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RADICAL REACTIONS OF ORGANOALUMINIUM COMPOUNDS: THE REACTION OF ALUMINIUM TRIPHENYL WITH BENZOPHENONE.

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The formation of radicals in the reactions of organometallic compounds is known to occur in at least two ways: by homolysis of the carbon-metal bond(1) and by electron transfer from the organic derivatives of the electropositive metals to unsaturated organic molecules(2).

In the course of a general investigation of the radical reactions of organoaluminium compounds we have observed a further mode of formation; namely, a facile homolysis of the carbon-oxygen bond in diphenylaluminium triphenylcarbinolate, formed by reaction of aluminium triphenyl with benzophenone.

Previous studies have shown that the reaction between aluminium triphenyl and benzophenone, in benzene, proceeds rapidly at 80° with the formation of diphenylaluminium triphenylcarbinolate dimer(3) which, on prolonged reaction, is decomposed to a complex mixture of hydrocarbons, the principal component of which is triphenylmethane(4,5).

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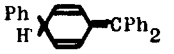
In the present investigation we have found that mixing benzene solutions of aluminium triphenyl and benzophenone results in the formation of the triphenylmethyl radical*. The radical is formed at room temperature and it's concentration slowly increases, a process catalysed by ultra-violet irradiation.

The principal products isolated from the reaction at 85°(0.92 mmoles $AlPh_3$:0.65 mmoles $Ph_2C{=}O$ in 4 ml. benzene) for three days were triphenylmethane(0.26 mmoles), p-phenyltriphenylmethane(0.16 mmoles) and p,p'-diphenyltriphenylmethane(0.10 mmoles), separated from the reaction mixture by acid hydrolysis and chromatography on alumina. In a separate experiment the reaction mixture was treated with deuterosulphuric acid to obtain deuterated hydrocarbons from organic moieties bound to aluminium. Triphenylmethane and the p-phenylated triphenylmethanes were found to be free from deuterium by mass spectrometry and must therefore be formed prior to the hydrolysis procedure. On the basis of these observations the following reaction scheme is proposed.

1. $Ph_2C{=}O + AlPh_3 \rightleftharpoons Ph_2C{=}O{\rightarrow}AlPh_3$

   $2\ Ph_2C{=}O{\rightarrow}AlPh_3 \longrightarrow (Ph_3COAlPh_2)_2$

2. $(Ph_3COAlPh_2)_2 \longrightarrow 2\ Ph_3C\cdot + PhAl{=}O + 2\ Ph\cdot$

3. $Ph_3C\cdot + Ph\cdot \longrightarrow$  (I).

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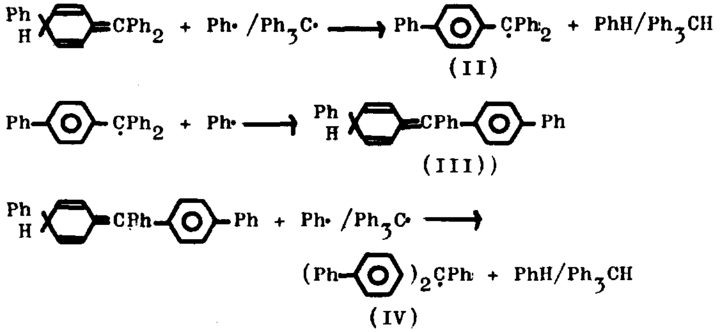
* The electron spin resonance spectrum was found to be identical with that of triphenylmethyl conventionally prepared from triphenylmethyl chloride and mercury in benzene.

4\.

5\.

6\.



Hydrogen abstraction by the p-phenylated triphenylmethyl radicals(II and IV) may occur by reactions analogous to those shown in steps 4 and 6, leading to the p-phenylated-triphenylmethanes, the overall result corresponding to radical isomerisation of (I) and (III). The initial steps in the reaction are rationalised by homolysis of diphenylaluminium triphenylcarbinolate(step 2) followed by radical phenylation of triphenylmethyl*(step 3) and the p-phenyltriphenylmethyl radical subsequently formed.

The spontaneous formation of the triphenylmethyl radical and isolation of triphenylmethane, p-phenyltriphenylmethane and p,p'-diphenyltriphenylmethane has also been noted in the reaction of triphenylcarbinol with aluminium triphenyl under similar reaction conditions. In this case diphenylaluminium triphenylcarbinolate formation occurs by a less ambiguous route: alcoholysis of the carbon-aluminium bond(7).

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* Radical phenylation of triphenylmethyl has recently been discussed in a study of the decomposition of phenylazo-triphenylmethane. This compound decomposes in a variety of solvents with the synchronous formation of triphenylmethyl and phenyl radicals(6).

It is of interest to note that the spontaneous formation of radicals in the reactions of Grignard(2,8), and alkyllithium(2) reagents with aromatic ketones is reported to proceed by electron transfer from the organometal to the ketone. In contrast, aluminium triphenyl reacts by addition to the ketone group and spontaneous radical formation occurs by homolysis of the adduct formed.

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