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GRIGNARD-LIKE REACTIONS OF ETHYNYL-LEAD COMPOUNDS: NEW ROUTES TO NN'-DIARYLURACILS.

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Although a number of alkynyl-lead compounds have been prepared, their reactions have not been described (1). The alkynyl-lead bond is in fact much more reactive than the alkyl-lead bond, and will take part in addition and substitution reactions similar to those of Grignard reagents. In contrast, in many reactions, alkynyl-magnesium compounds are less reactive than alkyl-magnesium compounds (2).

Triethylphenylethynyl-lead, $Et_3PbC{\equiv}CPh$, b.p. 94-97°/0.05 mm. (84% yield) and triethylhexynyl-lead, $Et_3PbC{\equiv}CBu$, b.p. 61-63°/0.05 mm. (75% yield), were prepared by treating triethyl-lead methoxide with the appropriate alkyne. The products are hydrolysed by air, and can be analysed by titration in aqueous acetone with hydrochloric acid.

They react exothermically with acid chlorides to give alkynyl ketones (eqn. 1). Thus acetyl chloride gives, respectively, methyl phenylethynyl ketone (I; R = Ph), b.p. 114-116°/14 mm. (78% yield), and methyl hexynyl ketone (I; R = Bu), b.p. 74-76°/14 mm. (84% yield). Under similar conditions, phenylethynylmagnesium chloride would give a relatively low yield of ketone, and a considerable amount of tertiary alcohol (2).

$$\mathrm{Et_3PbC{\equiv}CR} + \mathrm{Me.CO.Cl} \longrightarrow \mathrm{Et_3PbCl} + \underset{\text{(I)}}{\mathrm{Me.CO.C{\equiv}CR}} \qquad (1)$$

The ethynyl-lead compounds also reacted exothermically with phenyl isocyanate (eqn. 3). Hydrolysis of the oily product from triethylphenylethynyl-lead gave a white crystalline solid, m.p. 197–198°, which was identified by its analysis, molecular weight, and infrared, nuclear magnetic resonance, and mass spectra as being 1,3,6-triphenyluracil (III).

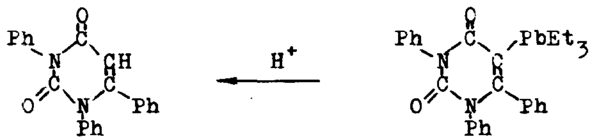
$$\mathrm{PhN{=}C{=}NPh} + \mathrm{PhC{\equiv}C.CO.OH} \longrightarrow \underset{\text{(II)}}{\mathrm{PhNH.CO.NPh.CO.C{\equiv}CPh}} \qquad (2)$$

$$\downarrow$$

$$\mathrm{Et_3PbC{\equiv}CPh} + \mathrm{2PhNCO} \longrightarrow \mathrm{Et_3Pb.NPh.CO.NPh.CO.C{\equiv}CPh} \qquad (3)$$

$$\downarrow$$

(III)



The same product can be prepared from diphenylcarbodiimide and phenylpropiolic acid. NN'-Diphenyl-N-phenylpropiolylurea (II), m.p. 139–140° is first obtained; if this is treated with triethyl-lead methoxide it undergoes ring closure to give the uracil (III). This compound may be the same as the unidentified yellow solid, m.p. 200–201°, which Tyabji obtained, along with other products, by treating phenylethynylsodium with phenyl isocyanate (3). Phenylethynylmagnesium bromide, on the other hand, reacts with phenyl isocyanate to form phenylpropiolylanilide, PhNH.CO.C≡CPh, in 90% yield (4). Triethylphenylethynyltin has been reported to undergo a series of consecutive reactions with phenyl isocyanate, perhaps of the type discussed here, but the reaction conditions and products have not been described (5).

Such differences in detail in the behaviour of the ethynyl derivatives of different metals may give the ethynyl-lead compounds some specific applications in synthesis.

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