to give rise to one electron or two electron transfer products is also found in benzyl halides(42).

An alternative explanation for the difference between the polarographic and the macroscopic reduction process is shown in the following scheme:

$$R_3\overset{+}{X} + 2e \longrightarrow R_3X^{-}:$$

$$R_3X^{-}: + R_3\overset{+}{X} \longrightarrow 2\,R_3\dot{X}$$

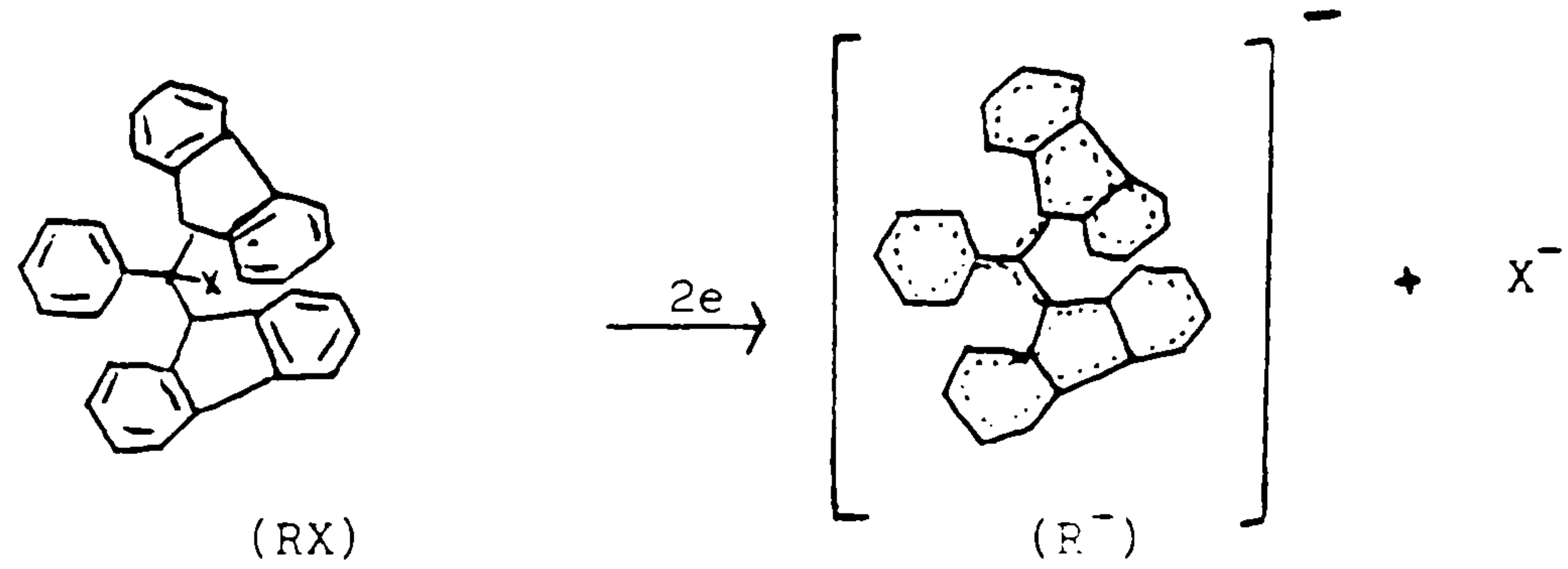
$$2\,R_3\dot{X} + Hg \longrightarrow 2\,R_2X + R_2Hg$$

$$R_3X^{-}: \longrightarrow R_2X + R^{-}:$$

$$R^{-}: + \overset{+}{H} \longrightarrow RH$$

The essence of this scheme is the reaction of the initially-formed carbanion with the unreacted sulphonium salt to give two radicals. This disproportionation system has recently been observed in cyclic voltammetric studies on a halogen compound which is reduced at a carbon-glass cathode to a highly stabilised benzyl type carbanion(42).

X = Hal



(RX) (R⁻)

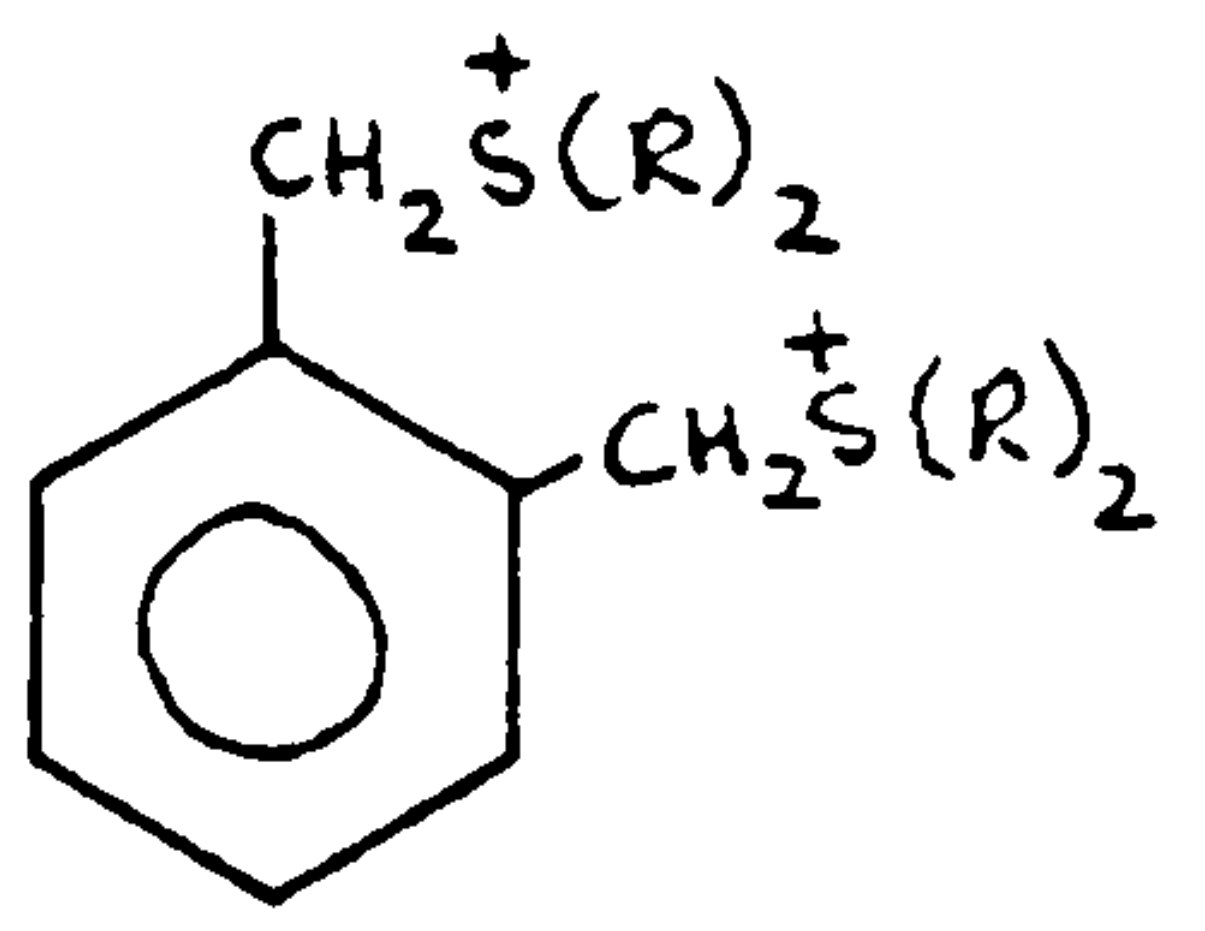
$$R^- + R\text{-}X \longrightarrow 2R^\cdot + X^-$$

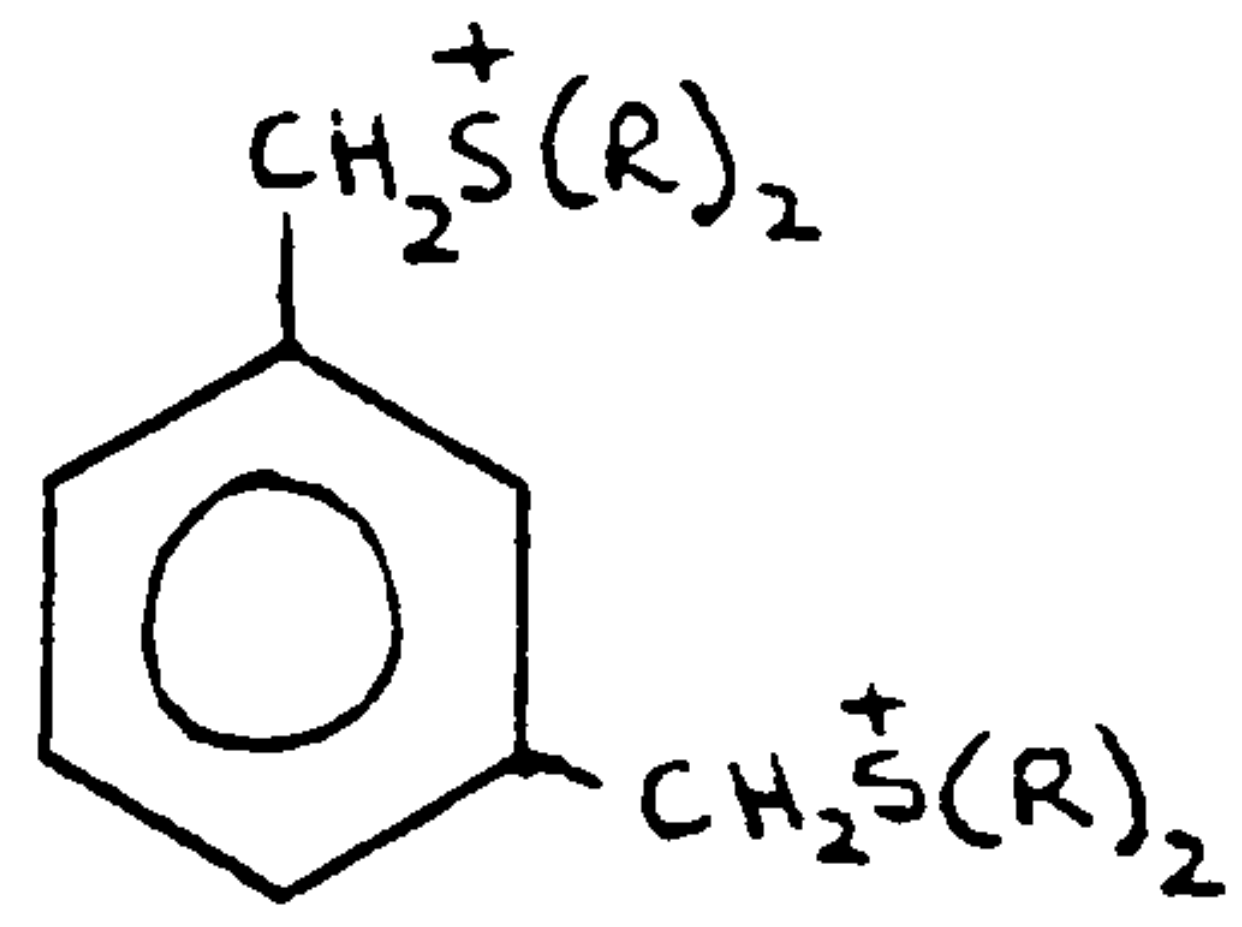
This reaction scheme has been put forward to account for the similar dichotomy of reaction products in the electrochemical reduction of alkylhalides.

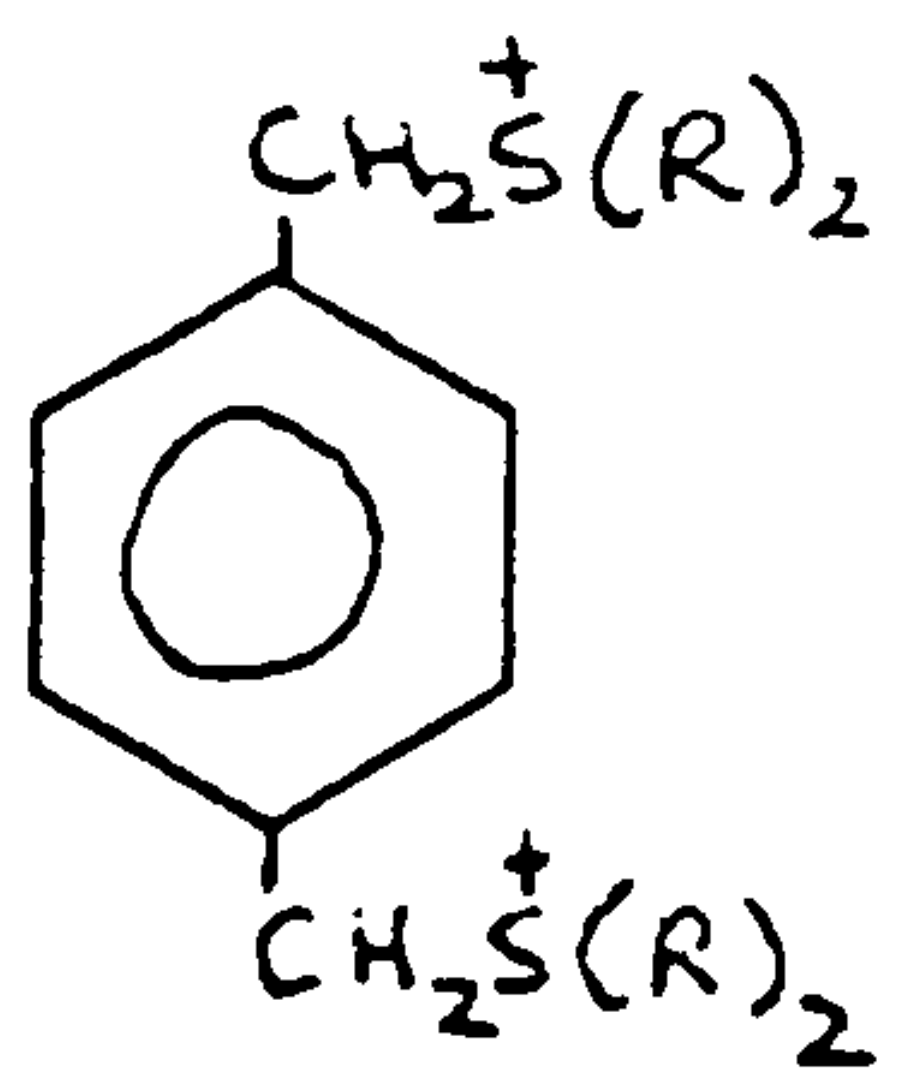
Under polarographic conditions where the concentration of substrate is very low ($10^{-3}$ to $10^{-4}$ M) the reaction process is diffusion controlled, and the opportunity for disproportionation is very small. In macroscopic reductions however, the concentration of substrate is much higher ($10^{-1}$ to $10^{-2}$ M), and the solution is vigorously stirred to remove products from the surface of the mercury surface and to create a new surface, so that the conditions are quite different and would be favourable to the disproportionation scheme.

If time had permitted and had facilities for cyclic voltammetry been available we would have attempted to test this mechanism by preparing analogous sulphonium salts to those used in the organic halide study.

## Xylylenebis-sulphonium salts

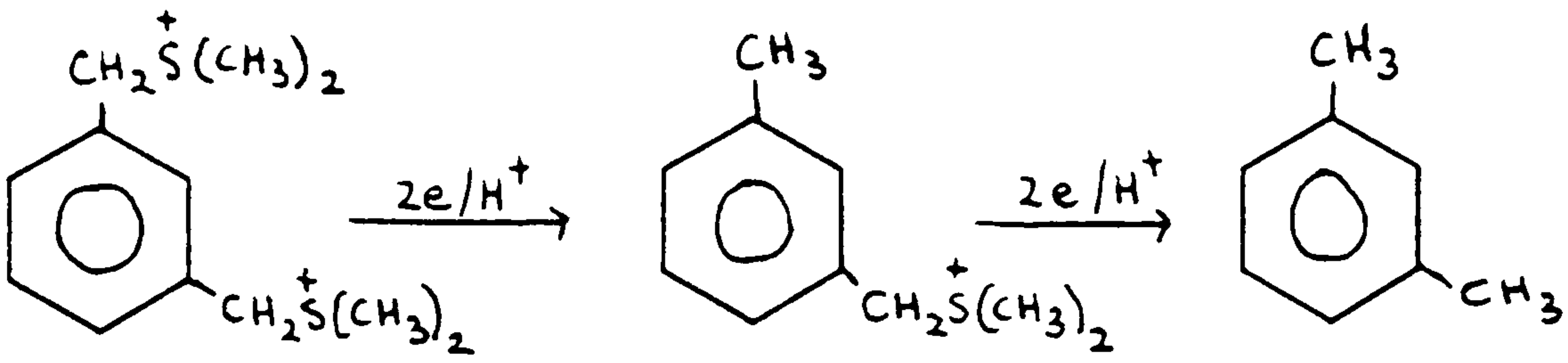






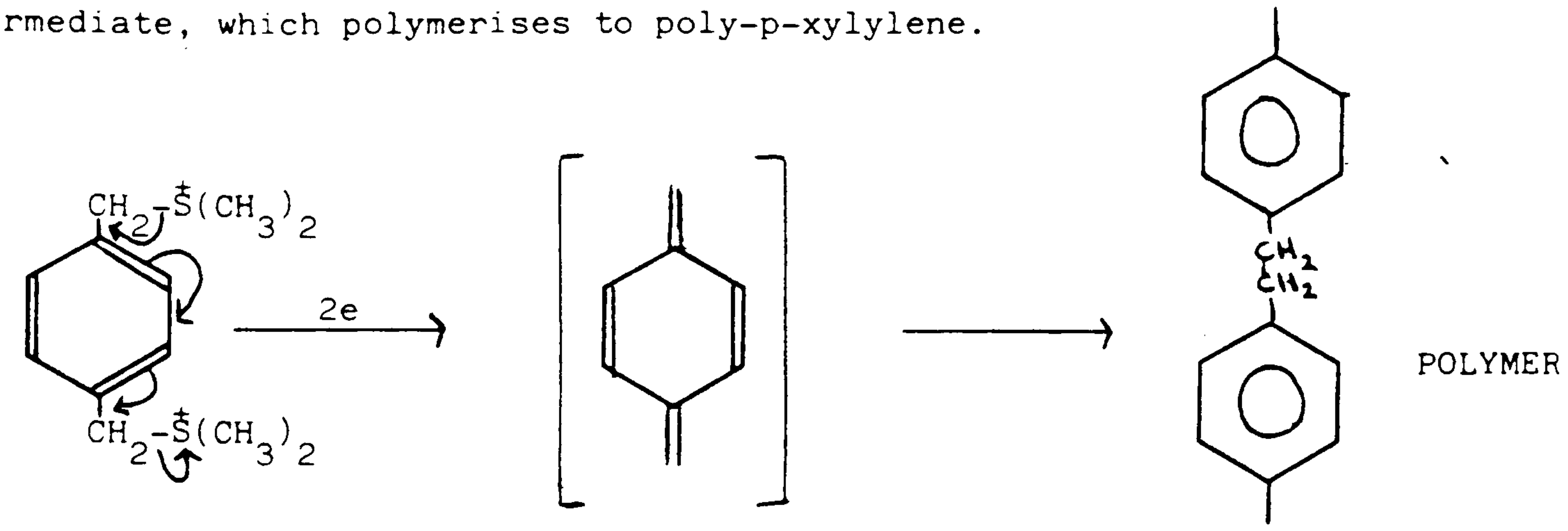
This series allows investigation of the intramolecular interaction of two benzyl sulphonium groups; i.e. the effect of reduction at one group on possible bond cleavage at the other group: it is unlikely that both groups will undergo simultaneous reduction.

Although Luttringhaus reported the $E_{\frac{1}{2}}$ values of a few p-xylylene sulphonium salts and Settineri et al. in patent literature reported the electrolysis of such salts to give poly-p-xylylene we decided to investigate the ortho-,meta- and para-bis-sulphonium salts in more detail. In particular we wished to see how the electrolysis of the ortho- and meta-compounds differed from that reported for the para-compound. In the meta-salt the two acyclic benzylic carbons, to a first approximation, cannot interact by a mesomeric mechanism and such group interaction should be less than that for the other two isomers. We therefore predicted that the meta-salt should behave similarly to the monosulphonium salts. The meta-isomer showed the expected behaviour. The polarogram of this salt consisted of what initially appeared to be a single wave but was actually two successive waves, each corresponding to two electrons, the join being a slight kink in the middle (see Fig. 3 ). The low $E_{\frac{1}{2}}$ value for the first wave of the meta-bis-salt is not unexpected and is due to the electron withdrawing inductive effect of the second sulphonium group; this value (-1.07 V) was appreciably lower than those of the parent benzyl (-1.28 V) and the m-tolyl (-1.33 V) monosulphonium salts. The second wave ($E_{\frac{1}{2}}$ = -1.25 V) is similar to that of the mono-salt.



This two-stage mechanism cleavage was confirmed by the following experiment. Macroscopic reduction at the potential corresponding to the top of the first wave ( E = -1.16 V) gave a current coulometry plot corresponding to approximately two electrons, and after dilution, polarographic analysis of the resultant solution gave a wave corresponding to that of the m-tolyldimethylsulphonium salt ($E_{1/2}$ = -1.34 V). This confirms the independent reduction of the two sulphonium groups. Macroscopic reduction at a cathode working potential corresponding to the upper plateau gave only m-xylene (97%). A number of reductions were effected at cathode potentials ranging between the first $E_{1/2}$ value and the plateau of the first polarographic wave, to see whether organomercury compounds could be formed but none were detected either by product analysis or by coulometry. We were surprised that no di-m-tolylmercury was formed and therefore we investigated the reduction of the m-tolyldimethylsulphonium salt. In contrast to the parent benzyl salt and its p-methyl isomer no organomercury product was formed. Reduction of m-xylylene dibromide was reported to give a single wave ($E_{1/2}$ = -1.32 V, 4 electrons) and reduction at the plateau potential gave only m-xylene(29). Our results suggest that this is also a two-stage reduction but the two waves merge to give a deceptively simple polarogram.

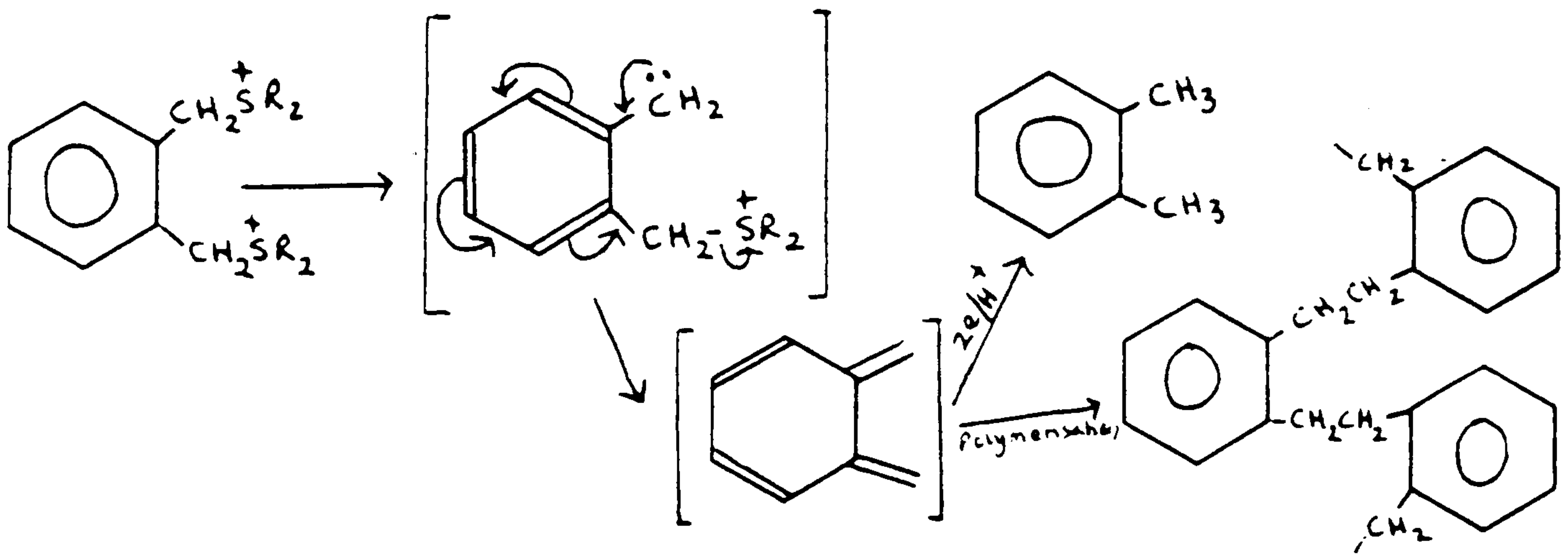
The polarogram of p-xylylenebis(dimethylsulphonium bromide) shows only one wave ($E_{1/2}$ = -0.99 V), significantly lower than that for the meta-isomer (-1.07 V), indicating a concerted mechanism. The wave height is only half that for the meta-isomer and corresponds to an overall two electron change, a value confirmed by coulometry. In this process reductive cleavage at one site causes concerted bond cleavage of the $C-\overset{+}{S}$ at the other group by delocalisation through the $\pi$-system to give a p-xylylene intermediate, which polymerises to poly-p-xylylene.



The polymer is insoluble in all common solvents and has been characterised by mass spectrometry and elemental analysis.

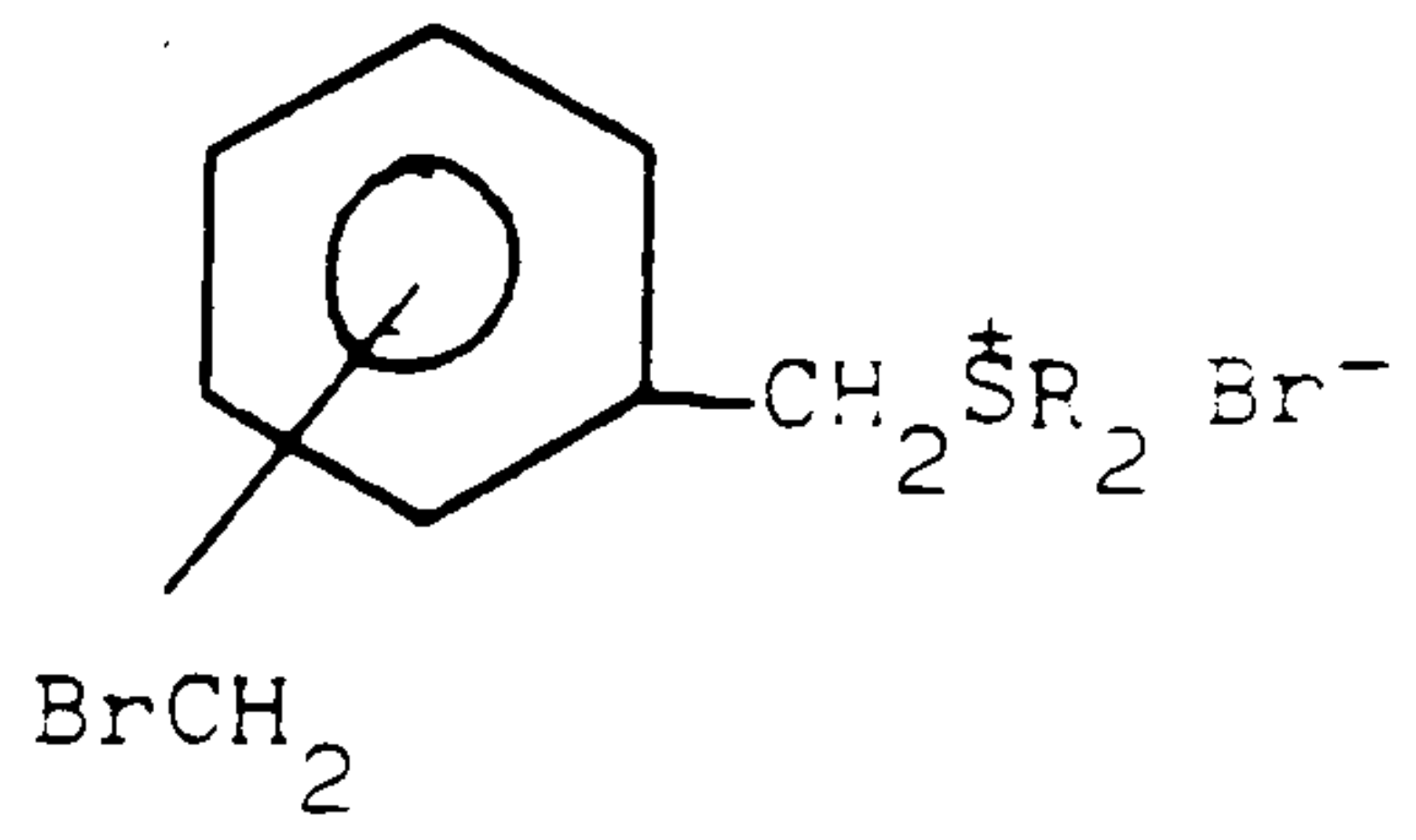
Covitz(29) obtained a similar polymer by electro-reduction of p-xylylene dibromide. He reported a two-wave polarogram (E½ = -0.8, -1.72 V), and ascribed the second wave to the reduction of the p-xylylene intermediate. The bis-sulphonium salts show no such second wave. A further difference between the dibromide and the bis-sulphonium salts is that the dibromo compound gives polymer and some p-cyclophane (5-10%); no p-cyclophane was detected from the bis-salts. We repeated the polarographic work of Covitz and confirmed his results with the dibromides.

The o-xylylenebis- salt exhibits two polarographic waves of the same diffusion current with E½ - -0.88 V and -1.15 V. Macroscopic electrolysis at the upper plateau potential, afforded a solid polymeric product (21%) and o-xylene (72%). The solid was not fully characterised but the mass spectrum suggested it is probably poly-o-xylylene. The following scheme is consistent with the results:



Reduction of o-xylylene dibromide at a mercury cathode is reported to give similar products.

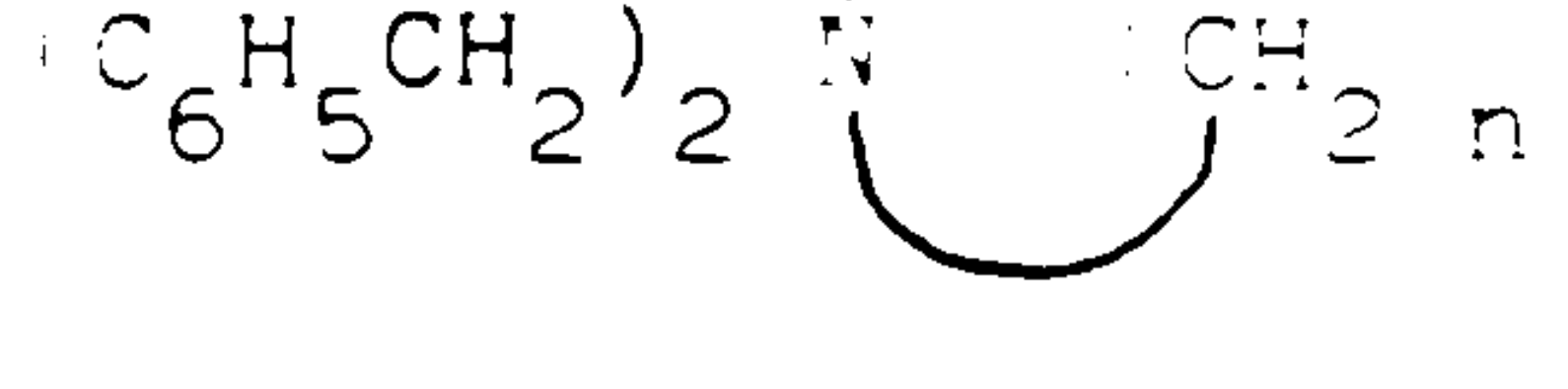
It was intended to examine the related bromomethyl sulphonium salts.

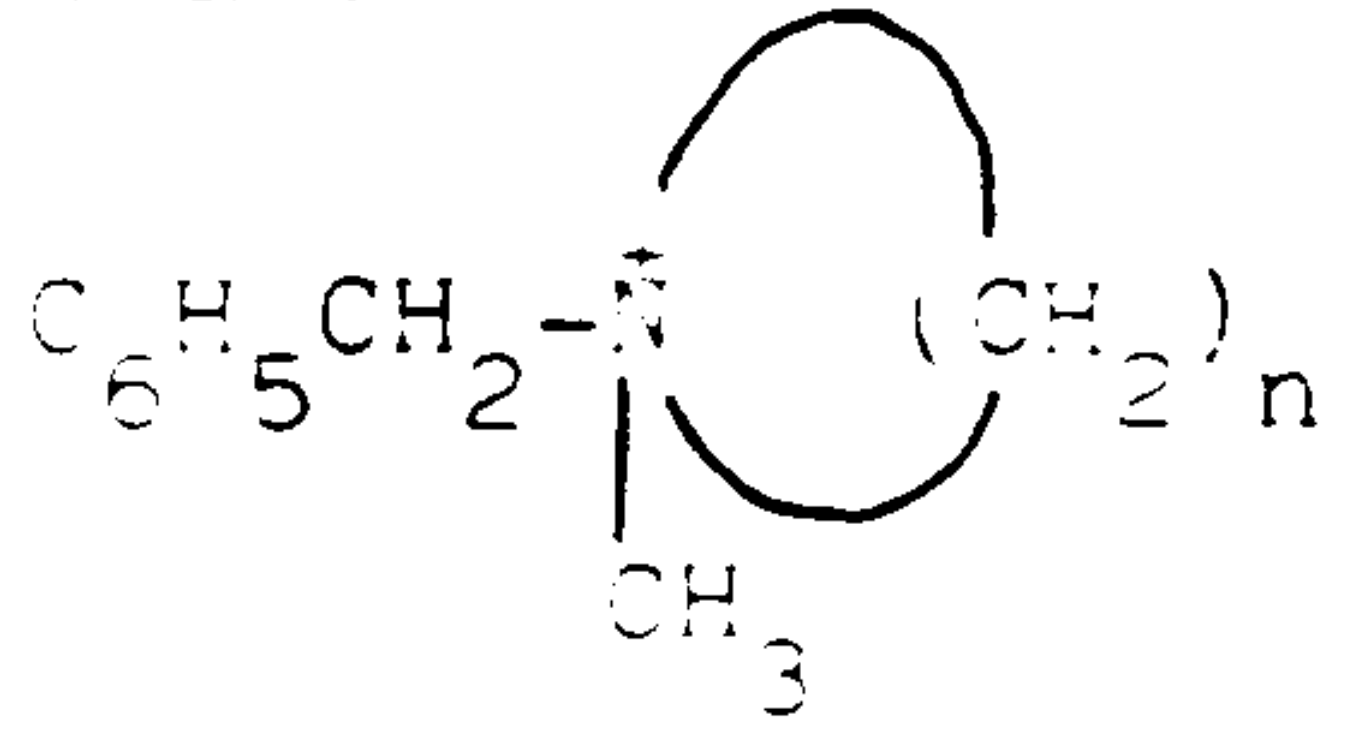


This would have allowed the relative ease of reduction of the halogen and sulphonium groups to be determined under the same condition. It would also be of interest to see if the ortho- and para- compounds would undergo concomitant cleavage of the two bonds to give the corresponding xylylene products. Covitz had shown that p-bromomethylbenzyltrimethylammonium bromide reduced and gave the same polarogram as p-xylylene dibromide. However, our attempts to prepare the salts were unsuccessful. In all cases a mixture of the mono- and bis-sulphonium salts resulted, despite using a large excess of the xylylene dihalide, and the desired salts could not be obtained pure.

Quaternary Ammonium Salts

These compounds are considerably more difficult to reduce than the corresponding sulphonium salts and tetraalkylammonium salts are often used as supporting electrolytes for the electrolysis of other salts in aqueous solutions. Even benzyltrimethylammonium salts are not reduced in aqueous solutions at potentials below that of general discharge. Because our results with sulphonium salts showed that the five- and six-membered sulphur ring group lowered the potential necessary for benzyl-$\overset{+}{S}$ bond cleavage, we prepared the analogous benzylammonium salts containing five and six rings. However neither of these salts reduced in aqueous solution below the hydrogen discharge potential.





n = 4 and 5

Due to the marked decrease in E½ values of the ortho- and para-xylylene-bis-sulphonium salts, we prepared the analogous isomeric xylylene-bis-ammonium salts. Again no polarographic wave due to the reduction of the C-$\overset{+}{N}$ bond was obtained.

Using sodium borohydride, Walcott(17) showed that the chemical reduction of C-$\overset{+}{N}$ bonds in ammonium salts was much more difficult than the corresponding C-$\overset{+}{S}$ bond in sulphonium salts; these differences in reactivity of the C-$\overset{+}{N}$ and C-$\overset{+}{S}$ bond can be attributed to the increased strength of the C-$\overset{+}{N}$ bond (248 kJ mol$^{-1}$ for C-N bond in amines and 233 kJ mol$^{-1}$ for C-S bond in sulphides).(43)

It is interesting that in the photochemical experiments, where we are dealing with an excited state, the ammonium salts showed a higher reactivity than the sulphonium salts (see later section on photochemistry).

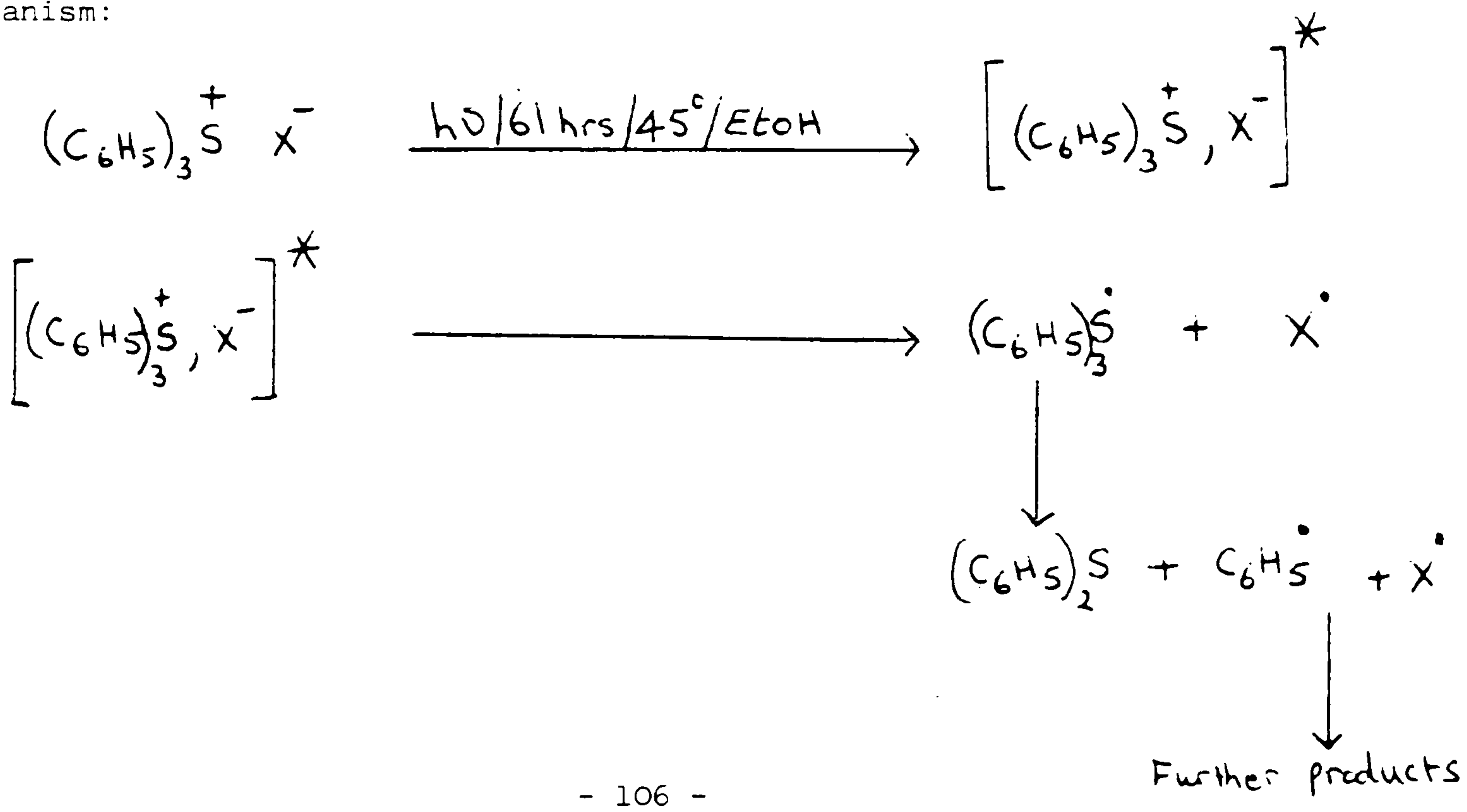
# PHOTOCHEMISTRY

## Introduction

On irradiation, molecules undergo excitation and have a different electronic distribution and reactivity in the excited state compared to the ground state. This enables transformations which may be impossible even at high temperatures in the ground state to be accomplished by u-v excitation at room temperature. In certain types of reactions, which proceed both thermally and photochemically, the stereochemistry of the products may be different in the two processes.

The photochemistry of certain classes of organo-sulphur compounds, such as thioketones and sulphones have been widely investigated. By contrast, however, sulphonium compounds have undergone less intensive study. The pattern that emerges is one in which the photolysis can involve homolytic or heterolytic cleavage of the Carbon-Sulphur bond.

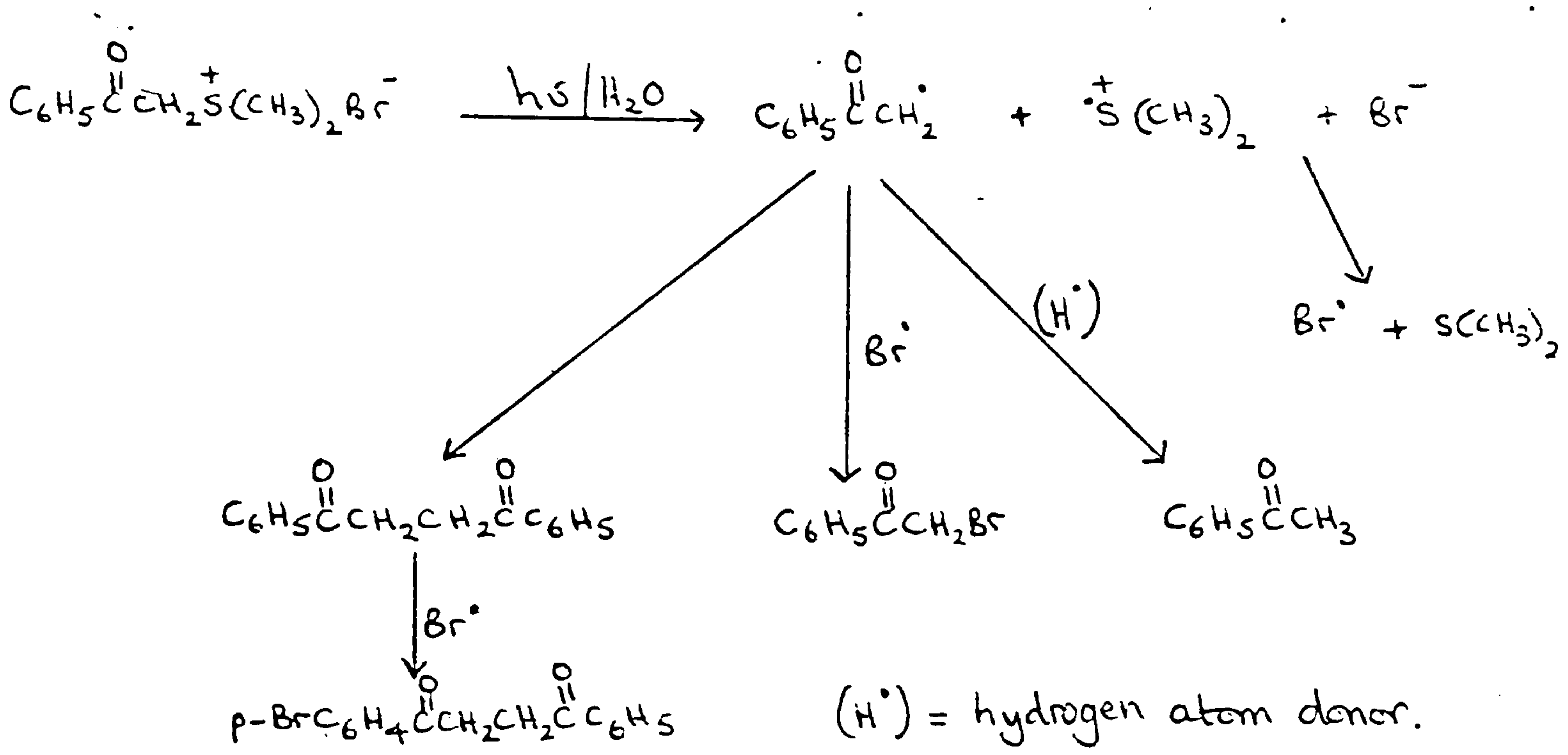
The photolysis of triphenylsulphonium salts was reported to yield radical products (44). The rate of reaction varied with the ease of electron transfer from the anion in accordance with a charge-transfer mechanism:



The following table shows how the anion $X^-$ influences the extent of reaction and product distribution.

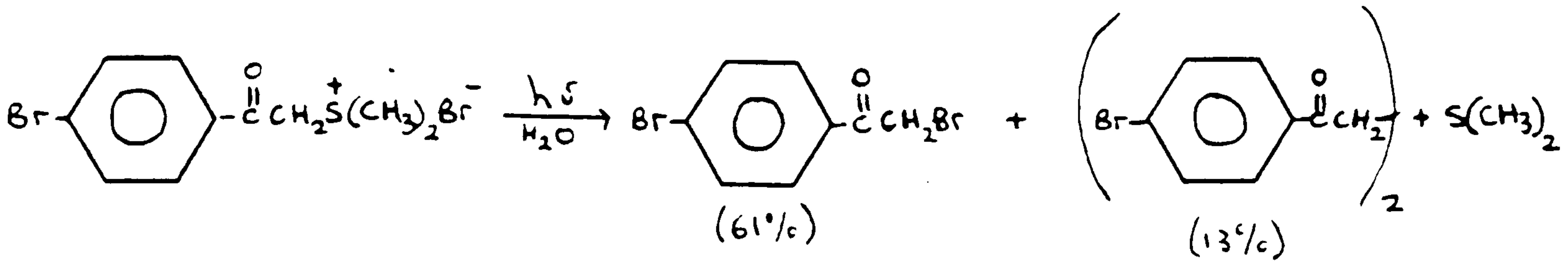
| $X^-$ | $(C_6H_5)_2S$% | $C_6H_5X$% | $C_6H_6$% | $(C_6H_5)_2$% | recovered salt% |
|---|---|---|---|---|---|
| Cl | 23 | 1 | 14 | 2.1 | 38 |
| Br | 37 | 12 | 24 | 1.4 | 24 |
| I | 47 | 36 | 31 | 1.4 | 4 |
| $NO_3$ | 30 | - | 34 | 1.4 | 29 |

Previous workers in this laboratory have shown that irradiation of phenacylsulphonium salts affords products resulting from the homolytic cleavage of the phenacyl carbon-sulphur bond(45 ) and the following scheme was proposed:

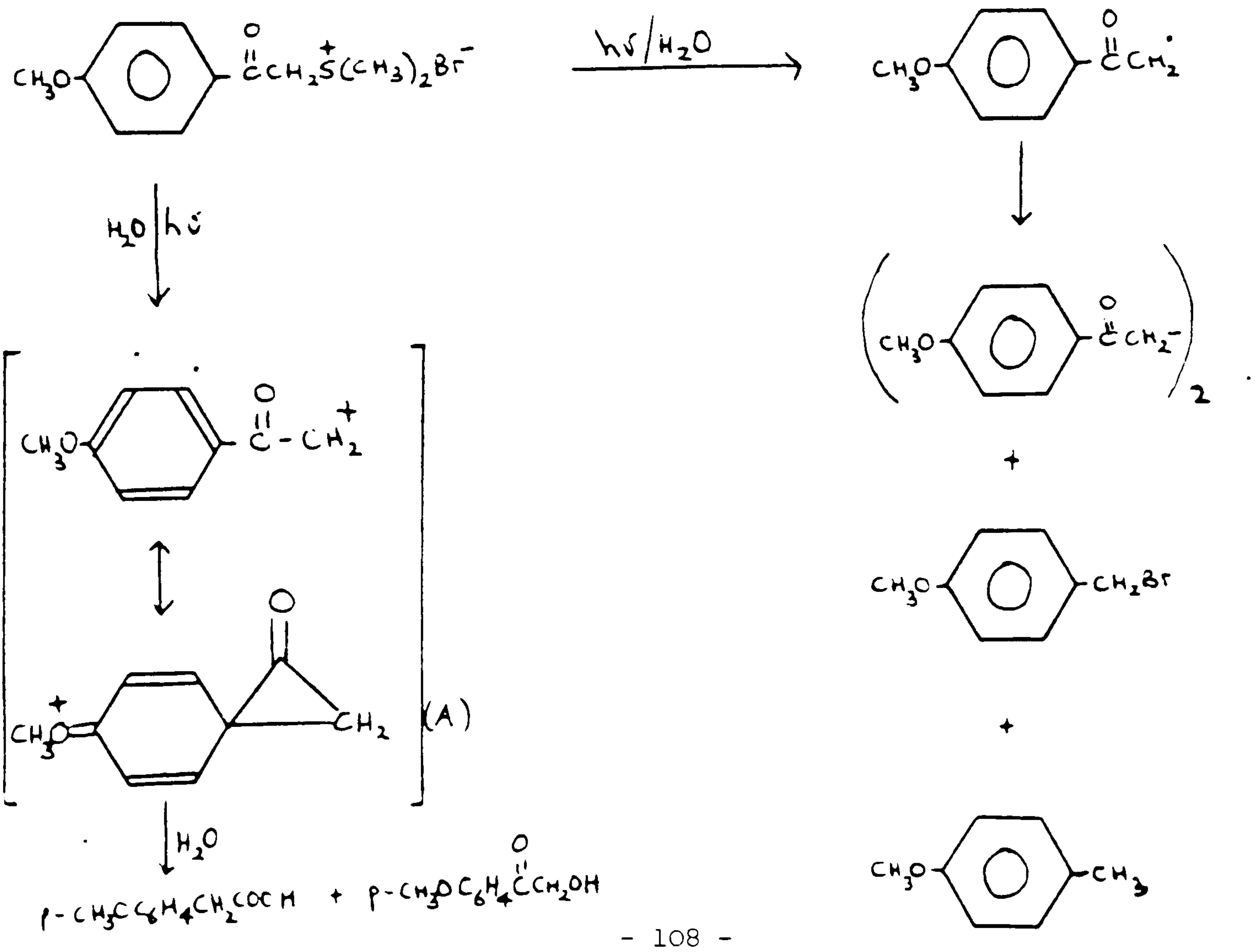


The formation of brominated products, when the counter ion was bromide, was attributed to the relative ease of oxidation of bromide ion to bromine atoms. The bromine atom may combine with the phenacyl radical to give phenacyl bromide, or attack dibenzoylethane to give 1-benzoyl-2-(p-bromobenzoyl)ethane. It was established that phenacyl bromide was not on the main reaction pathway to the 'normal' products of the reaction.

Substituents had a marked effect on the reaction: photolysis of p-bromophenacylsulphonium bromide gave p-bromophenacyl bromide as the major product.

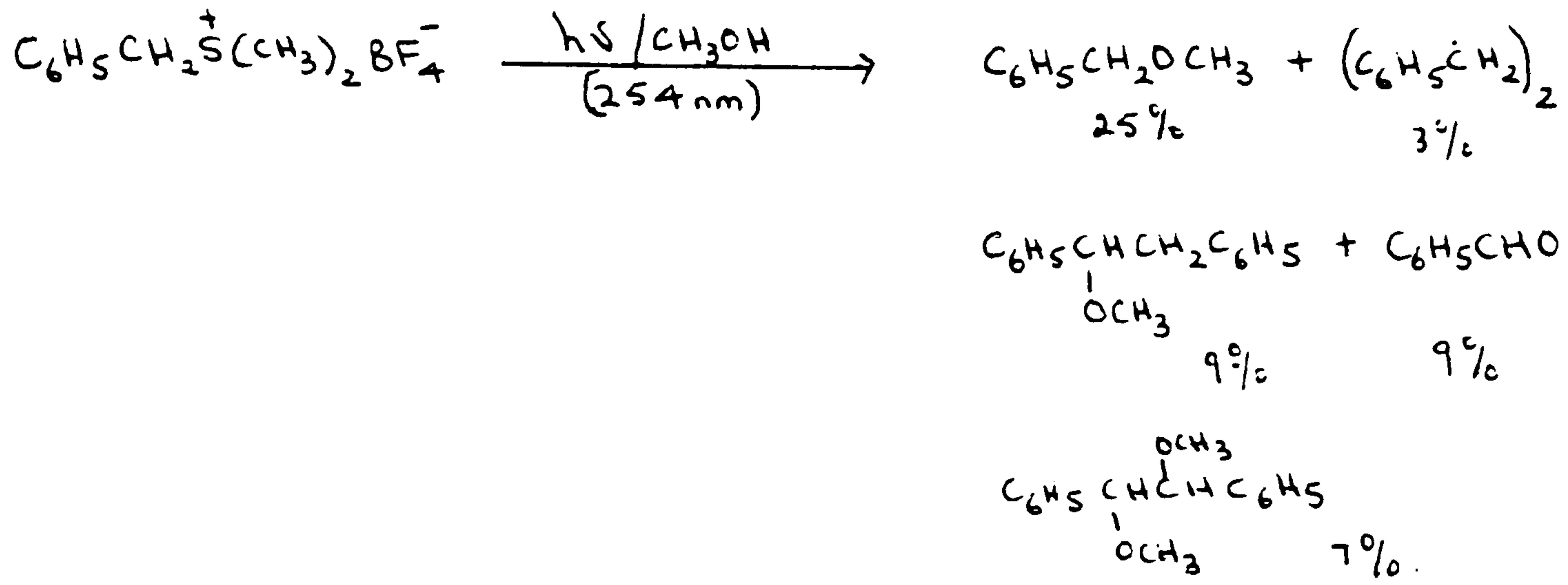


The dimer product must have arisen from a homolytic process, as could the p-bromophenacylbromide but the authors suggested that the latter might also have been formed by an $S_N2$ reaction of bromide anion on the excited sulphonium cation i.e. a heterolytic process. p-Methoxyphenacyldimethylsulphonium bromide gave largely radical derived products, but there were appreciable amounts of p-methoxyphenacyl alcohol and p-methoxyphenylacetic acid, both of which were explained on the basis of a carbonium ion intermediate. (A).



The involvement of the anion in these processes was minimised by using an inert anion (e.g. hydrogensulphate) and the photolysis of phenacycldimethylsulphonium hydrogensulphate in water led to a high yield of dimer and the absence of products arising from the anion.(46)

Benzyldimethylsulphonium tetrafluoroborate, in methanol, behaved rather differently and the major products were benzyl methyl ether, with a small amount of diphenylethane,



$$C_6H_5CH_2\overset{+}{S}(CH_3)_2BF_4^- \xrightarrow[(254\,nm)]{h\nu/CH_3OH} \underset{25\%}{C_6H_5CH_2OCH_3} + \underset{3\%}{(C_6H_5\dot{C}H_2)_2}$$

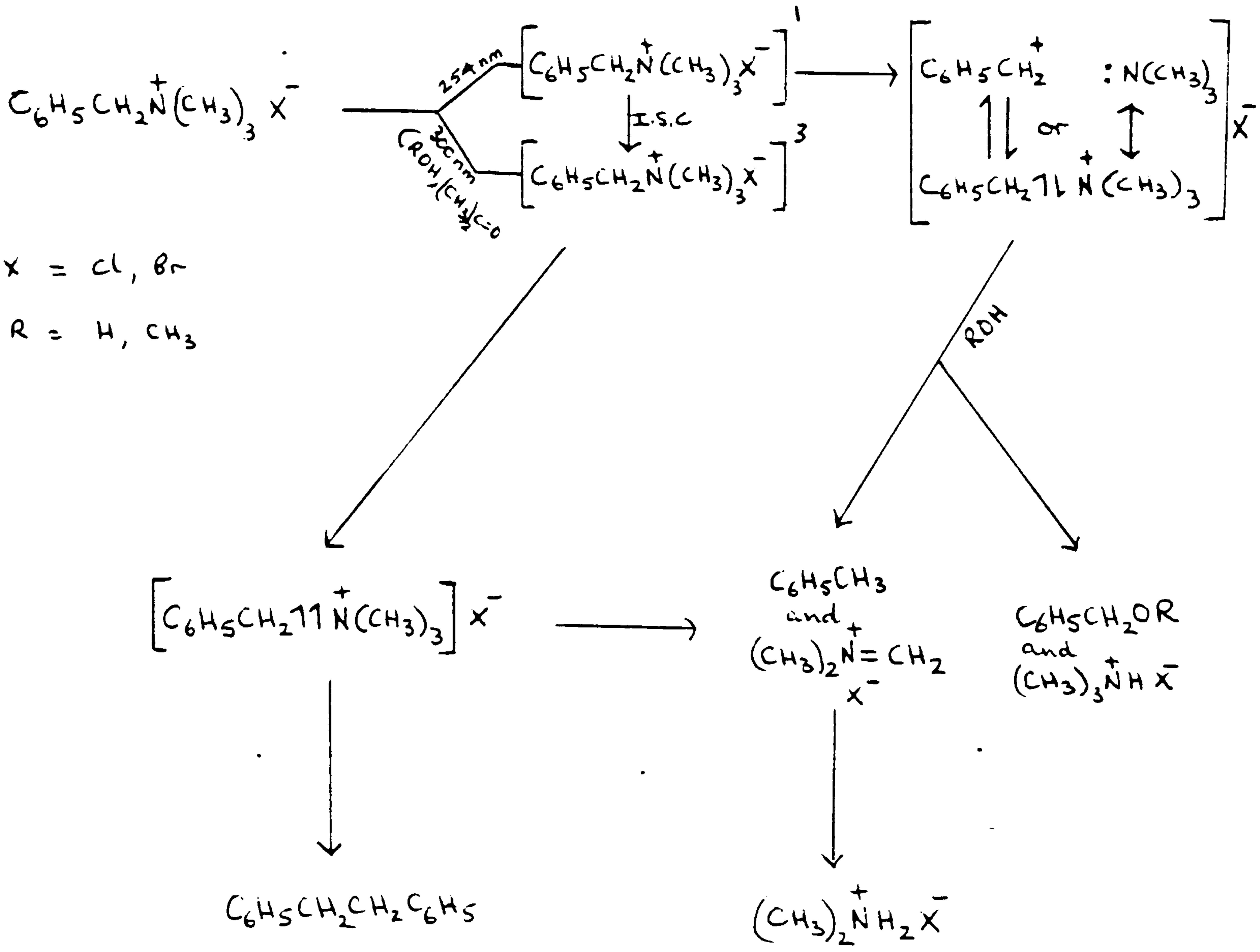
$$\underset{9\%}{C_6H_5\underset{OCH_3}{CH}CH_2C_6H_5} + \underset{9\%}{C_6H_5CHO}$$

$$\underset{7\%}{C_6H_5\underset{OCH_3}{CH}\overset{OCH_3}{CH}C_6H_5}$$

and both heterolytic and homolytic cleavages were proposed to account for product formation. The products were postulated to arise from an initial $\pi\rightarrow\pi^*$ excitation(47).

A single experiment on benzyldimethylsulphonium bromide in aqueous solution was reported by Laird and Williams(46). The system required acetone as sensitiser and the products were, benzyl alcohol, toluene, bibenzyl and benzyl bromide.

The photolytic decomposition of benzylammonium salts has been investigated.(48) By detailed sensitisation and quenching studies, McKenna et al. established the photolysis of benzyltrimethylammonium bromide in aqueous and aqueous/tert-butanol solution: benzyl alcohol, benzyl t-butyl ether, and some toluene were produced by a singlet pathway, and the following scheme was proposed to account for the products.



These workers proposed that both homolytic and heterolytic mechanisms were operating concurrently.

The desire to correlate electrochemical reduction with photochemical cleavage of the C-$\overset{+}{S}$ bond lead us to investigate the excited state chemistry of the benzyl type sulphonium salts, in particular the xylylenebis-sulphonium salts.

## EXPERIMENTAL

### General Procedure for the Photochemical Experiments

The experiments were carried out in the apparatus shown in Figure 5 (p 112). The sulphonium salt (5 mmoles) was dissolved in distilled water (200 $cm^3$) in the reaction vessel and the solution degassed with nitrogen for 20 minutes, and then acetone (5 $cm^3$) was added to sensitise the reaction. When the solution was irradiated, a fine precipitate was usually deposited on the cooling-jacket of the lamp. After one hour, the irradiation was stopped and the cooling-jacket removed and cleaned by washing with acetone, in which the deposit was quite soluble. The cooling-jacket was replaced and the irradiation recommenced. This procedure was repeated at hourly intervals until it was judged, from the absence of deposit on the cooling-jacket, that most of the starting material had reacted. The acetone washings were examined by tlc and glc and compared with standards.

### The Work-up Procedure

The aqueous mixture was extracted with ether and the extract combined with the acetone washings, dried and analysed by gas liquid chromatography. The residual aqueous solution was evaporated under reduced pressure to remove all traces of ether and its uv spectrum recorded. Evaporation under reduced pressure, to dryness, gave the unreacted sulphonium salt. The weight of sulphonium salt recovered by evaporation correlated well with the estimated value from uv measurements.

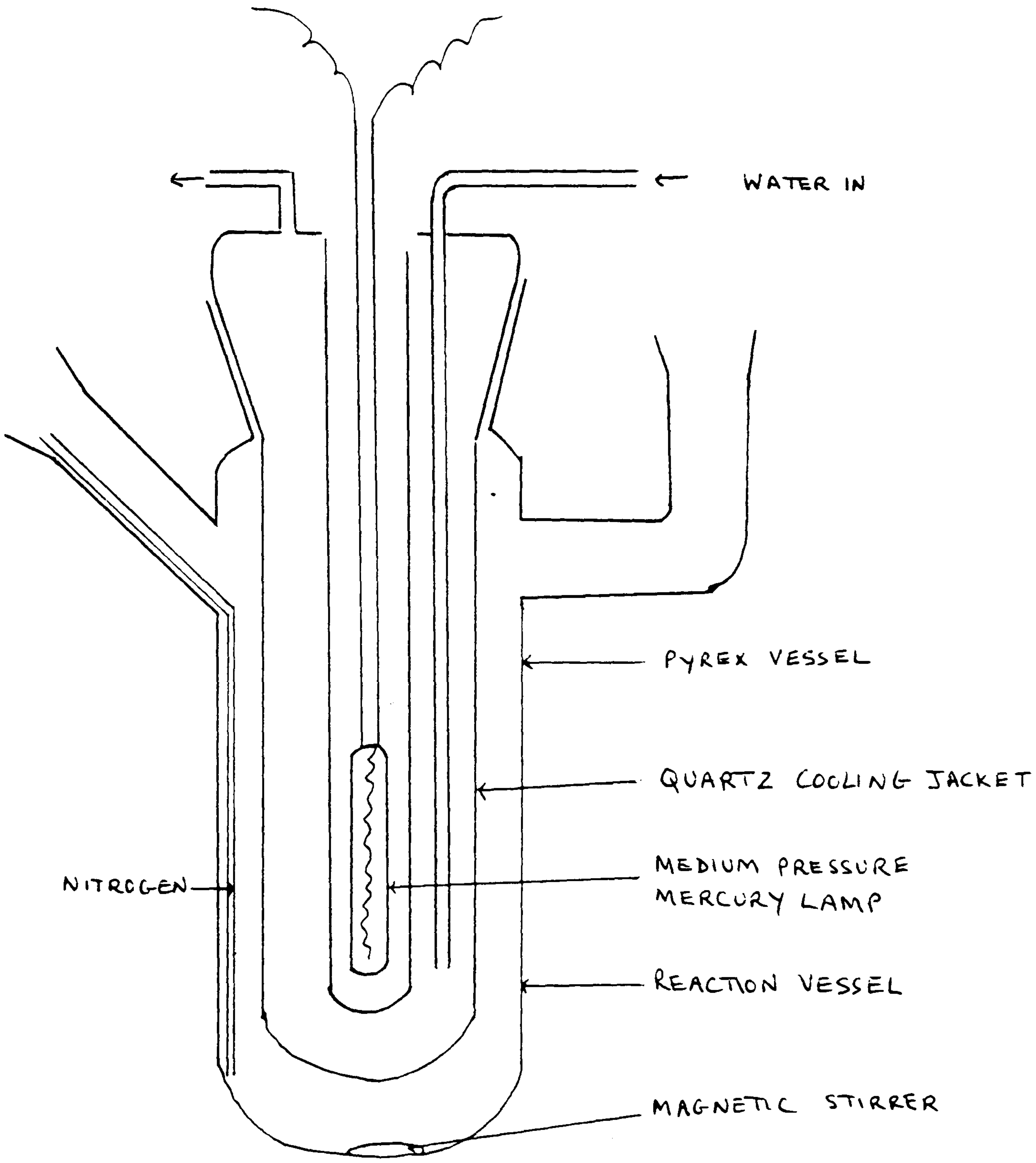


FIG 5 DIAGRAM OF THE U.V. IRRADIATION APPARATUS

## Photolysis of benzyldimethylsulphonium bromide

Benzyldimethylsulphonium bromide (1.2 g) was dissolved in water (200 cm$^3$) and acetone (5 cm$^3$) added as a sensitiser. After 3 hours of irradiation there was no obvious sign of reaction: the solution was unclouded and there was little or no smell of dimethyl sulphide. The irradiation was continued overnight and the mixture was extracted with ether. Glc analysis of the ether extract showed traced traces of benzyl alcohol, toluene and bibenzyl.

$$C_6H_5CH_2\overset{+}{S}(CH_3)_2Br^- \longrightarrow C_6H_5CH_2OH + C_6H_5CH_3$$
$$+ (C_6H_5CH_2)_2$$

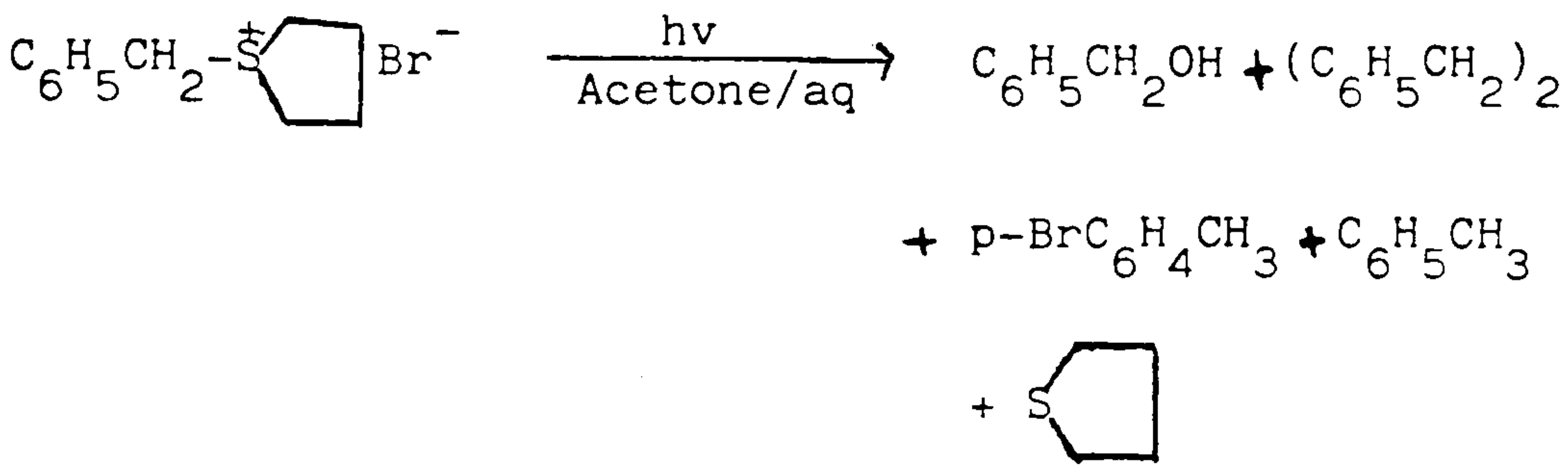
Examination of the aqueous fraction by uv showed 98% unreacted salt. Evaporation of the aqueous fraction gave 97% unreacted starting material. The glc analyses were carried out using a Silar 5 cp column at 170°C; nitrogen carrier gas (60 cm$^3$/min).

## "Dark reaction" of benzyldimethylsulphonium bromide

The possibility of any of the products, particularly the benzyl alcohol, arising from simple hydrolysis ("dark reaction") of the initial substrate, was tested by allowing a solution of the salt (1.2 g in 200 cm$^3$ water) to stand for 15 hours in the dark. The solution was extracted with ether. Work-up of the mixture showed the absence of all the products produced in the irradiation of this sulphonium salt. Recovered salt 1.2 g (100%).

## Photolysis of 1-benzylthioniacyclopentane bromide

A solution of 1-benzylthioniacyclopentane bromide (1.2 g) in water (200 $cm^3$) containing acetone (5 $cm^3$) was irradiated for 5½ hours and worked up according to the general procedure. Examination of the extract by tlc, using benzene as eluant, showed that bibenzyl and benzyl alcohol were the major products, together with small amounts of toluene and p-bromotoluene.



The ether extract was concentrated under vacuo, at room temperature, marker was added (6-methylheptanol), and the mixture was made up to a known volume with ether and analysed by glc, using a Silar 5 cp column at 170°; nitrogen carrier gas (60 $cm^3$/min), and the following yields were estimated:

| | |
|---|---|
| Toluene | 47 mg |
| bibenzyl | 100 mg |
| benzyl alcohol | 220 mg |
| p-bromotoluene | 40 mg |
| thiacyclopentane | 353 mg |

## Determination of unreacted starting material

After extraction of the aqueous mixture from photolysis with ether, the aqueous layer was diluted to a known volume and the uv spectrum recorded. Comparing the absorbance with a calibration graph the amount of unreacted salt was 15%.

## 'Dark reaction' of 1-benzylthioniacyclopentane bromide

A solution (5 mmoles in 200 $cm^3$) water) was allowed to stand in the dark overnight. The solution was extracted with ether. Analysis of the aqueous layer by polarography and by uv spectroscopy showed that no decomposition of the salt had occurred. The possibility of hydrolysis can also be ruled out by the earlier experiments in which irradiation in the absence of the sensitiser showed virtually no decomposition of the salt.

## Attempted detection of the benzyl radical and thiacyclopentane radical cation using ESR spectroscopy

(This experiment was kindly carried out by Dr. A. Oduwole at Queen Mary College, University of London).

1-benzylthioniacyclopentane bromide (6 mg) was dissolved in water (0.5 $cm^3$) and the solution was degassed by means of 3 freeze-thaw cycles and sealed in an esr tube. The solution was irradiated at room temperature in the cavity of the esr spectrometer using a medium pressure lamp. The esr spectra were recorded over a period of several hours but no signals due to radical formation were detected. The above procedure was repeated, this time using acetone as a sensitiser, and again no radicals were detected although photodecomposition had occurred, since the resultant solution had become turbid. Even lowering the temperature to -196° C gave spectra devoid of radical or radical cation signals.

## Photolysis of p-chlorobenzyldimethylsulphonium chloride

Irradiation of this salt (1.2 g) in the normal manner, for 5½ hours and extraction with ether and analysis by glc, (Silar 5 cp column at 170°) gave the following products:

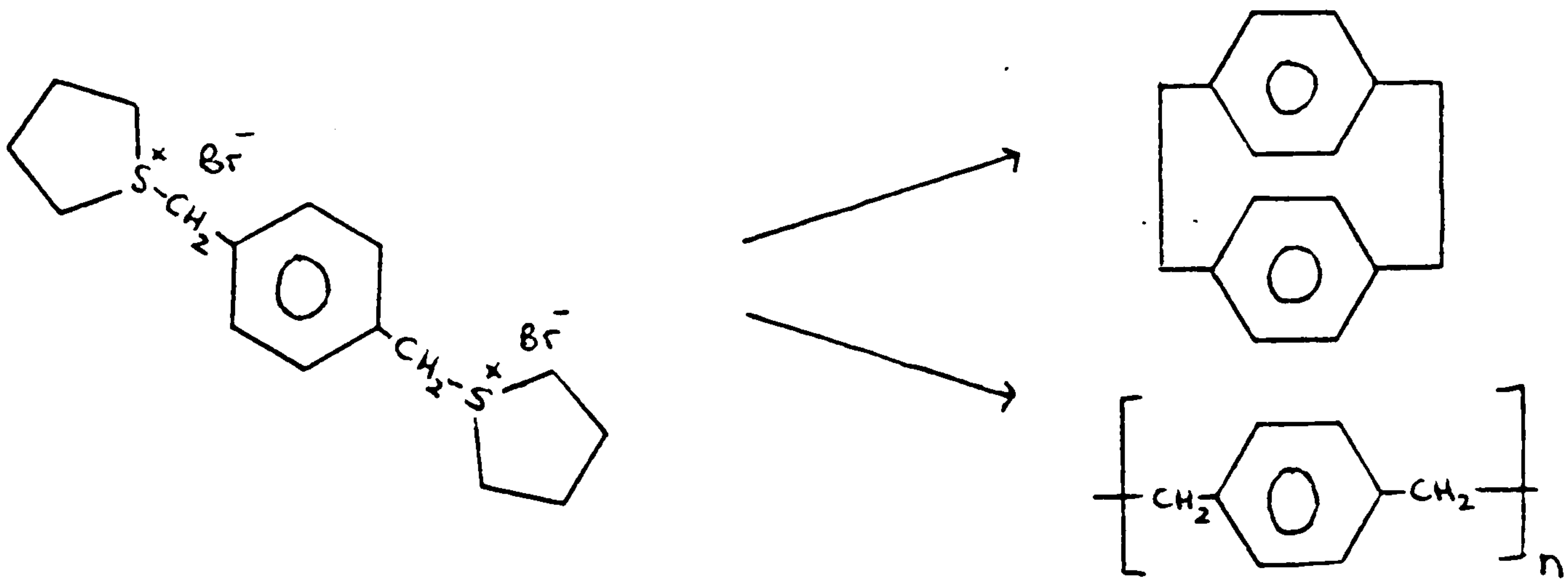
$$\begin{aligned} p\text{-}ClC_6H_4CH_2\overset{+}{S}(CH_3)_2Cl^- \longrightarrow\ & p\text{-}ClC_6H_4CH_2\text{-}CH_2C_6H_4Cl\text{-}p && 92\% \quad (1) \\ & + p\text{-}ClC_6H_4CH_2OH && 3\% \\ & + p\text{-}ClC_6H_4CH_2Cl && 3\% \end{aligned}$$

Unreacted sulphonium salt = 2% (uv spectrum analysis)
The dimer was isolated.
Elemental analysis for dimer (1) :

Calculated %C = 66.93 Found%C = 67.01
%H = 4.78 %H 4.63

## Photolysis of p-xylylenebis(1-thioniacyclopentane bromide)

The salt (2 g) was photolysed according to the general procedure, for 5 hours. During this time a suspension of fine particles and "filmy material" were observed. The mixture was filtered and the two components were isolated. The aqueous mixture was extracted with ether and chromatographed, and a trace of p-xylene was detected.



The infra-red spectrum of the "filmy material" gave the following bands: 2800-3800(s); 1400-1510(s); and 820 $cm^{-1}$ (p-substituted benzene). The mass spectrum showed a regular degradation pattern consisting of peaks centred at: 726, 624, 520, 415, 311, 207, 105 and is consistent with the poly-p-xylylene structure.

The $^{1}H$ nmr, infra-red and mass spectra of the second component are consistent with it being p-cyclophane.
$\delta$ values (ppm): 3.09(s), 6.47(s)
The infra-red spectrum had a band at 800 $cm^{-1}$, characteristic of p-disubstituted benzenes.
Mass spectrum: (m/e) 208 (molecular ion), 104 (base peak).

elemental analysis: Calculated %C = 92.31 Found %C = 92.28

%H = 7.69 %H = 8.09

Yield of p-cyclophane, 337 mg.

Yield of poly-p-xylylene, 80 mg.

This corresponds to a conversion of 98.7%. (Based on 1.80 g of reacted salt.)

Unreacted salt 0.2 g.

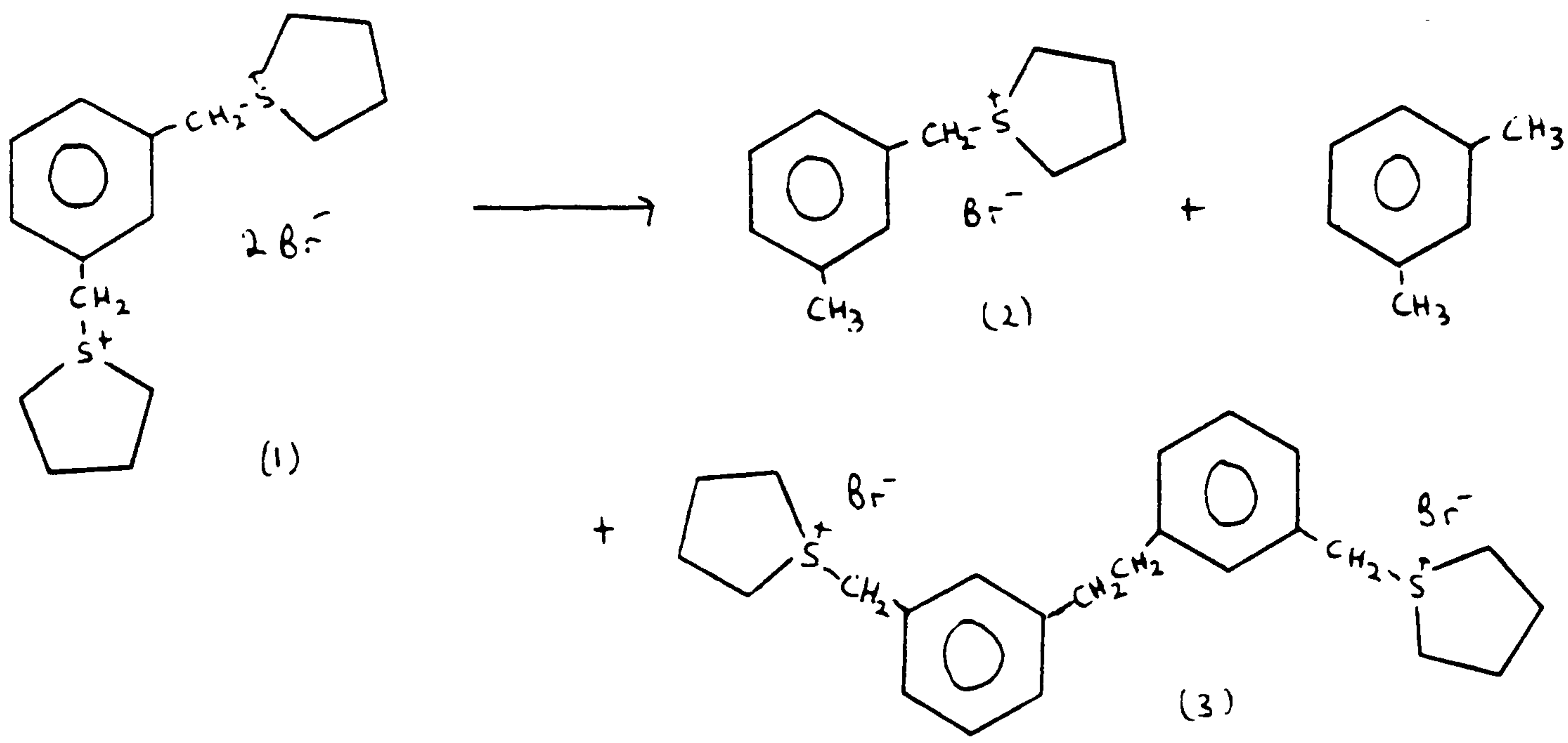
### Photolysis of o-xylylenebis(1-thioniacyclopentane bromide)

Irradiation of an aqueous acetone (200:5cm$^3$) solution of the salt (2 g) for 10 hours, showed no apparent reaction.

The mixture was extracted with ether and examined by glc; a trace of o-xylene was detected. The polarographic current of the solution after dilution, corresponded to 98% unreacted starting material.

### Photolysis of m-xylylenebis(1-thioniacyclopentane bromide)

Irradiation of this salt (2 g) as outlined in the general procedure gave the following results:



The solution was extracted with ether: the ether extract contained only a trace of m-xylene. The aqueous layer was worked up using column chromatography (silica, ethanol as eluent), to separate (1), (2) and (3) salts. Order of elution 2, 1 and 3.

Irradiation of a solution of (2) for the same period of time (5) hours have only a trace of m-xylene. The structure of 3 was assigned from $^1$H nmr only.

## Effect of anion and concentration on ease of reduction

When photolysis occurs the products that are insoluble in the aqueous solution cause it to become opaque. A series of irradiations were carried out in which various amounts of anion, detailed below, were added to the solution of the sulphonium bromide salt. Visually there appeared to be no change in the reaction rate, except with iodide.

| Anion | Equivalents |
|---|---|
| Br | 1, 10, 20 |
| F | 1, 20 |
| Cl | 1, 20 |
| I | 1,20 |
| $NO_3$ | 1,20 |

Although this was rather a qualitative method of evaluation, it was sufficient to show clearly that none of the added ions had a marked effect on the ease of reaction. The only case where an effect was observed was when iodide ion was added: a definite decrease in the rate of photolysis was noticed. Similar results were observed by Laird in the photolysis of phenacyl sulphonium salts.(46)

## Photolysis of benzyltrimethylammonium bromide

Benzyltrimethylammonium bromide (1.13 g) in 200 cm$^3$ water was irradiated for 4½ hours, according to the general procedure, using acetone (5 cm$^3$) as a sensitiser. The decomposition of the substrate was much faster than the corresponding benzyldimethylsulphonium salt; the salt appeared to react at much the same rate as the 1-benzylthioniacyclopentane salt. No change in the pH was detected. The mixture was extracted with ether and the extract analysed by glc. The aqueous fraction was evaporated in vacuo. Tlc of the resulting mixture, using ethanol as eluant showed the presence of three salt components. These were separated on a silica column using ethanol as eluent; each component was identified by its nmr spectrum. The dimethylammonium bromide was also identified by its mass spectrum and derivatisation to N,N-dimethyl-p-toluenesulphonamide.

$$\begin{array}{lcll}
C_6H_5CH_2\overset{+}{N}(CH_3)_3Br^- & \xrightarrow[\text{acetone}/H_2O]{h\nu} & C_6H_5CH_2OH \;+ & C_6H_5CH_3 \\
 & & \quad 45\% & \quad 28\% \\
 & & (C_6H_5CH_2)_2 & \\
 & & \quad 22\% & \\
 & & (CH_3)_2\overset{+}{N}H_2Br^- \;+ & (CH_3)_3\overset{+}{N}HBr^- \\
 & & \quad 30\% & \quad 64\%
\end{array}$$

The amount of unreacted starting material, detected by uv absorption, was 4%.

## Test for a possible "dark" reaction

A solution of benzyltrimethylammonium bromide (1.13 g) in aqueous acetone (200: 5 cm$^3$) was maintained at room temperature for 12 hours. The aqueous mixture was extracted with ether and the aqueous layer after dilution was analysed by uv spectroscopy. The absorption remained identical to that of the initial solution. Evaporation under reduced pressure, gave only the starting material (1.12 g).

## Photolysis of benzyltrimethylammonium bromide in the absence of a sensitiser

The irradiation of a solution of benzyltrimethylammonium bromide (1.13 g) without acetone sensitisation, for 4½ hours, according to the general procedure, led to the following products.

$$C_6H_5CH_2\overset{+}{N}(CH_3)_3\ Br^- \xrightarrow[H_2O]{hv} \underset{12\%}{C_6H_5CH_3^{*}} + \underset{10\%}{(C_6H_5CH_2)_2^{*}}$$

$$+ (CH_3)_2\overset{+}{N}H_2\ Br^- + (CH_3)_3\overset{+}{N}H\ Br^-$$

* identified by glc analysis (conditions as before).

## Photolysis of benzyltriethylammonium bromide

A solution of benzyltriethylammonium bromide (1.36 g) in water/acetone (200: 5 $cm^3$) was irradiated as before for 5 hours. The final pH of the solution was unchanged. The products were estimated as described earlier.

$$C_6H_5CH_2\overset{+}{N}(C_2H_5)_3\ Br^- \xrightarrow[acetone/H_2O]{hv} \underset{36\%}{C_6H_5CH_2OH} + \underset{27\%}{C_6H_5CH_3}$$

$$\underset{18\%}{(C_6H_5CH_2)_2} + (C_2H_5)_3\overset{+}{N}H\ Br^-$$

The amount of unreacted starting salt, calculated on the basis of uv measurements, was 145 mg.

## Test for a possible "dark" reaction

Benzyltriethylammonium bromide (1.36 g) was dissolved in aqueous acetone (water 200 $cm^3$: acetone 5 $cm^3$) and the uv absorption determined. The solution was allowed to stand in the dark overnight. After extraction with ether the uv absorption of the aqueous solution was unchanged. Evaporation of the solution under reduced pressure led to the recovery of the salt (1.33 g).

## Photolysis of m-methylbenzyltrimethylammonium bromide

A solution of m-methylbenzyltrimethylammonium bromide (1.22 g, 5 mmoles) in water/acetone (200/5 $cm^3$) was irradiated for 5 hours according to the general procedure. The final solution was alkaline (pH 9.5). The ether extract of the solution was analysed by glc and the aqueous fraction was analysed by column chromatography.

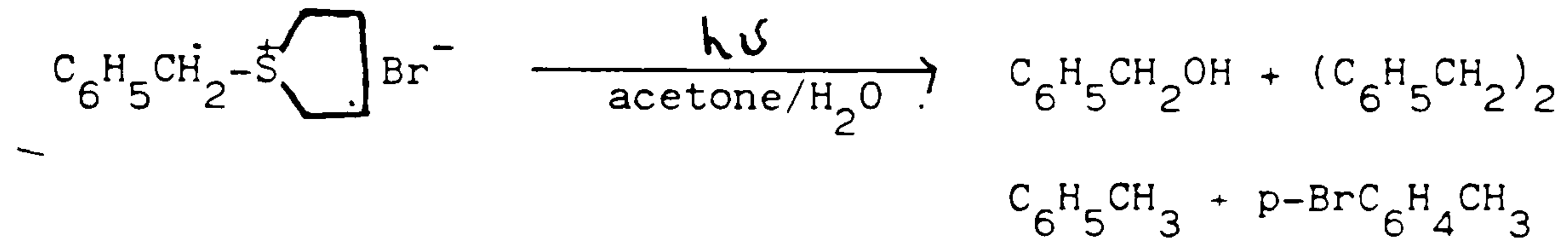
Products:

m-xylene (86%)
m-methylbenzyl bromide (trace)
$(CH_3)_3\overset{+}{N}HBr^-$ (89%)
unreacted salt (11%) (uv absorption)

There was also a small peak in the glc chromatograph with a retention time corresponding to that expected for 3,3'-dimethylbibenzyl.

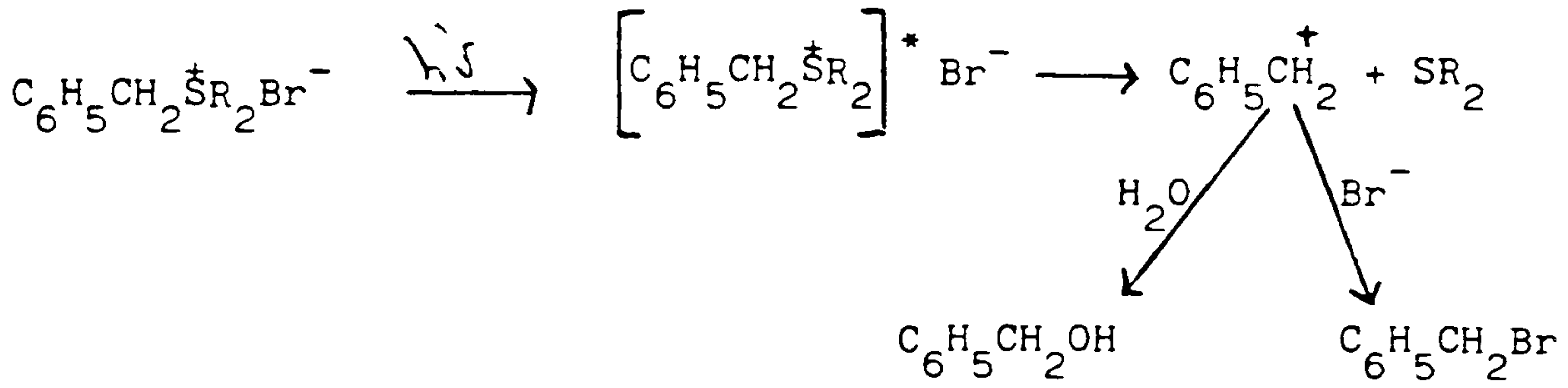
## DISCUSSION

Photolysis of the parent benzyldimethylsulphonium salts, in aqueous solution, using a medium pressure mercury lamp for ten hours gave no decomposition, whereas the same acetone sensitised solution gave only slight decomposition to afford traces of benzyl alcohol, toluene and bibenzyl. Because of the much higher electrochemical reactivity of the 1-benzylthioniacyclopentane salt than the benzyldimethylsulphonium salt we investigated whether it would prove similarly more reactive in the excited state and experiments confirmed this. Thus the photochemical decomposition of the 1-benzylthioniacyclopentane bromide went almost to completion in 5 hours. However, even in this case a sensitiser was necessary.

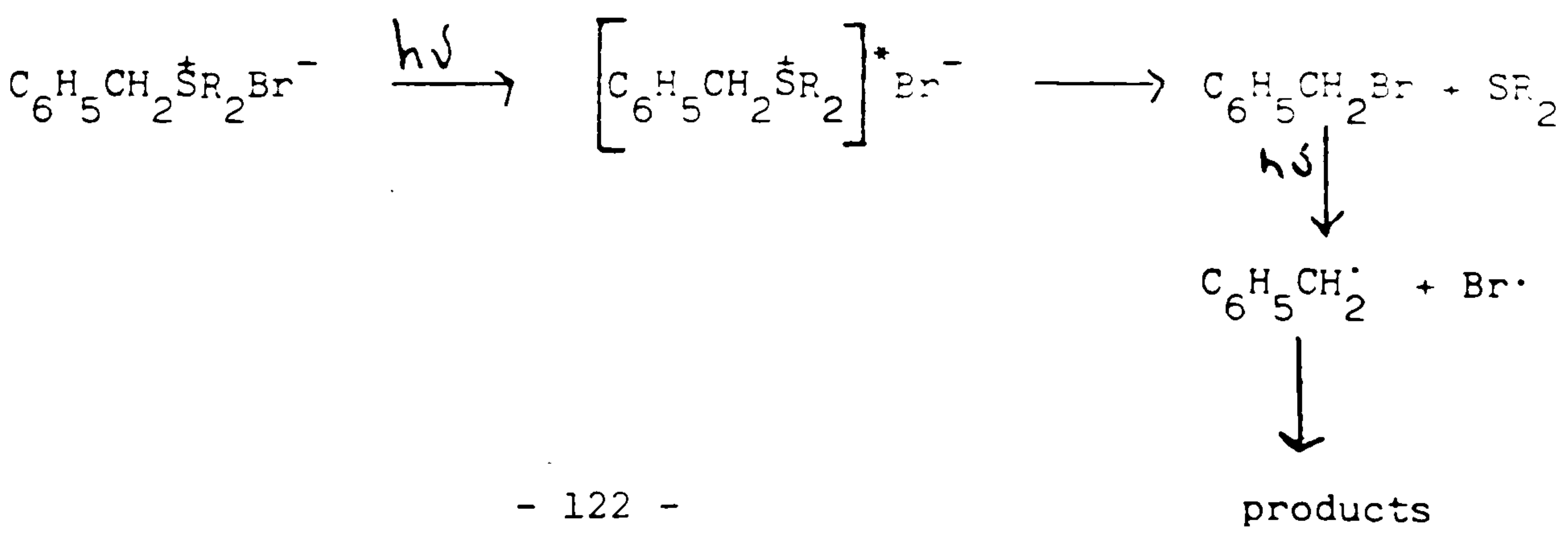


There are several possible mechanisms for the cleavage of the C-$\overset{+}{S}$ bond:

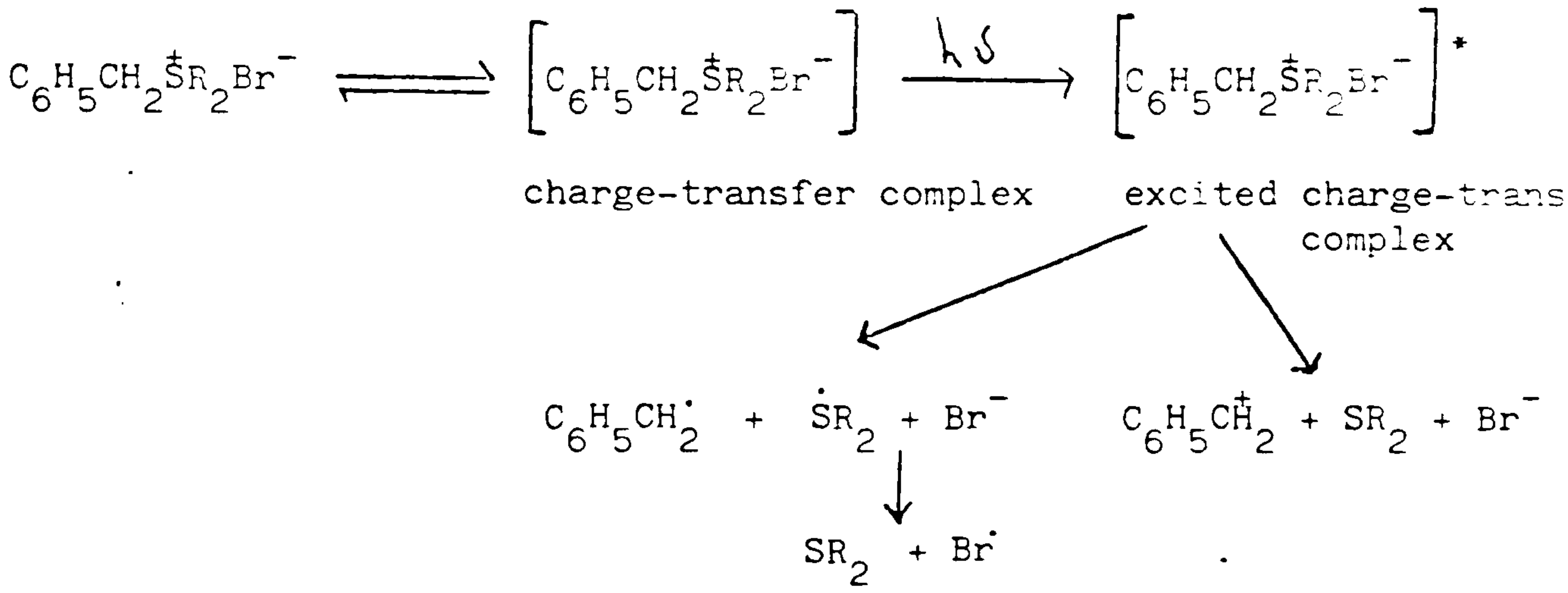
(1) Heterolysis of the C-$\overset{+}{S}$ to give the benzyl carbonium ion:



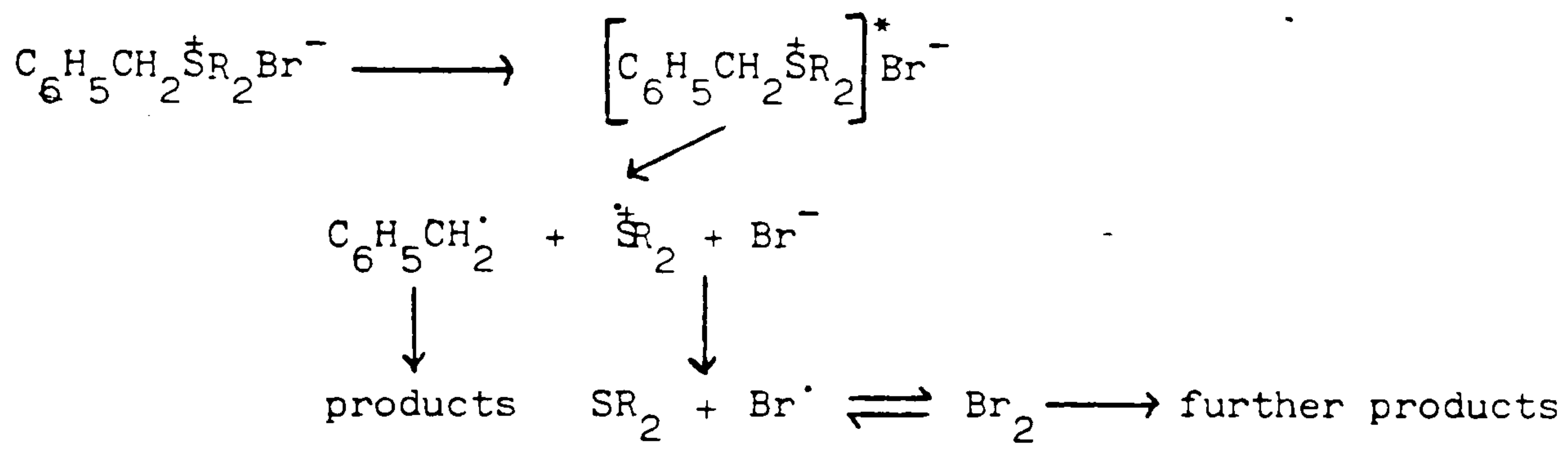
(2) Nucleophilic attack ($S_N2$) by bromide ion on an excited benzyl salt to give benzyl bromide which then undergoes homolysis.



(3) Formation of an excited charge-transfer complex, which undergoes further reaction:



(4) Homolysis of the $C-\overset{+}{S}$ bond leading to the benzyl radical:



Mechanisms (2) and (3) both involve the anion in the cleavage of the $C-\overset{+}{S}$ bond. The rates of reaction for such processes should be dependent upon the concentration and the nature of the anion. We therefore changed the concentration and the type of anion but found no significant difference in the rate of reaction. Aqueous solutions of 1-benzylthioniacyclopentane bromide were irradiated in the presence of other anions, for example: chloride, iodide, fluoride and tosylate. There was no apparent change in the rate of decomposition except in the presence of iodide which significantly reduced the rate of decomposition, possibly by quenching the excitation. Adding an excess of bromide ion did not appear to enhance the photolysis. Therefore mechanisms (2) and (3) may be disregarded. Further evidence against mechanism (2) is (a) no benzyl bromide was detected in the reaction product, (b) the photolytic decomposition of a suspension of benzyl bromide in water was much slower than the solution of the sulphonium salt and gave only traces of toluene and bibenzyl.

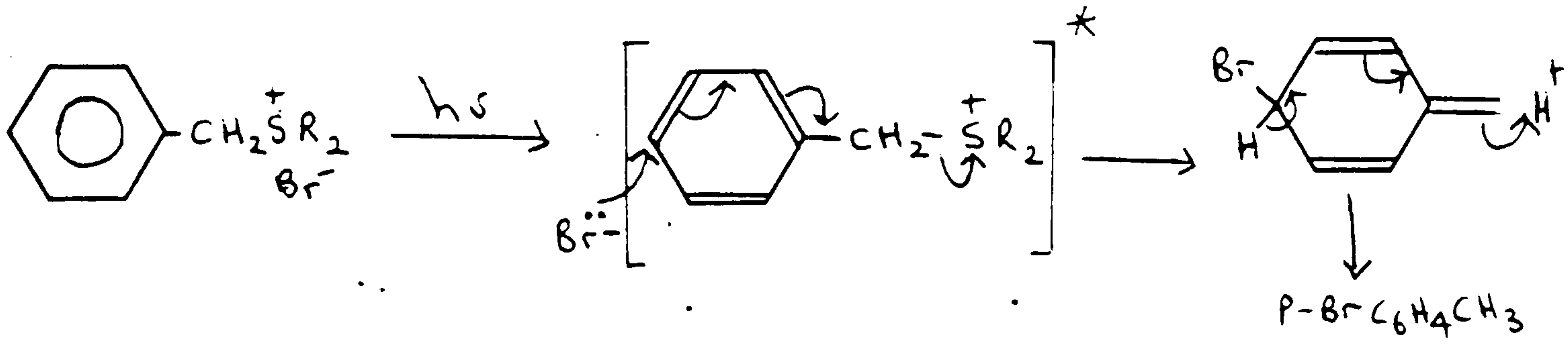
From the products formed, it appears that both heterolytic and homolytic mechanisms are proceeding concurrently. It is difficult to account for the formation of benzyl alcohol except by a heterolytic process. Mechanism (1) involves heterolysis to give a benzyl carbonium intermediate followed by reaction with a water molecule to give the benzyl alcohol.

The formation of bibenzyl is readily accommodated by the dimerisation of the benzyl radicals. Benzyl radicals are relatively unreactive and in the absence of a good hydrogen atom donor usually form the dimer. Toluene, which is only a minor product in the photolysis, can arise from the benzyl radical by hydrogen atom abstraction and possible hydrogen atom donors include bibenzyl and unreacted sulphonium salt substrate. Water is a very poor hydrogen atom donor in radical reactions. Another possible route for the formation of toluene is by oxidation of an anion e.g. bromide by benzyl radicals to give the carbanion, which is then protonated:

$$\begin{array}{ccc} C_6H_5CH_2^{\cdot} + :Br^- & \longrightarrow & C_6H_5CH_2^-: + \dot{Br} \\ & & \big\downarrow H^+ \\ & & C_6H_5CH_3 \end{array}$$

The p-bromotoluene, which is also a minor product, may arise by bromination of the toluene. p-Bromo products were also observed in the photolysis of phenacylsulphonium bromide by Laird and Williams(45). This bromination is probably electrophilic substitution because free radical (bromination) substitution generally replaces the $\alpha$-hydrogens. In this case the source of electrophilic bromine is molecular bromine.

However, any bromine formed should be scavenged by the acetone sensitiser which is present in relatively large amounts. Another possibility is the bromination of some of the sulphonium salt which then undergoes photolysis. However, this again is subject to the restriction mentioned above that the bromine is most likely to be scavenged by the acetone. Also relevant is the fact that we failed to detect any para-bromo salt in the recovered unreacted sulphonium salt, by either uv or nmr methods; nor did we detect any 4,4'-dibromobibenzyl. A mechanism which might account for the p-bromotoluene without involving molecular bromine is the following scheme:



This $S_N2'$ type mechanism would also require that the rate of formation of the p-bromotoluene should be dependent upon the concentration of the bromide ion. It might be concluded that the earlier experiments showed that the photolysis was insensitive to bromide ion concentration, and would therefore rule out this mechanism. However, since this is only a minor product, any concentration dependence may not have been detected in the earlier experiments.

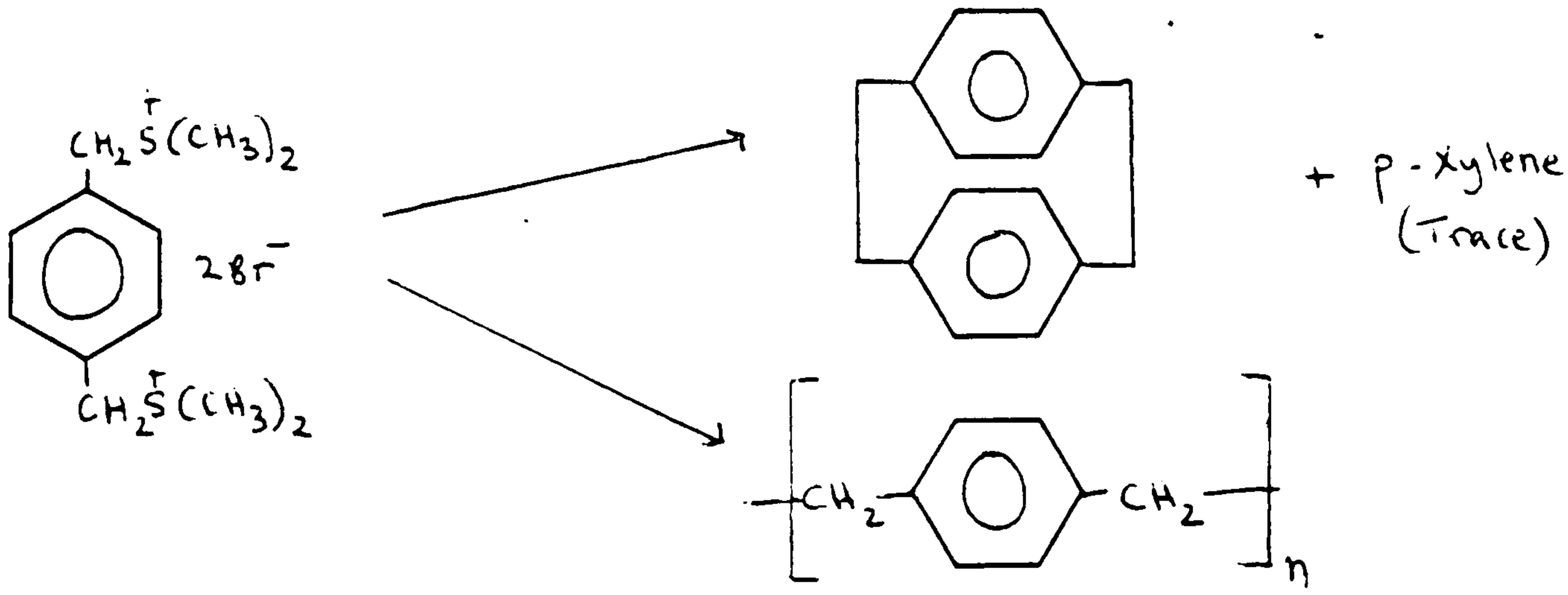
The photolyses of p-substituted benzyldimethylsulphonium salts were appreciably faster than the unsubstituted salt, which reacted very slowly. The p-chloro salt gave p,p'-dichlorobibenzyl (main product), p-chlorobenzyl chloride and p-chlorobenzyl alcohol; the p-methyl salt afforded p-bitolyl (main product), p-methylbenzyl bromide and p-benzyl alcohol. The most salient feature of these results for the p-substituted benzyl salts is the very large production of dimer ( 90%). This is again consistent with the radical scheme. Methyl and chloro-substituents have very different polar properties and would be expected to affect heterolytic processes very differently, whereas both substituents stabilise radicals. This could account for (a) the apparent ease of photolysis relative to the unsubstituted benzyl salt,

(b) the increased amount of radical product and

(c) the much higher proportion of dimer compound to p-substituted toluene.

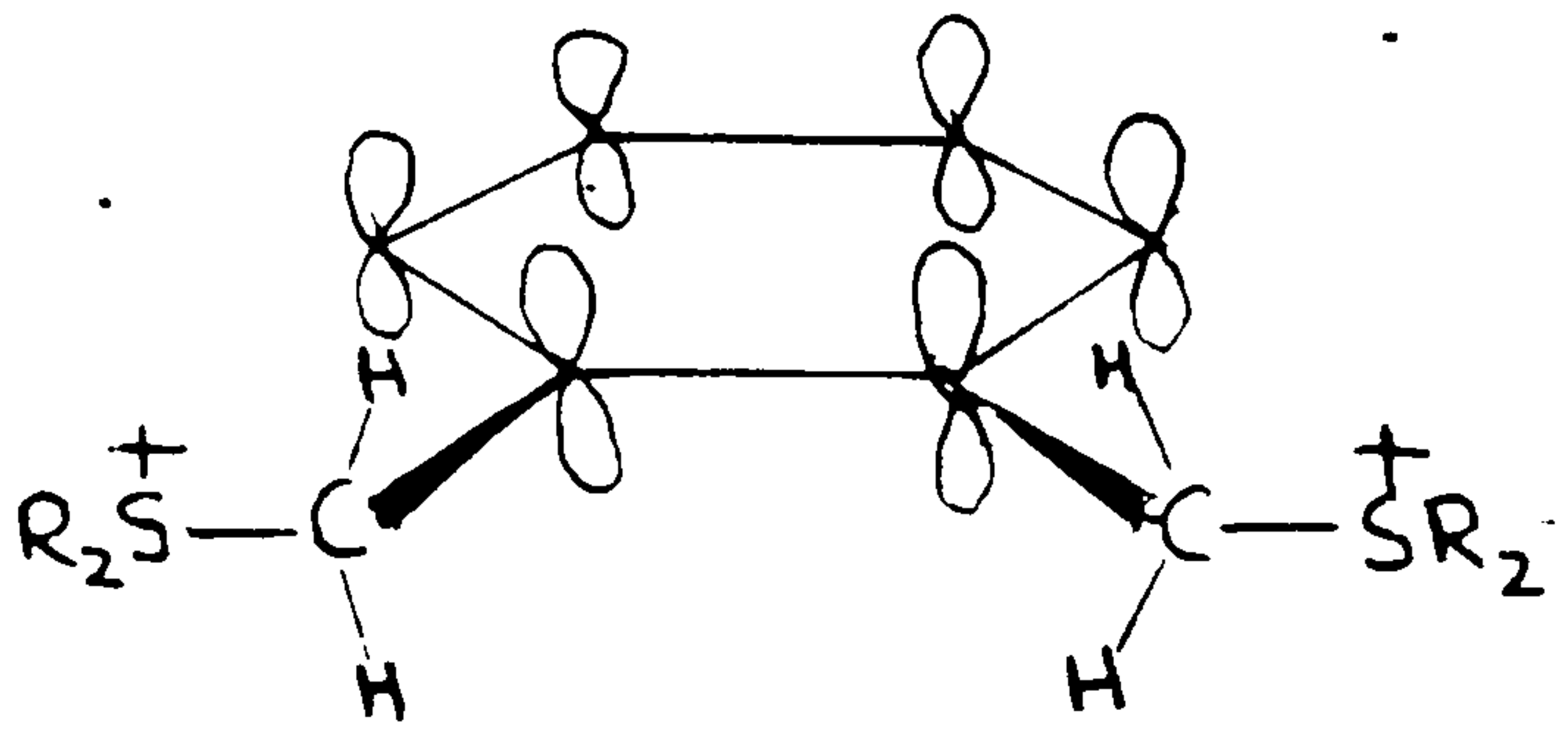
These observations parallel our results on the electrolysis of the salts: although dimer was seldom formed, the proportion of the dibenzylmercury product was enhanced by p-substituents.

We were particularly interested in the bis-sulphonium salts because of our results on the electrolysis of these compounds. The p-bis-dimethylsulphonium salt undergoes photolysis faster than the benzyl-dimethylsulphonium salt and contrary to the electrolysis experiments, gives largely the p-cyclophane together with some polymer and a trace of p-xylene.



As in electrolysis, the reaction (excitation) at one group leads to reaction involving both the salt groups. There was no evidence for the formation of any of the mono-salt (p-methylbenzyldimethylsulphonium bromide) during the reaction (cf. the m-bis salt). The p-cyclophane and p-xylylene polymer almost certainly derives from the p-xylylene intermediate and it is interesting that the two methods of generation, electrolysis and photolysis, give rise to very different proportions of dimer and polymer. This suggests that the p-xylylene monomer differs either in state and/or in environment in the two processes. We suggest the following explanation. In the electrolytic reduction, the p-xylylene is generated at the mercury surface to which it is initially adsorbed, together with many other p-xylylene molecules. This is conducive to polymerisation. In the photolysis experiments the p-xylylene at the moment of its formation is surrounded by salt and solvent molecules and in a "more dilute" environment compared to the p-xylylene molecules formed at the mercury surface. Therefore in solution polymerisation would tend to be less favourable and dimer formation more likely.

In contrast to the p-xylylene-bis-salt the ortho isomer was almost inert to photolysis under the same conditions. This contrasts also with the electrolytic reduction of this salt, where the ortho isomer was the most reactive.. The considerable steric and electrostatic repulsions between the two sulphonium groups may favour conformations which are unfavourable to delocalisation of electrons of the C-S bond over the aromatic $\pi$ orbitals.



In this conformation the sulphonium groups are at a maximum separation, but the C-S bonds are, to a first approximation, orthogonal to the aromatic $\pi$ orbitals.

The meta-bis-salt also differs from the other isomers; photolysis gives mainly the mono-salt (m-methylbenzyldimethylsulphonium bromide), together with traces of the bis-dimer salt; no m-methylbenzyl alcohol was detected. This contrasts markedly with the photolysis of the mono-sulphonium salts (benzyldimethylsulphonium bromide and 1-benzylthioniacyclopentane bromide) where over half of the product was benzyl alcohol.

The relationship with electrolysis is even more apt insofar as the main product of photolysis of the meta-bis salt is the mono salt, which was also the product in the potential controlled electrolysis. The isolation of such a large amount of the m-methylbenzyldimethylsulphonium bromide suggested that it was rather inert to photolysis. We therefore prepared this salt and subjected it to photolysis under the same conditions. There was no obvious sign of reaction and extraction with ether gave only a trace of m-xylene. This inertness is in contrast to the relatively high reactivity of the p-methylbenzyldimethylsulphonium salt. This difference may be due to the fact that in the resulting benzyl radical there is some delocalisation of the unpaired electron at the o- and p- position but not at the m- position and thus substituents at the m- position will have less effect than those at the o- and p- positions. This is an area for further study. A parallel difference in the behaviour of m-methyl and p-methyl isomer was noted in the electrolytic reductions: the para isomer showed a marked tendancy to form the organomercury compound whereas the meta compound gave none.

## Photolysis of quaternary benzylammonium salts

Previous photochemical studies on phenacyl sulphonium and ammonium salts showed that the breaking of the C-$\overset{+}{S}$ bond is much easier than the C-$\overset{+}{N}$ bond. Similar differences were observed in some ground state reactions, e.g. benzyldimethylsulphonium salts are readily reduced by sodium borohydride and sodium in liquid ammonia to the corresponding hydrocarbon, whereas the ammonium salts are much less reactive(17). Also the electrochemical studies described earlier in their report showed a similar difference in reactivity.

However, our investigation of the benzyltrialkylammonium salts showed that these decompose more readily than the analogous sulphonium salts.

The unsensitised photolysis of benzyltrimethylammonium bromide gave toluene and bibenzyl. Under similar conditions the corresponding sulphonium salt (benzyldimethylsulphonium bromide) showed no decomposition. When acetone was used as a sensitiser, photolysis of the sulphonium salt was only slightly enhanced, whereas acetone sensitised photolysis of the ammonium salt went almost to completion to yield benzyl alcohol, toluene and bibenzyl. These results are at variance with those of McKenna et al.(48) who reported that it was the unsensitised photolysis reaction which afforded the three benzyl based products, whilst the sensitised reaction gave only toluene and bibenzyl. They postulated that the benzyl alcohol must arise from the singlet state whereas our results suggest that it arises from the triplet excited state.

The photolysis of benzyltriethylammonium salt affords a similar yield of the three benzyl based products. This suggests that the excitation of both the compounds is similar, presumably $\pi \rightarrow \pi^*$. However, whereas the photolysis of benzyltrimethylammonium bromide gave rise to both the trimethylammonium salt, $(CH_3)_3NHBr$, and the dimethylammonium salt, $(CH_3)_2NH_2Br$, photolysis of benzyltriethylammonium bromide gave only triethylammonium bromide, $(C_2H_5)_3NHBr$ ; no diethylammonium salt, $(C_2H_5)_2NH_2Br$, was detected.

m-Methylbenzyltriethylammonium bromide was photolysed to compare results with the corresponding sulphonium salt. Again it was much more reactive than the sulphonium salt. The products were m-xylene, trimethylammonium bromide and unreacted substrate: no dimer or m-methylbenzyl alcohol was detected. It is most likely that the m-xylene arises from a m-xylyl radical which undergoes very efficient hydrogen transfer from a hydrogen donor, although it is difficult to identify the hydrogen donor from the products.

It is important to record that the discovery of the higher reactivity of the benzylammonium salts compared with the sulphonium salts was made late in this investigation and there was little time available to explore this interesting area. The suggestion that the difference in reactivity of the phenacylsulphonium and ammonium salts was due to the $C-\overset{+}{S}$ bond being weaker than the $C-\overset{+}{N}$ bond cannot be advanced to account for the present results from the benzyl salts.

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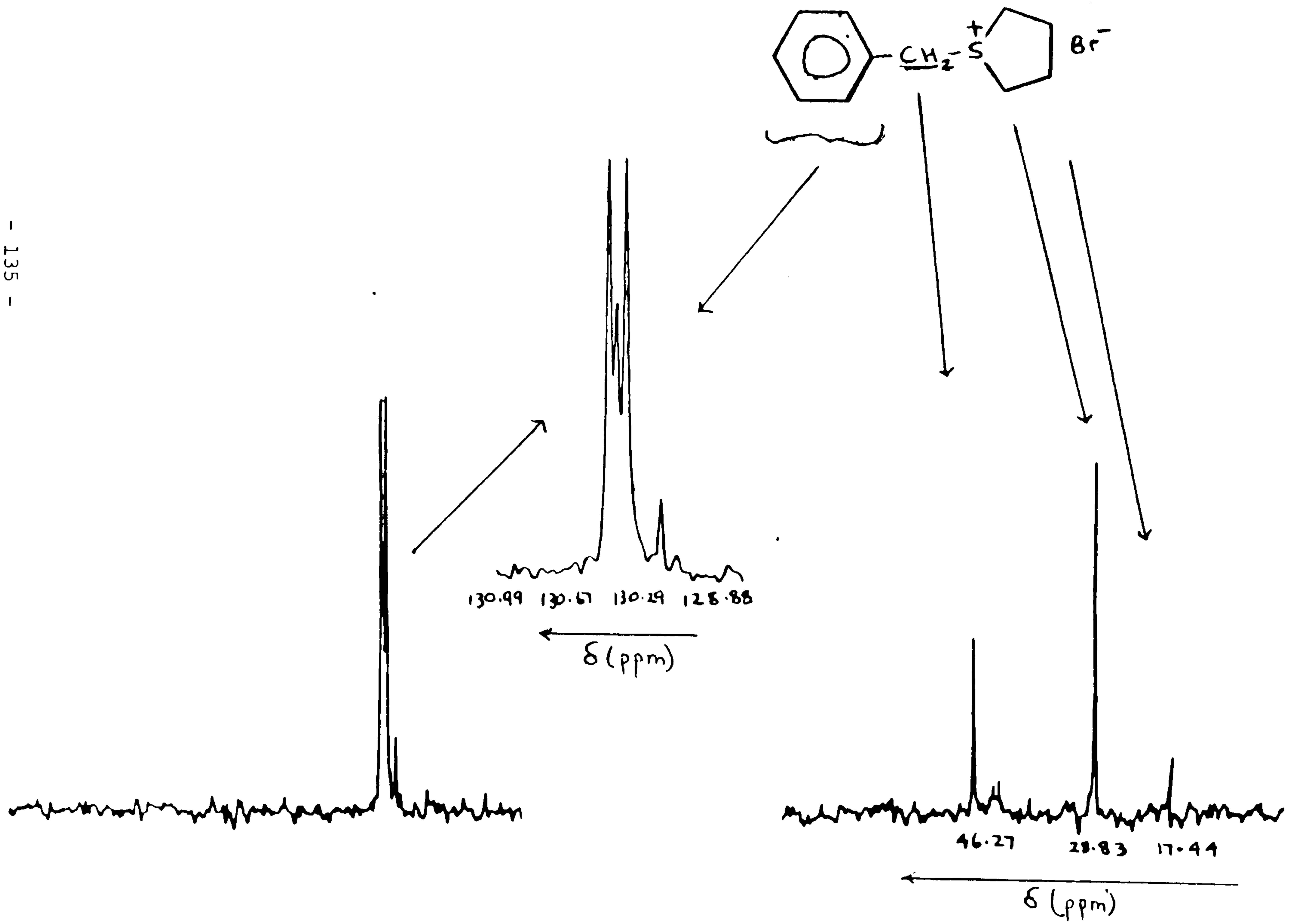
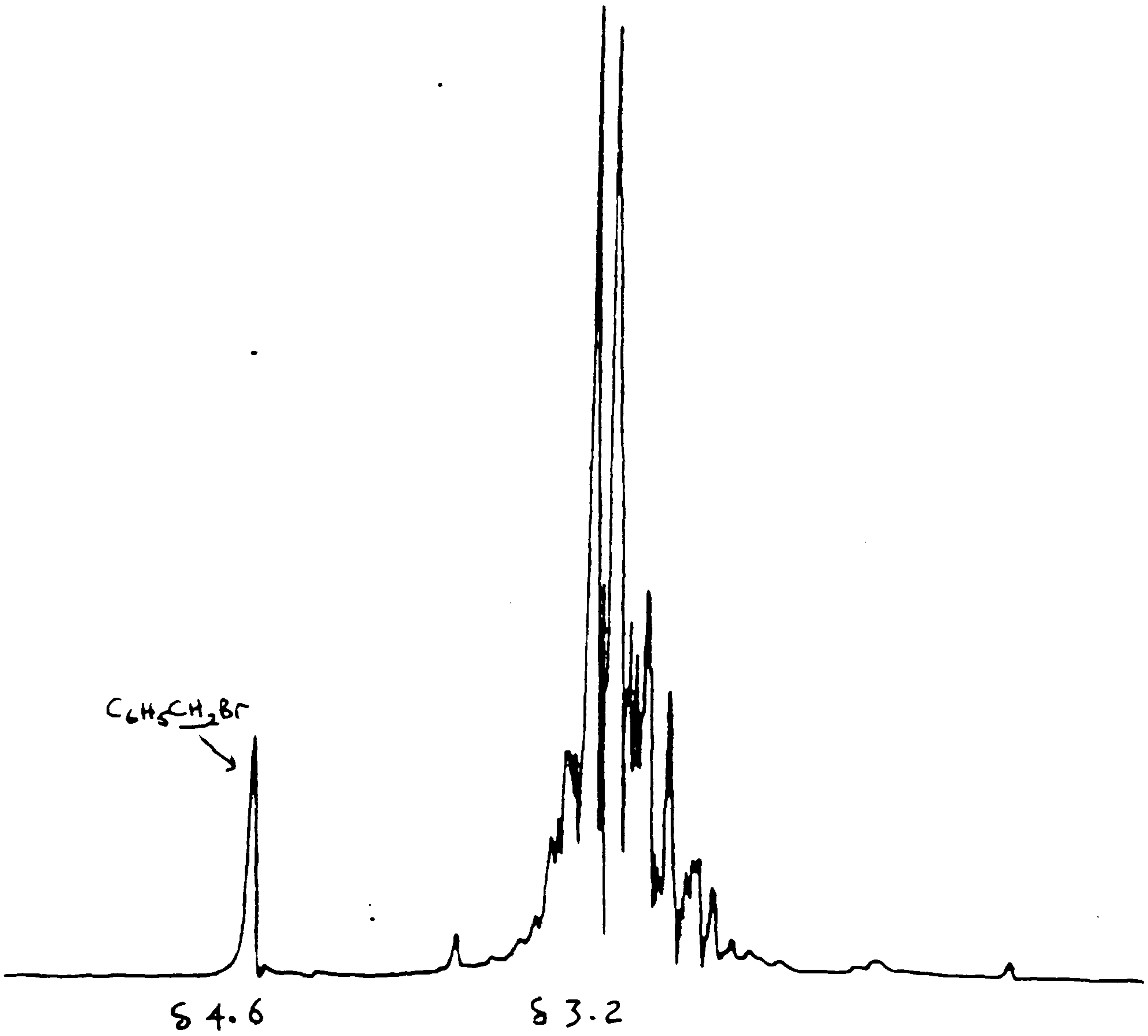
# APPENDIX

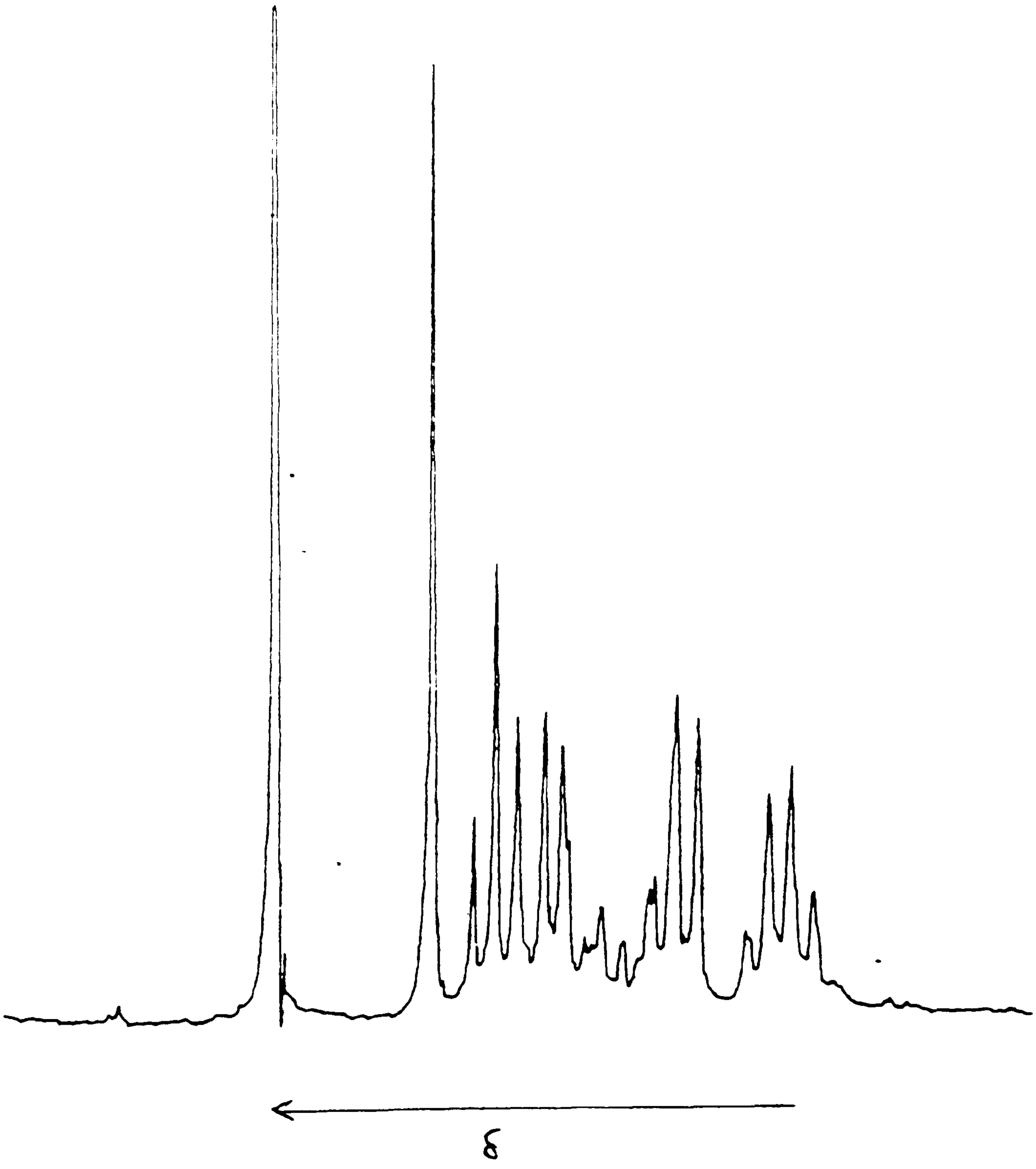
$^{13}C$ nmr spectrum of 1-benzylthioniacyclopentane bromide



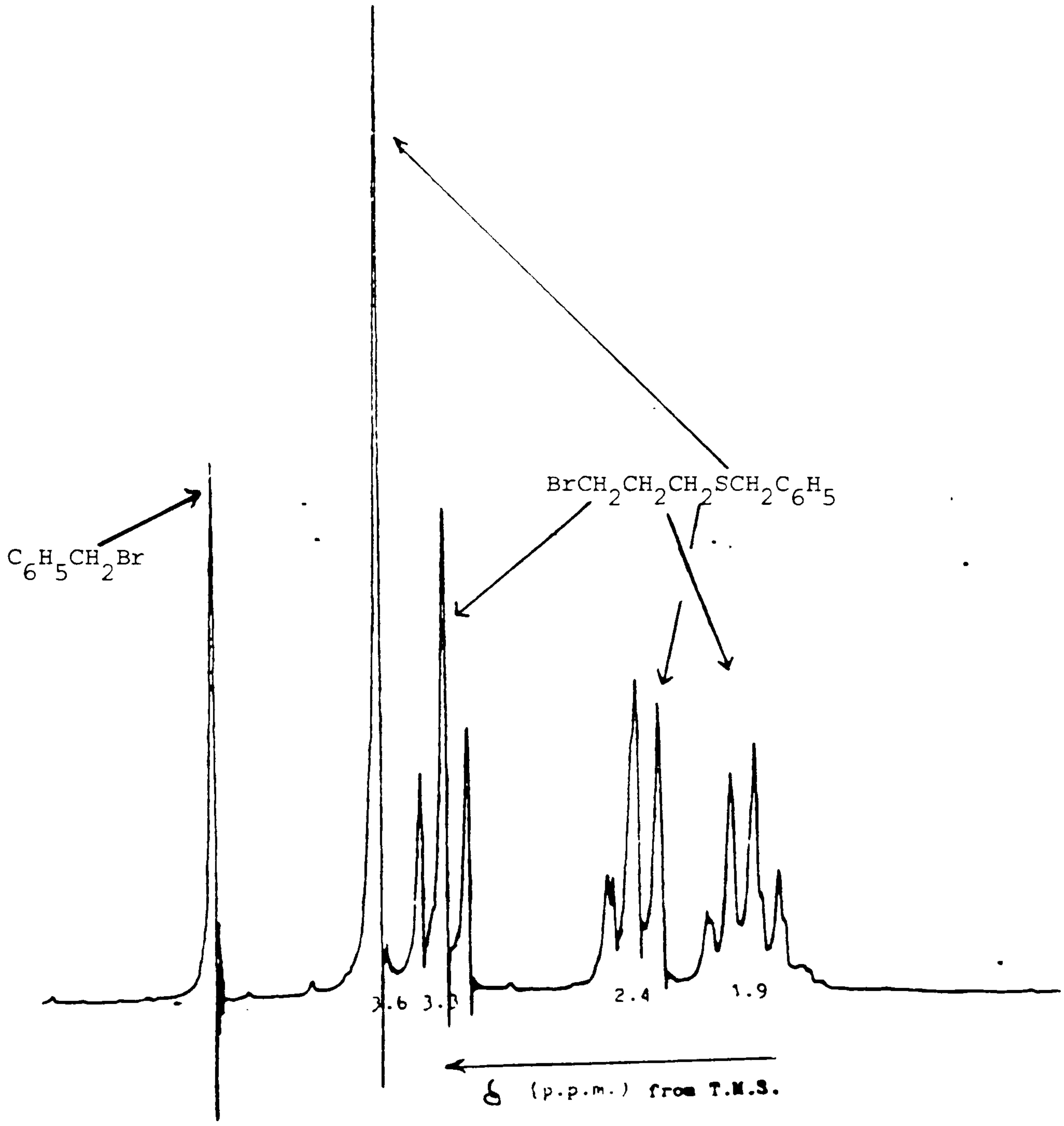
$^1$H nmr spectrum of mixture of benzyl bromide and excess thietane after one hour.



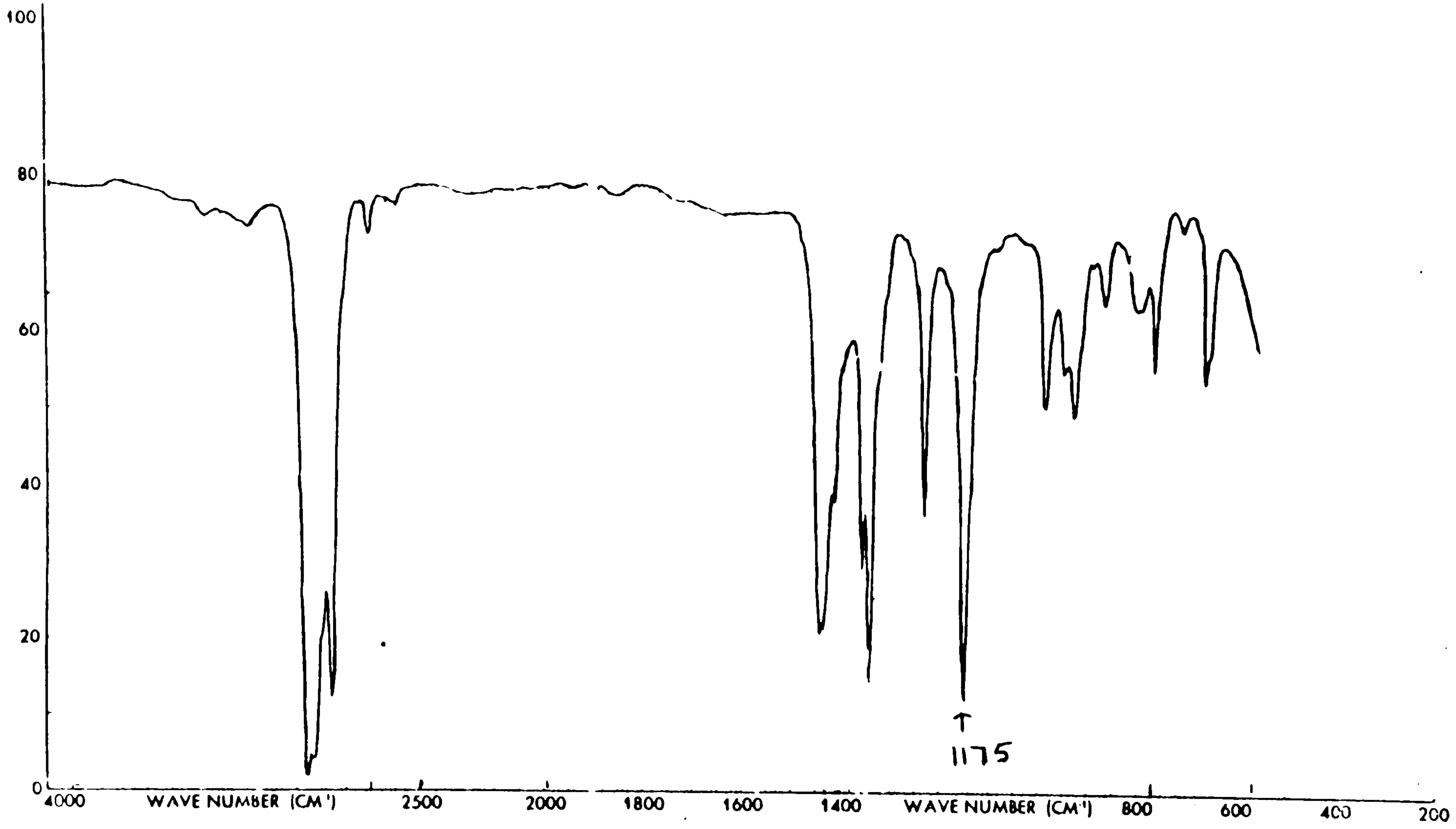
$^1H$ nmr spectrum of mixture of thietane and excess benzyl bromide after one week, showing new multiplets.



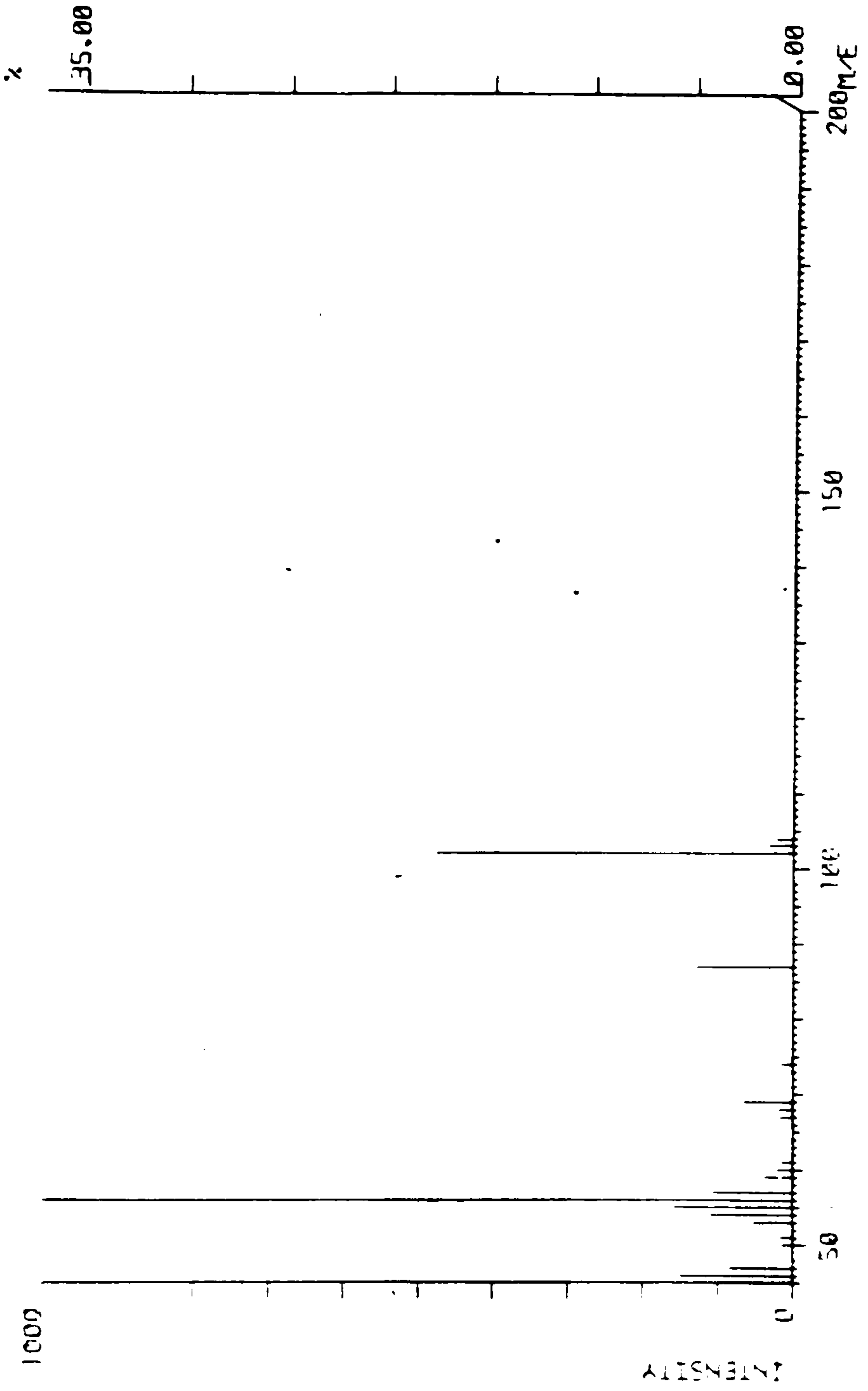
$^1$H nmr spectrum of mixture of thietane and excess benzyl bromide after three weeks.



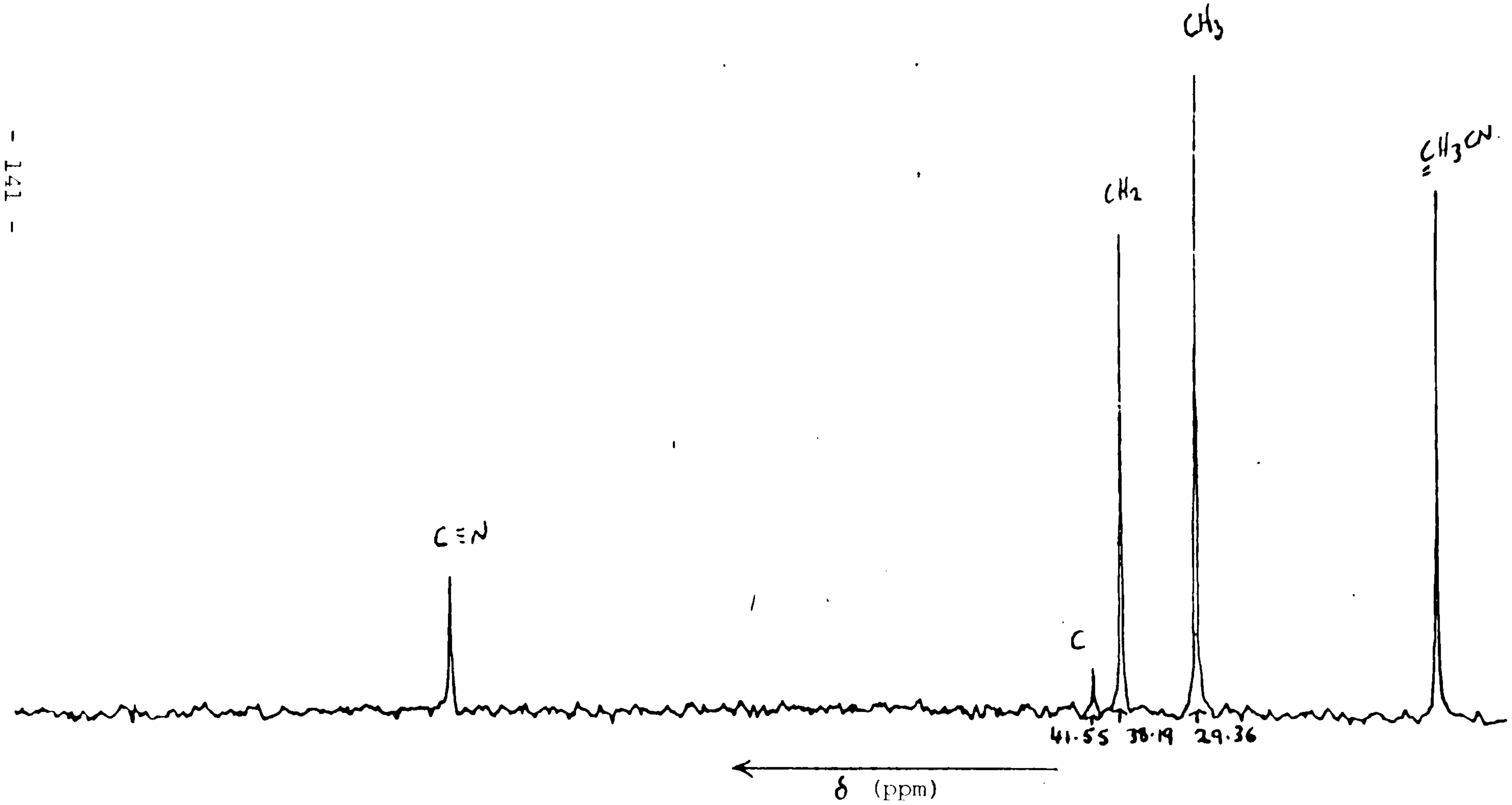
Infra-red spectrum of 3,3-dimethylthietane



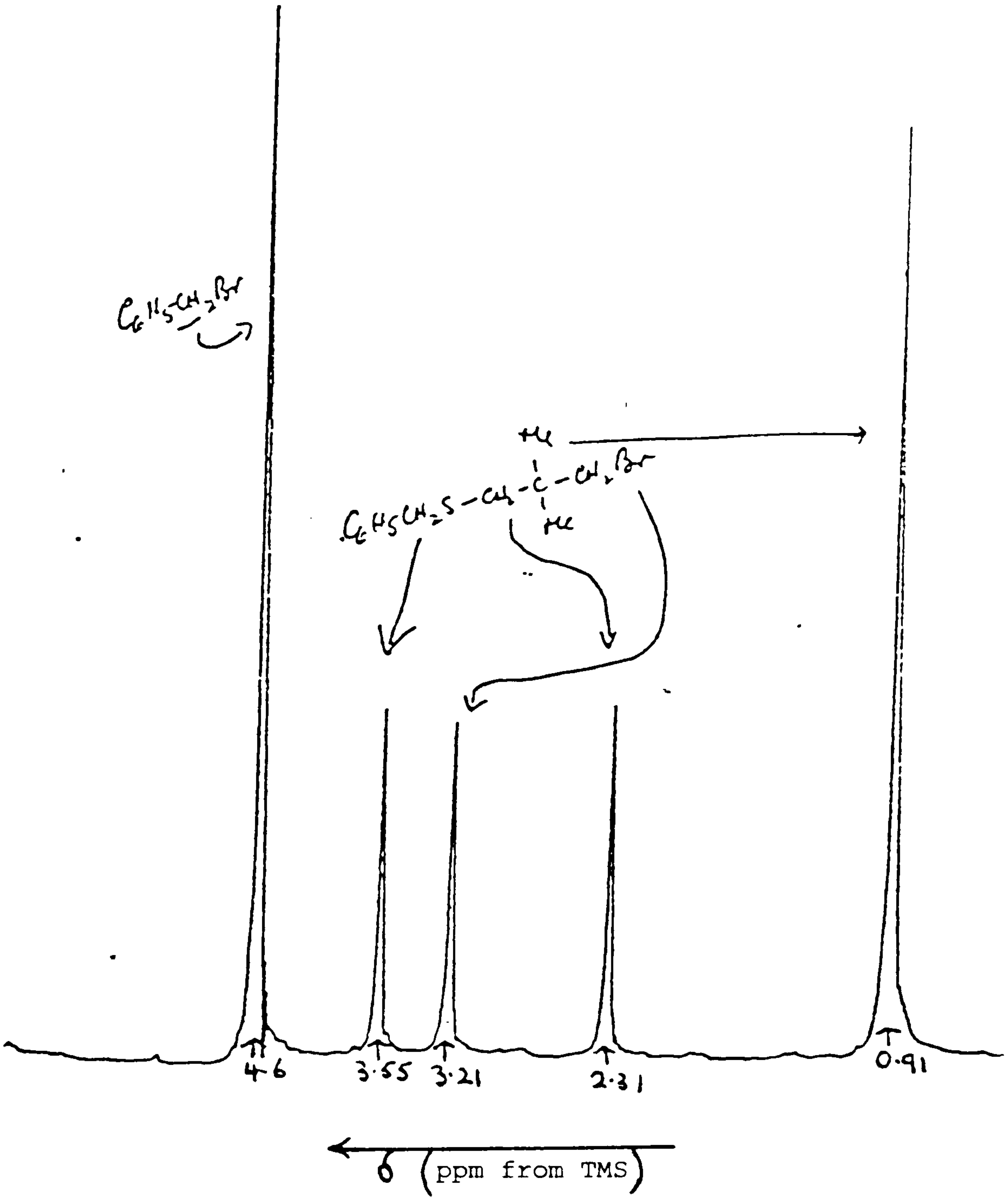
Mass spectrum of 3,3-dimethylthietane



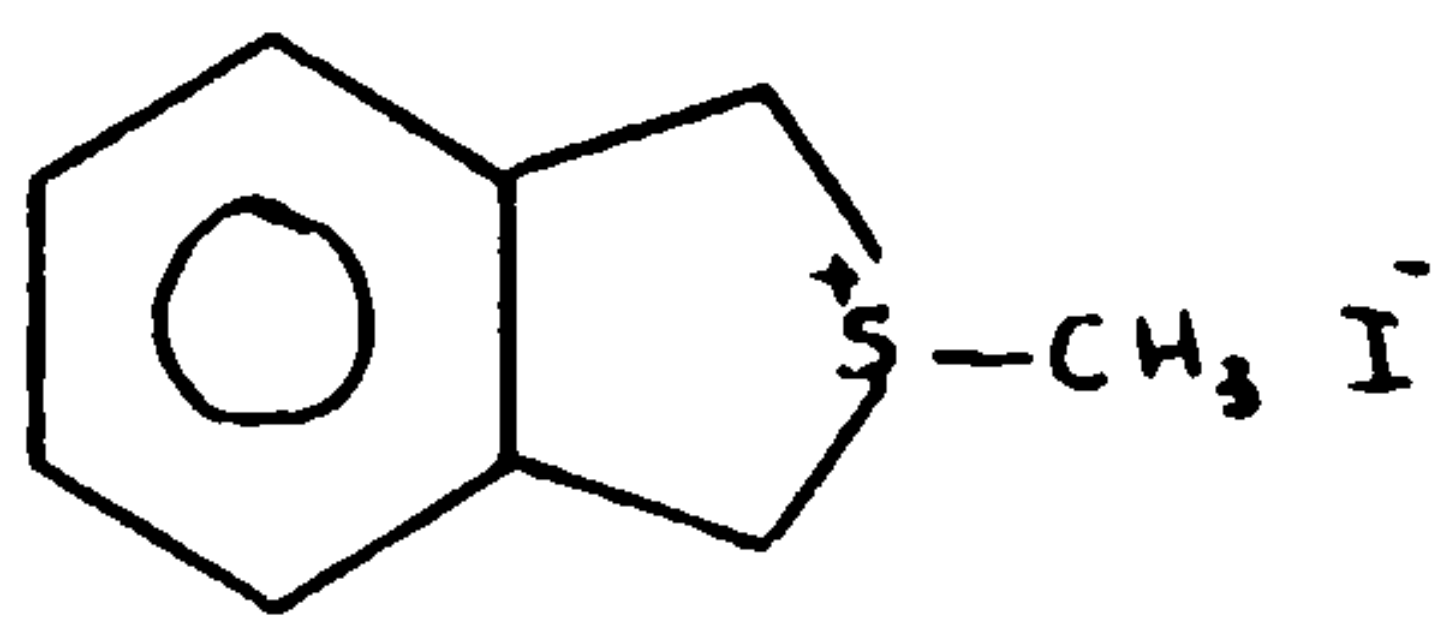
$^{13}C$ nmr spectrum of 3,3-dimethylthietane in acetonitrile

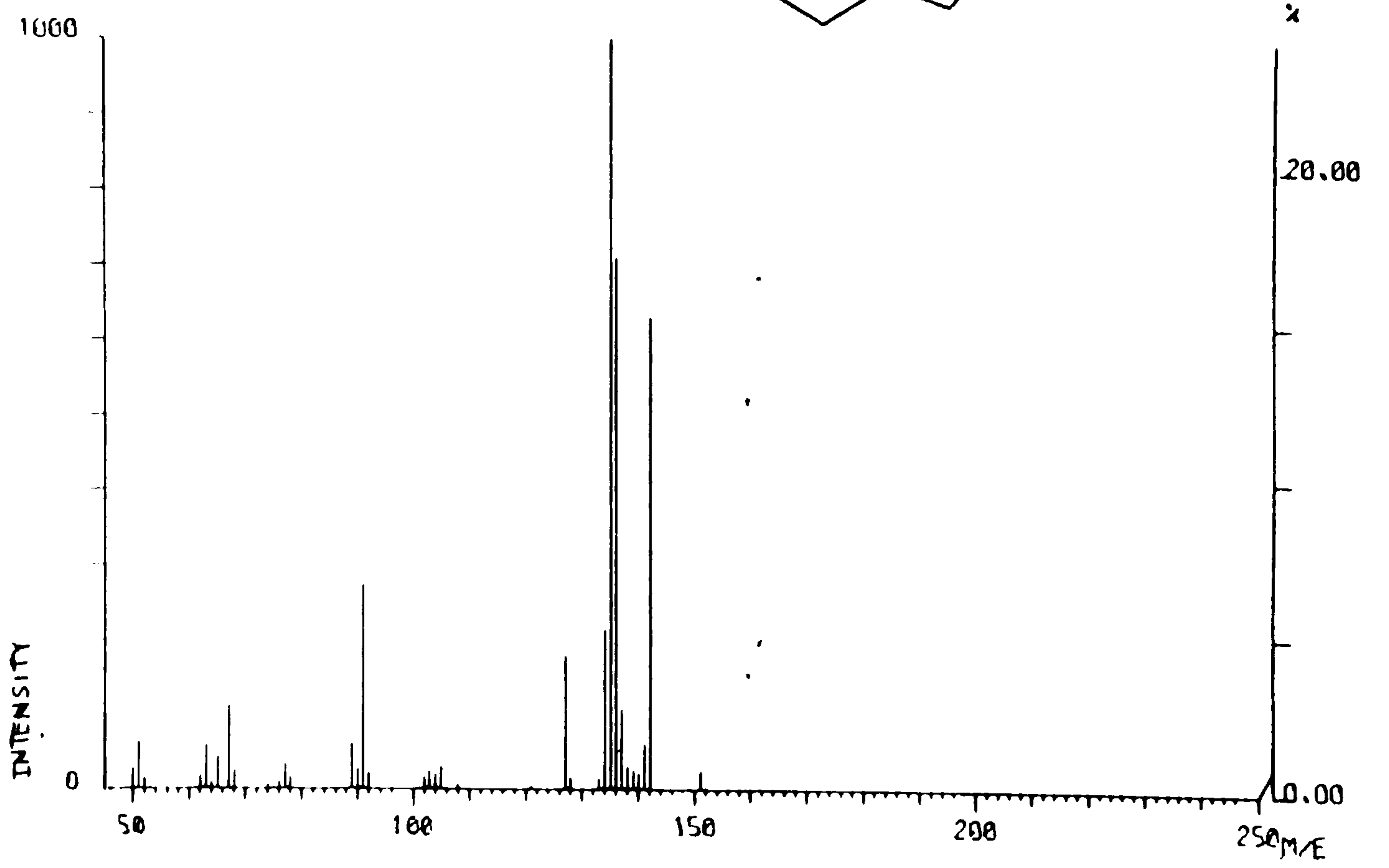


$^1$H nmr spectrum of mixture resulting from reaction between 3,3-dimethylthietane and benzyl bromide.

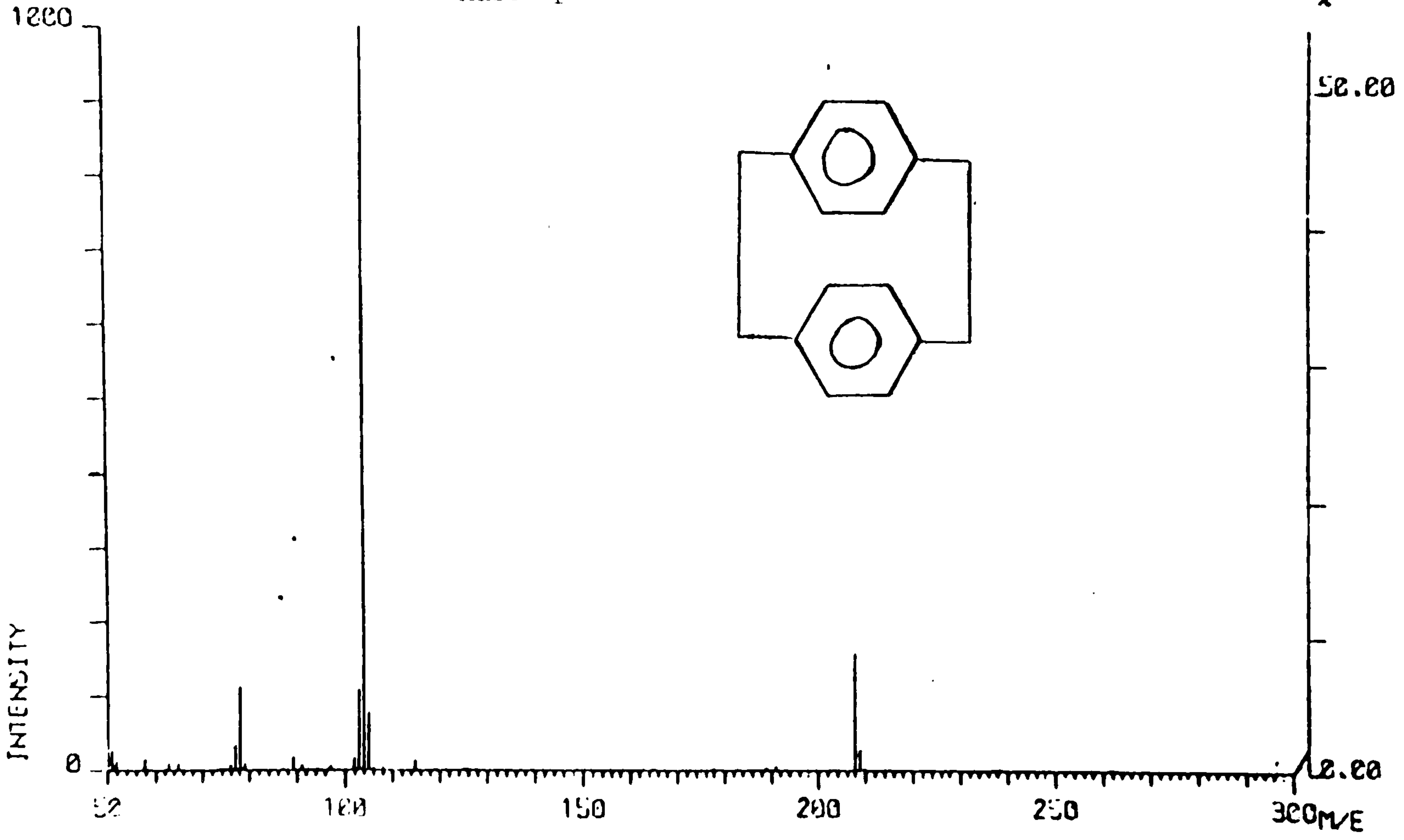


Mass spectrum of

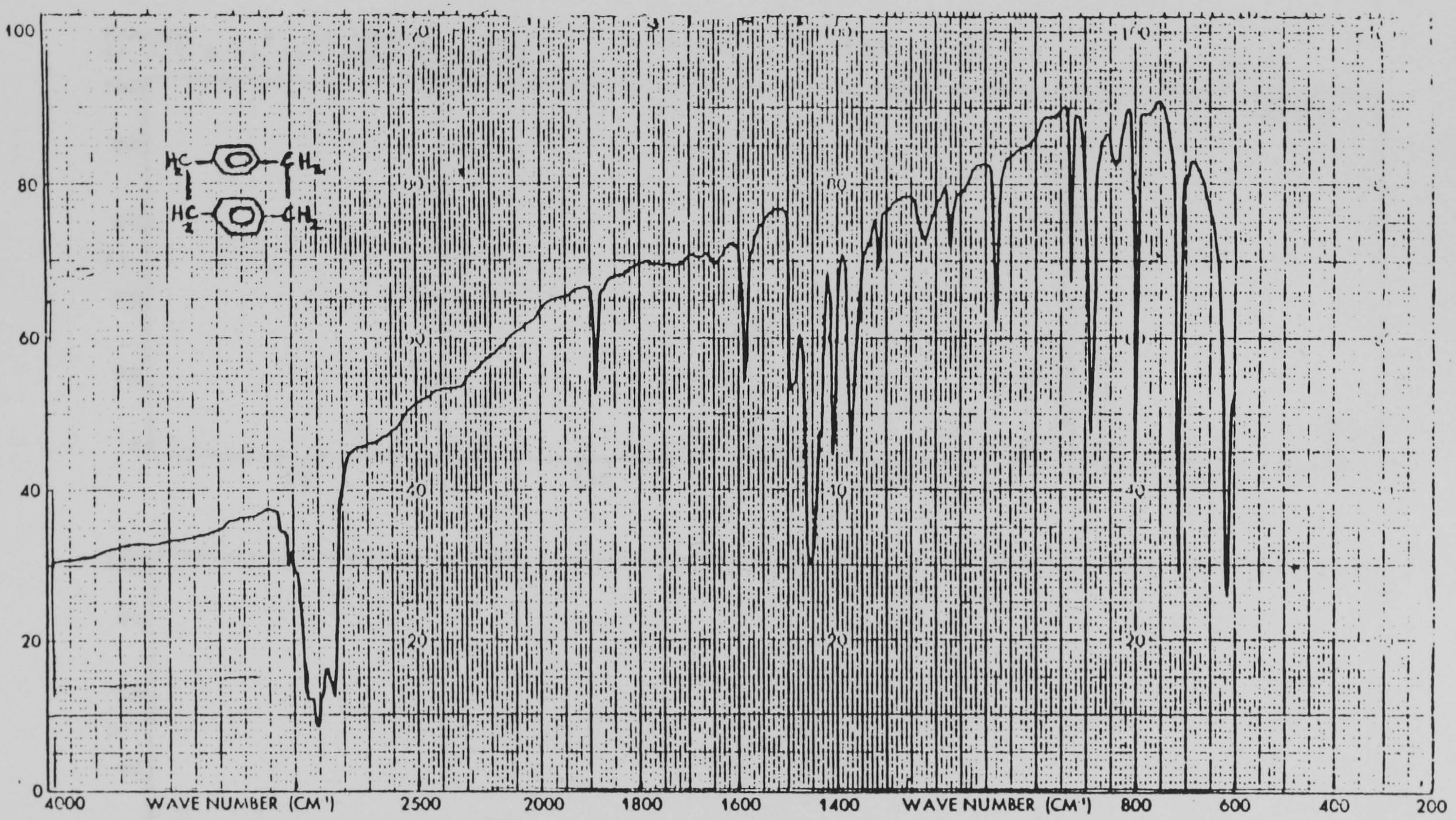




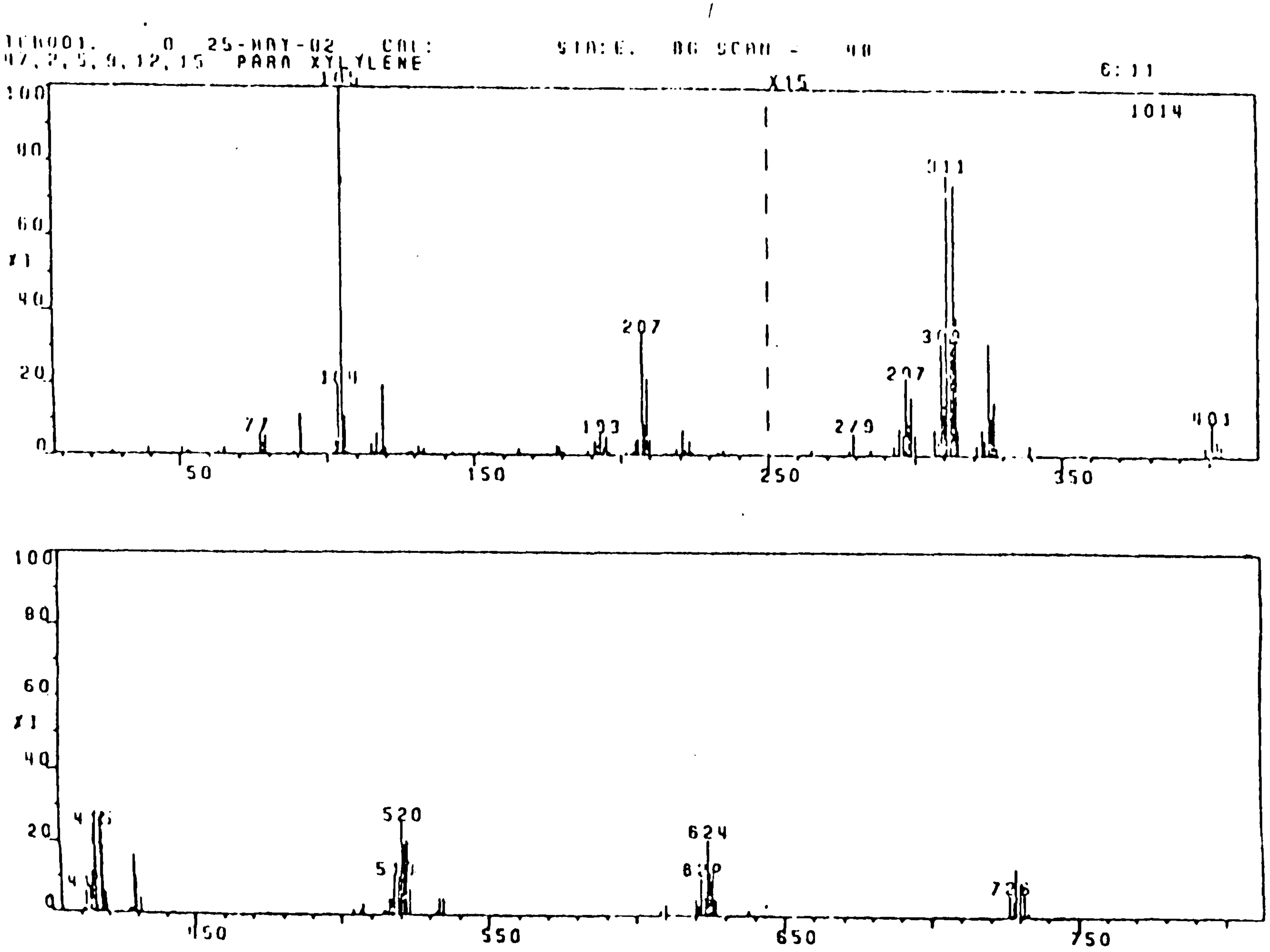
Mass spectrum of p-cyclophane



Infra-red spectrum of p-cyclophane



Mass spectrum of polymer from p-xylylenebis(1-thioniacyclopentane bromide)



Mass spectrum of polymer from photolysis of p-xylylenebis(1-thionacyclopentane bromide)

```
001.0          RT 0: 6:11   25-MAY-82    TIC:519      A
               BASE INT.:1014      B/G SCAN:40        S
               47,2,5,9,12,15  PARA XYLYLENE

 MASS   %AR.       ABS          MASS   %AR.       ABS
        MOD.       AREA                MOD.       AREA

 27.1   1.58        16         155.9   0.69         7
 38.9   1.78        18         165.0   1.78        18
 40.9   0.30         3         165.9   0.49         5
 49.0   0.49         5         166.9   0.49         5
 50.9   1.68        17         176.0   0.10         1
 51.9   0.59         6         176.9   0.20         2
 53.0   0.99        10         177.9   2.76        28
 63.0   1.08        11         178.9   2.37        24
 65.0   1.97        20         179.9   0.99        10
 75.0   0.10         1         180.9   0.79         8
 76.0   0.10         1         188.9   1.38        14
 77.0   5.52        56         189.9   0.89         9
 77.9   2.86        29         190.9   3.55        36
 78.9   5.13        52         192.0   2.96        30
 79.9   0.20         2         193.0   5.72        58
 80.9   0.99        10         194.0   2.17        22
 89.9   0.20         2         195.0   5.03        51
 90.9  11.05       112         196.0   1.08        11
 92.0   1.28        13         201.9   0.89         9
102.0   0.69         7         202.9   0.69         7
103.0   4.24        43         204.0   1.09        11
104.0  18.84       191         205.0   4.64        47
105.1 100.00      1014         206.0   4.83        49
106.0  10.75       109         207.0  33.43       339
107.0   0.59         6         207.9   8.78        89
115.0   3.06        31         208.9  21.40       217
116.0   0.89         9         209.9   4.93        50
117.0   6.02        61         211.0   0.49         5
118.0   1.87        19         215.0   0.20         2
119.0  19.43       197         216.9   0.49         5
119.9   2.17        22         217.9   0.20         2
127.0   0.20         2         218.9   1.78        18
128.0   0.59         6         219.9   0.79         8
129.0   1.28        13         221.0   6.80        69
129.9   0.10         1         222.0   1.68        17
131.0   2.07        21         223.0   3.85        39
132.9   0.20         2         224.0   0.99        10
133.0   1.70        18         230.9   0.10         1
134.0   0.10         1         233.0   0.69         7
139.0   0.10         1         235.0   1.48        15
141.0   0.49         5         236.0   0.10         1
143.0   0.59         6         237.0   0.10         1
145.0   0.10         1         264.9   0.10         1
151.9   0.59         6         277.9   0.10         1
152.9   0.20         2         278.9   0.39         4
153.9   0.20         2         285.0   0.10         1
154.9   0.59         6         292.9   0.20         2
```

```
  MASS   %AR.    ABS        MASS   %AR.     ABS
         MOD.    AREA              MOD.     AREA

 294.9   0.49      5        515.0   0.10       1
 296.0   0.39      4        515.9   0.30       3
 296.9   1.38     14        517.0   0.30       3
 297.9   0.59      6        517.9   0.69       7
 298.9   1.08     11        519.0   0.69       7
 299.9   0.39      4        519.9   1.68      17
 305.9   0.49      5        521.0   1.28      13
 307.9   0.30      3        521.9   1.38      14
 308.9   2.07     21        522.9   0.49       5
 309.9   0.99     10        532.0   0.10       1
 310.9   5.13     52        533.1   0.30       3
 311.9   2.47     25        534.1   0.30       3
 313.0   4.93     50        608.0   0.10       1
 314.0   2.56     26        609.9   0.20       2
 315.0   0.49      5        619.9   0.30       3
 320.9   0.20      2        620.9   0.20       2
 322.9   0.49      5        622.0   0.69       7
 324.0   0.30      3        623.0   0.39       4
 324.9   2.07     21        623.9   1.38      14
 325.9   0.69      7        624.9   0.79       8
 326.9   0.99     10        626.0   0.99       9
 328.0   0.20      2        626.9   0.30       3
 329.0   0.20      2        637.8   0.10       1
 330.0   0.20      2        726.4   0.39       4
 400.0   0.10      1        727.7   0.30       3
 401.0   0.59      6        728.9   0.89       9
 402.0   0.10      1        730.2   0.59       6
 403.0   0.30      3        731.3   0.59       6
 404.0   0.20      2        732.6   0.10       1
 410.9   0.10      1
 412.0   0.39      4
 413.0   0.49      5
 413.9   0.79      8
 415.0   1.58     16
 415.9   1.87     19
 417.0   1.78     18
 417.9   1.87     19
 419.0   0.39      4
 427.0   0.10      1
 428.0   0.10      1
 428.9   1.08     11
 429.9   0.69      7
 430.9   0.30      3
 503.9   0.10      1
 506.0   0.10      1
 507.0   0.20      2
 513.9   0.10      1
```

Infra-red spectrum of poly-p-xylylene