UNIVERSITY OF LONDON

'CERTAIN PROPERTIES OF ALKENE AND ALKYNE ALCOHOLS'

by

TREVOR MORGAN COOK, M.Sc., F.R.I.C.

A thesis presented for the degree of
DOCTOR OF PHILOSOPHY
of the University of London.

Northern Polytechnic,
London, N.7.

July, 1965

Summary of Thesis entitled

"Certain Properties of Alkene and Alkyne Alcohols"

by T.M. Cook

The importance of a knowledge of the basic strength of oxygen in organic compounds has been recognised in recent years. Assessment of the basic function of oxygen has been achieved, in particular, by the determination of the solubility of hydrogen chloride in saturated alcohols, phenols, ethers, carboxylic acids, esters and esters of inorganic acids. Particular application has been found in the accurate description of reaction mechanisms in the organic chemistry of inorganic non-metal halides, including those of phosphorus, silicon and boron.

This thesis presents an extension of this work by the measurement of the solubility of hydrogen chloride in a range of alkene and alkyne alcohols and their esters at various temperatures using a modified technique. It also presents a study of the interactions of certain of these alcohols with phosphorous trihalides under precisely controlled experimental conditions.

It has been shown that terminal unsaturation in the carbon chain close to the oxygen atom gives rise to a considerable reduction in the solubility of hydrogen chloride and this is attributed to a decrease of electron density on oxygen, thus:-

$$CH{\equiv}C\ CH_2\ OH \ll CH_2{=}CH\ CH_2\ OH \ll CH_3\ CH_2\ CH_2\ OH$$

The effect is decreased on moving the unsaturation centre farther from the oxygen atom, for example:-

$$CH_2{=}CH\ CH_2\ OH \ll CH_3\ CH_2\ CH_2\ OH$$

$$CH_2{=}CH\ CH_2\ CH_2\ OH < CH_3\ CH_2\ CH_2\ CH_2\ OH$$

$$CH_2{=}CH\ CH_2\ CH_2\ CH_2\ OH \eqsim CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ OH$$

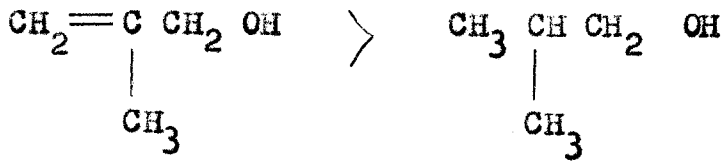
and similarly,

$$CH{\equiv}C\ CH_2\ OH \ll CH_3\ CH_2\ CH_2\ OH$$

$$CH{\equiv}C\ CH_2\ CH_2\ OH < CH_3\ CH_2\ CH_2\ CH_2\ OH$$

Alkyl substitution at the terminal carbon atom reduces the effect of unsaturation considerably, and substitution in the side chain may actually reverse the effect, for example:-

$$CH_3\ CH{=}CH\ CH_2\ OH \eqsim CH_3\ CH_2\ CH_2\ CH_2\ OH$$



These observations are discussed and possible explanations presented.

Carboxylic acid esters of alkene and alkyne alcohols showed similar solubility features, for example:-



where R = n-butyl

Changes in the R group gave similar solubility changes to the corresponding esters of saturated alcohols.

Interaction of alkene and alkyne alcohols with phosphorus trihalides have been studied, and the help from a knowledge of the basic strength of the alcoholic oxygen atom in the choice of experimental conditions and in the accurate description of reaction sequences and mechanistic characteristics is illustrated.

Systematic dealkylation of alkenyl and alkynl esters of phosphorous acid with hydrogen halides has thrown further light on the mechanisms of the replacement steps.

The example given is the stepwise dealkylation of tri-(3-methylallyl)-phosphite:

$$(R^3O)_3P + HCl \longrightarrow (R^3O)_2PHO + R^3Cl$$

$$(R^3O)_2PHO + HCl \longrightarrow R^3OPHO(OH) + R^3Cl + \text{a little } R^1Cl$$

$$R^3OPHO(OH) + HCl \longrightarrow H_3PO_3 + R^3Cl + \text{predominantly } R^1Cl$$

where R^3 = 3-methylallyl R^1 = 1-methylallyl.

The reactive nature of the intermediates and certain products, always tending to, and not infrequently giving rise to fires and explosions, has added considerably to the time required for the experimental work.