CCLV.—*The Alleged Existence of Triphenyldialkylpentaphosphines.*

By Bertie Kennedy Blount.

In a recent paper (*Compt. rend.*, 1931, **192**, 592) Grignard and Savard described the preparation of compounds of type (III) by means of the following series of reactions :

$$\underset{\text{(I.)}}{(C_6H_5)_3PO} + PCl_5 = \underset{\text{(II.)}}{(C_6H_5)_3PCl_2} + POCl_3 \quad . \quad . \quad \text{(A)}$$

$$(C_6H_5)_3PCl_2 + 2RMgX = (C_6H_5)_3P(MgX)_2 + 2RCl \quad . \quad . \quad \text{(B)}$$

$$(C_6H_5)_3P(MgX)_2 + 2R'OH = \underset{\text{(III.)}}{(C_6H_5)_3PR'_2} + 2MgXOH \quad . \quad . \quad \text{(C)}$$

$$(R = CH_3 \text{ or } C_2H_5 ;\ X = I \text{ or } Br ;\ R' = CH_3,\ C_2H_5, \text{ or } n\text{-}C_3H_7)$$

The products are stated to be white crystalline solids, apparently perfectly stable.

The existence of such compounds, having five ordinary hydrocarbon groups attached to one phosphorus atom, would have great theoretical interest in connexion with problems of valency and stereochemistry, and an attempt was accordingly made to repeat this work. The authors describe the conversion of triphenylphosphine oxide (I) into the corresponding dichloride (II) as being accomplished by means of phosphorus pentachloride in toluene, the product separating as an oil which was washed with water and sodium bicarbonate solution and crystallised from benzene or alcohol. The yield of the triphenylphosphine dichloride (described as white crystals, m. p. 176°, hydrolysed by boiling water) is not stated. On attempting to repeat this preparation, a chlorine-free product was obtained, which proved to be the regenerated oxide. This raised the question as to whether a compound of the type of triphenylphosphine dichloride would tolerate the action of water and of sodium bicarbonate solution, and it was therefore prepared by an independent method in order that this point might be investigated. Grignard and Savard state that triphenylphosphine dichloride has not previously been described, and appear therefore to have overlooked the work of Michaelis and Soden (*Annalen,* 1885, **229**, 302), who, by the direct action of chlorine on triphenylphosphine, obtained it as a syrup, which they were unable to purify owing to the extreme readiness with which it was hydrolysed by moisture.

The compound has now been obtained by a modification of Michaelis and Soden's method as white crystals, which are exceedingly sensitive to moisture, and become sticky on standing in the air for a few seconds, hydrogen chloride being evolved. This property made it difficult to prepare the substance in a condition suitable for analysis, but its constitution is adequately proved by the facts (1) that a solution of triphenylphosphine in carbon tetrachloride instantaneously decolorises a solution of chlorine in the same solvent up to (but not exceeding) an equimolecular proportion, a precipitate of the dichloride separating, and (2) that on hydrolysis it yields triphenylphosphine oxide. It appears, therefore, that Grignard and Savard's compound, m. p. 176°, cannot have been triphenyldichlorophosphine.

Attempts to carry out reactions (B) and (C) with triphenylphosphine oxide showed that it did not react. With authentic triphenylphosphine dichloride, a complex reaction took place (see p. 1893), and reactions of this type will be studied in greater detail later. No evidence was obtained of the formation of the triphenyldialkylpentaphosphines described by Grignard and Savard.

EXPERIMENTAL.

Attempted Repetition of Grignard and Savard's Preparation.—Triphenylphosphine oxide (4 g.) was dissolved in toluene (100 c.c.), and finely powdered phosphorus pentachloride (5 g.) was added gradually, with shaking. After standing for a time, the toluene was decanted from the oil, which was washed with ether and treated successively with ice and sodium bicarbonate solution. The oil soon solidified to a white crystalline mass, which was filtered off and washed with a little ether; yield 1·6 g. The substance was chlorine-free, and on recrystallisation from toluene it gave pure triphenylphosphine oxide, identified by its m. p. and mixed m. p.

Preparation of Triphenylphosphine Dichloride by a Modification of Michaelis and Soden's Method.—Triphenylphosphine (2·62 g.) was dissolved in pure dry carbon tetrachloride (10 c.c.) and treated with the theoretical amount of chlorine in the same solvent. Heat was evolved, and the compound separated either in a crystalline condition or as an oil which soon crystallised. It could also be prepared by leading a stream of chlorine on to the surface of a solution of triphenylphosphine in benzene, in which case it separated as an oil. The purest sample obtained melted indefinitely at 90—100°.

Hydrolysis of Triphenylphosphine Dichloride to Triphenylphosphine Oxide.—A small quantity of the dichloride was kept under cold water for an hour, with occasional stirring, and filtered off; on crystallising the residue from toluene, pure triphenylphosphine oxide was obtained. A further small quantity of the dichloride was exposed to the air on a watch-glass for 24 hours, the lumps being occasionally broken up. Crystallisation of the product from toluene gave the pure oxide.

Subjection of Triphenylphosphine Oxide to the Reactions described by Grignard and Savard.—Triphenylphosphine oxide (2·78 g.) was added to an excess of ethylmagnesium iodide in benzene, and the mixture boiled for some hours, during which no apparent reaction took place. After addition of alcohol and heating for a further ½ hour, the product was decomposed by means of dilute acid, and the benzene layer separated and dried. The residue left on evaporation solidified at once, and, after being pressed on porous plate, melted at 148—152°. Crystallisation from toluene gave 1·7 g. of pure oxide, m. p. 154° [Grignard and Savard give 155—157°, but during the present work an m. p. higher than 154° (uncorr.) was never obtained].

Reaction between Triphenylphosphine Dichloride and Ethylmagnesium Iodide under the Conditions described by Grignard and Savard.—A benzene suspension of triphenylphosphine dichloride, prepared from triphenylphosphine (2·62 g.), was added to an excess of ethylmagnesium iodide in benzene, and the mixture treated as described above. The product, after treatment with dilute acid, separated into three layers: an upper benzene layer, an aqueous layer, and a heavy oil, insoluble in water and benzene, which separated partly at the bottom and partly at the benzene-water interface. The oil at the bottom was run off, and as much as possible of the oil at the interface was removed by alternate shaking and separation. The benzene layer was then separated and dried. If any of the compound described by Grignard and Savard as triphenyldiethylpentaphosphine (III; $R' = C_2H_5$) had been formed in the reaction, it would have passed into the benzene layer, since they describe it as soluble in this solvent. Evaporation of the benzene solution, however, gave only a small quantity of material which consisted of triphenylphosphine oxide mixed with a trace of a pungent oil. The latter was separated by stirring with cold ether, in which triphenylphosphine oxide is sparingly soluble.

The insoluble oil was dissolved in alcohol, filtered from suspended impurities, and precipitated by addition of much ether. The ethereal mother-liquors on partial evaporation deposited a very small quantity of glistening, dark brown, rectangular leaflets, m. p.

129°, which were not further examined. On standing with ether, the insoluble portion crystallised, and, after being pressed on porous plate to remove a dark-coloured oil, was twice recrystallised by dissolving it in alcohol and gradually precipitating it with ether, and finally crystallised from acetone–light petroleum (b. p. 80—100°). It formed aggregates of compact prisms, m. p. 162—163°, and, dissolved in hot water, gave with silver nitrate a precipitate of silver iodide. It was proved by mixed m. p. not to be triphenylethylphosphonium iodide (m. p. 164—165°, Michaelis and Soden, *loc. cit.*). Analysis indicated that the substance was either very complicated or impure.

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