The Reaction between α-Halogenometallic Compounds and *ortho*-Acylanilines: Synthesis of Indoles

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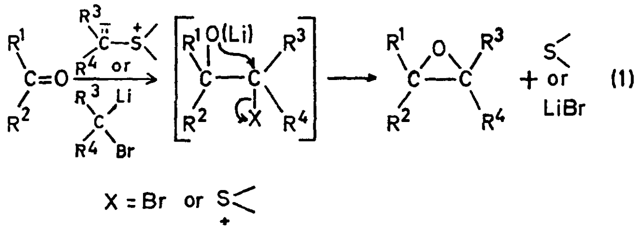
Summary Indoles may be obtained by treating *o*-acylanilines in ether–THF with diazomethane and MgI_2 (LiI) or with dibromomethane and Li–Hg.

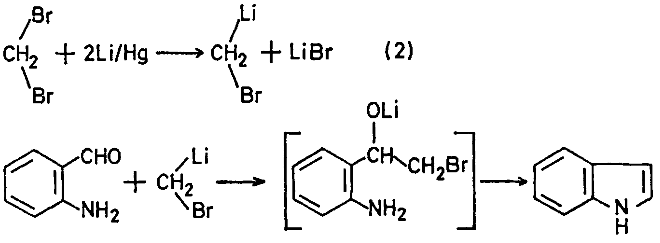
Recently we have reported the similarity in behaviour between α-halogenolithium compounds and sulphonium ylides which both yield oxirans on reaction with aldehydes and ketones (reaction 1).[1]

On the other hand, sulphonium ylides have been shown to react with aromatic *o*-aminocarbonyl compounds leading to the corresponding indoles.[2]

We now report that bromolithium methane generated *in* *situ* by treatment of dibromomethane in THF with Li–Hg reacts at room temperature with *o*-aminobenzaldehyde to give indole in 25% yield and starting material (reaction 2).

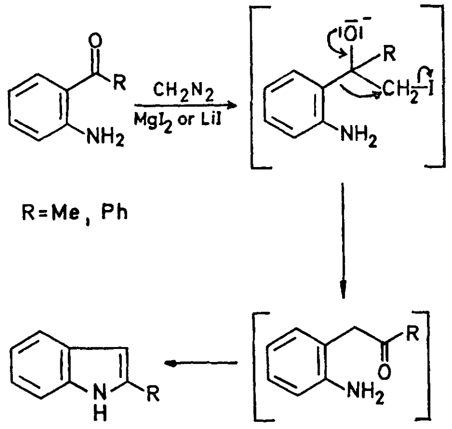


Diazomethane has been reported to react readily with MgI_2 or LiI in ether to give $CH_2IMgI$and CH_2ILi, respectively.[3] We have shown that both organometallic species generated *in situ* give rise to indoles on reaction at room temperature with *o*-aminobenzaldehyde, *o*-aminoacetophenone, or *o*-aminobenzophenone in an ether–THF solution.



With *o*-aminoacetophenone and *o*-aminobenzophenone in addition to traces of the 3-methyl- and 3-phenyl-indoles, respectively, the corresponding 2-substituted derivatives were formed by rearrangement probably by the pathway shown in the Scheme.

A rearrangement of this kind has been already reported for sulphonium and arsonium ylides.[4] It is not possible at present to establish if this rearrangement is, at least in part, also operative in the case of *o*-aminobenzaldehyde.



Scheme

In a typical experimental procedure a solution of 21 mmol of CH_2N_2 in dry ether was added dropwise over 2 h to a stirred solution of 21 mmol of dry MgI_2 or LiI and 7 mmol of the *o*-acylanilines in 60 ml of dry THF at 0°. The reaction mixture was then allowed to remain 2 h at 30° before work-up. In all cases studied indoles were obtained in a 30—40% yields. However, no effort has been made to increase the yields and in all cases a considerable amount of starting material was recovered. No reaction was observed when CH_2N_2 and the *o*-acylanilines were allowed to react under the same conditions in the absence of metal salts.

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