

CHLOROCARBENE : A NOVEL METHOD OF GENERATION.

REACTION WITH o-HYDROXYPHENYL BENZYL KETONES.

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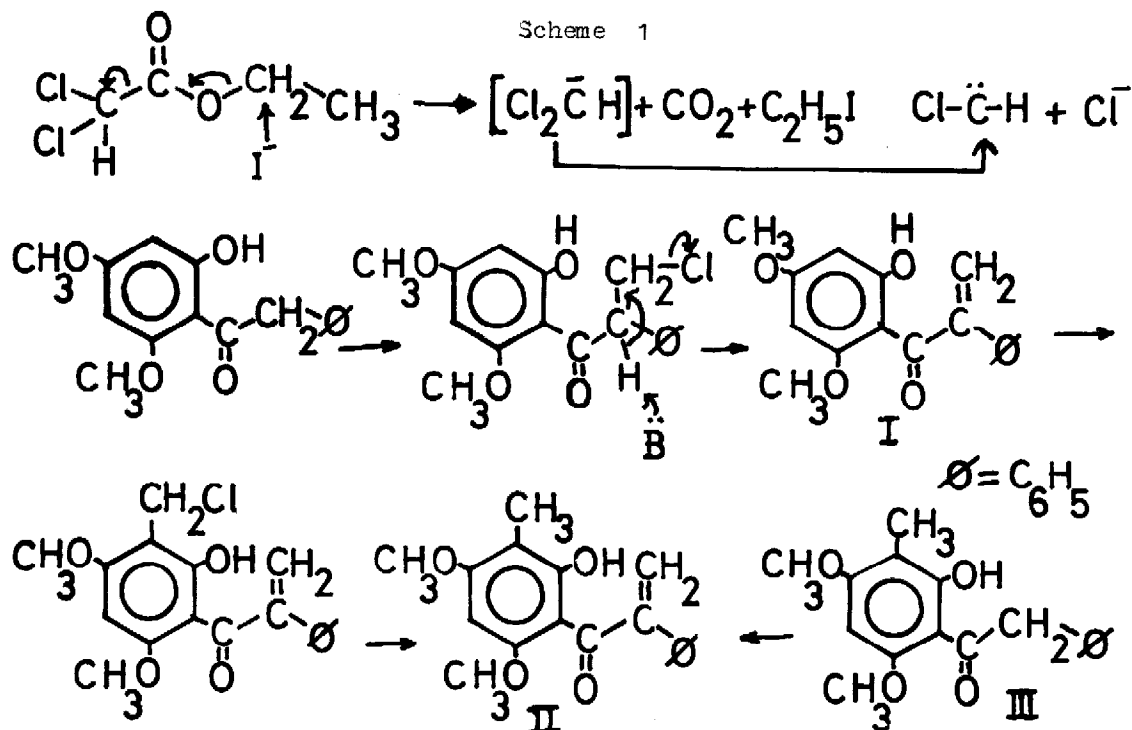
Diiodomethane undergoes nucleophilic displacement of iodide groups when reacted with o-hydroxyphenyl benzyl ketones in the presence of potassium carbonate yielding isoflavanones¹. In an attempt to synthesise 2-carbethoxy-isoflavanones, ethyl dichloroacetate was refluxed with 2-hydroxy-4,6-dimethoxyphenyl benzyl ketone under similar conditions but no change could be observed even after 100 hr. Addition of sodium iodide helped the reaction to be completed in 35 hr. However, the reaction product was a very complex mixture on TLC. Careful column chromatography gave two pure compounds A & B in addition to other impure fractions.

Compound A, m.p. 90-91^o, λ MeOH 290 nm, ν OH 3280 cm⁻¹, ν CO 1680 cm⁻¹; NMR: δ 3.42 and 3.8 (each s, 2OCH₃), between δ 7.09 and 7.83 (7 aromatic H), δ 12.31(s, -OH). A characteristic absorption at δ 5.79 and 6.03 (each d, J = 2 Hz) showed the presence of a vinyl group (=CH₂). Based on these facts, structure I has been assigned to compound A.

Compound B, m.p. 131-132^o, λ MeOH at 293 nm; ν OH 3380 cm⁻¹, ν CO 1700 cm⁻¹; NMR: δ 2.14(s, C-CH₃), δ 3.7 and 3.77 (each s, 2OCH₃), between δ 7.25 and 7.31 (6 aromatic H), δ 5.81 and 6.05 (each d, J=2 Hz, vinyl group (=CH₂) and δ 13.98(s, -OH). This data could be explained by assigning structure II to compound B.

The structures of A and B reveal that the reaction is not one of nucleophilic substitution. Their formation can be explained on the basis that iodide ion attacks ethyl dichloroacetate resulting in the formation of chlorocarbene as shown in scheme 1. Chlorocarbene² could add or insert at the different reactive positions^{1,3} of phenyl benzyl ketones;

Compound A is likely to have formed by insertion of chlorocarbene at the reactive α position followed by dehydrochlorination while compound B could have formed by insertion of chlorocarbene at the reaction 3 position of compound A followed by ionisation and hydride ion abstraction. Structure II has been confirmed by the formation of compound B when III¹ was subjected to the above reaction.



Experimental evidence for the proposed role of iodide ions has been provided by trapping carbon dioxide generated when ethyl dichloroacetate, sodium iodide and acetone were refluxed under nitrogen atmosphere. In the absence of either sodium iodide or ethyl dichloroacetate, evolution of carbon dioxide did not occur. Reactions with other substrates are in progress.

R E F E R E N C E S

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