

Abstract of Thesis

Six known substituted 1-phenylpyrazoles have been prepared and each one formylated in the reactive 4-position using dimethylformamide and phosphoryl chloride. The yields obtained are a further justification of the general applicability of this method for the preparation of substituted 1-phenylpyrazole-4-aldehydes.

The following reactions have been carried out with each aldehyde:-

- A Oxidation to the corresponding acid.
- B Condensation with acetophenone.
- C Condensation with malonic acid.
- D Condensation with aniline.
- E Condensation with o-phenylenediamine.

The interest in each series of reactions was in noting the influence of the alkyl and aryl substituents on the reactivity of the aldehydic group. Steric effects were most noticeable in the condensations with aniline - reaction taking place only with the two mono-substituted aldehydes - and to a lesser extent in the condensations with malonic acid and o-phenylenediamine - a decrease in yield with increasing size of substituents being observed. In the condensations

with acetophenone the yields were high but the order was a reversal of that to be expected from a consideration of steric effects. It has been shown that this may be due to a Cannizzaro side-reaction taking place during the condensations with the mono-substituted aldehydes. The oxidation of the aldehydes to the corresponding 4-carboxylic acids has been shown to be the best method yet available for preparing these compounds.

The mechanism of the formylation reaction was also studied. The reactive intermediates involved in the formylation of the six substituted 1-phenylpyrazoles have been isolated and characterised. The ionic structures are all similar and are of the type postulated by Smith (1955) for the reactive intermediate involved in the formylation of indole. On the basis of the evidence obtained, a mechanism for the formylation reaction has been proposed which combines the mechanisms proposed by Smith (1954) and Silverstein (1955).

The following new compounds have been prepared and characterised:-

4-Formyl-3-methyl-1-phenylpyrazole.

4-Formyl-3-methyl-1,5-diphenylpyrazole.

4-Formyl-1,3,5-triphenylpyrazole.

B-(3-methyl-1-phenyl-4-pyrazolyl)acrylic acid.

B-(5-methyl-1-phenyl-4-pyrazolyl)acrylic acid.

B-(3,5-dimethyl-1-phenyl-4-pyrazolyl)acrylic acid.

B-(3-methyl-1,5-diphenyl-4-pyrazolyl)acrylic acid.

B-(5-methyl-1,3-diphenyl-4-pyrazolyl)acrylic acid.

B-(1,3,5-triphenyl-4-pyrazolyl)acrylic acid.

H-(3-methyl-1-phenyl-4-pyrazolylmethylidene)aniline.

N-(5-methyl-1-phenyl-4-pyrazolylmethylidene)aniline.

1-phenyl-3-(3'-methyl-1'-phenyl-4'-pyrazolyl)prop-2-en-1-one.

1-phenyl-3-(5'-methyl-1'-phenyl-4'-pyrazolyl)prop-2-en-1-one.

1-phenyl-3-(3',5'-dimethyl-1'-phenyl-4'-pyrazolyl)prop-2-en-1-one.

1-phenyl-3-(3'-methyl-1',5'-diphenyl-4'-pyrazolyl)prop-2-en-1-one.

1-phenyl-3-(5'-methyl-1',3'-diphenyl-4'-pyrazolyl)prop-2-en-1-one.

1-phenyl-3-(1',3',5'-triphenyl-4'-pyrazolyl)prop-2-en-1-one.

- 1,3-diphenyl-5-(3'-methyl-1'-phenyl-4'-pyrazolyl)pyrazoline.
 1,3-diphenyl-5-(5'-methyl-1'-phenyl-4'-pyrazolyl)pyrazoline.
 1,3-diphenyl-5-(3',5'-dimethyl-1'-phenyl-4'-pyrazolyl)
 pyrazoline.
 1,3-diphenyl-5-(3'-methyl-1',5'-diphenyl-4'-pyrazolyl)
 pyrazoline.
 1,3-diphenyl-5-(5'-methyl-1',3'-diphenyl-4'-pyrazolyl)
 pyrazoline.
 1,3-diphenyl-5-(1',3',5'-triphenyl-4'-pyrazolyl)pyrazoline.
 3-methyl-1,1',3'-triphenyl-4,5'-bipyrazolyl.
 5-methyl-1,1',3'-triphenyl-4,5'-bipyrazolyl.
 3,5-dimethyl-1,1',3'-triphenyl-4,5'-bipyrazolyl.
 3-methyl-1,1',3',5'-tetraphenyl-4,5'-bipyrazolyl.
 5-methyl-1,1',3,3'-tetraphenyl-4,5'-bipyrazolyl.
 1,1',3,3',5'-pentaphenyl-4,5'-bipyrazolyl.
 2-(3-methyl-1-phenyl-4-pyrazolyl)benzimidazole.
 2-(5-methyl-1-phenyl-4-pyrazolyl)benzimidazole.
 2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)benzimidazole.
 2-(3-methyl-1,5-diphenyl-4-pyrazolyl)benzimidazole.
 2-(5-methyl-1,3-diphenyl-4-pyrazolyl)benzimidazole.
 2-(1,3,5-triphenyl-4-pyrazolyl)benzimidazole.
 2-(1-phenyl-4-pyrazolyl)benzimidazole.

The dichlorophosphates and hexachloroplatinates of the cation of the intermediate involved in the formylation of the six substituted 1-phenylpyrazoles as well as the chloride of the cation of the intermediate involved in the formylation of 1-phenylpyrazole.

The picrates and tetraphenylborates of the cation of the intermediate involved in the formylation of 3-methyl-1-phenylpyrazole and 1-phenylpyrazole.