71. *Free Radicals and Radical Stability. Part VI. The Reactions of Triphenylmethoxides.*

By Sydney T. Bowden and Tudor John.

Lithium and rubidium triphenylmethoxides have been prepared by direct interaction of the metals with triphenylcarbinol. The sodium derivative can be prepared by boiling a xylene solution of the carbinol with sodium.

Although there is a fundamental difference in the electronic condition of the metal in the methoxides and the polar triphenylmethides, the metal atom of the former is also endowed with considerable reactivity. Potassium triphenylmethoxide reacts with benzyl bromide and methyl sulphate to form the benzyl and the methyl ether of triphenylcarbinol, respectively.

The functional analogy between the magnesium halide radical, –MgX, and the alkali metals is reflected in the reactions of potassium triphenylmethoxide, $CPh_3{\cdot}OK$, and the corresponding magnesium bromide derivative, $CPh_3{\cdot}OMgBr$. Although the latter does not yield ethers of triphenylcarbinol on treatment with methyl iodide and benzyl bromide, it reacts with acetyl chloride to form triphenylmethyl chloride. This is also produced by the action of carbonyl chloride, owing to the thermal instability of the intermediate chloroformate.

Phenoxymagnesium bromide, $MgBr{\cdot}OPh$, reacts with carbonyl chloride to give a good yield of phenyl carbonate. This reaction provides a convenient method of synthesising those substituted alkyl or aryl carbonates which cannot be prepared by the usual method involving the preliminary treatment of the hydroxyl compound with alkali metal.

According to Hemilian (*Ber.*, 1874, **7**, 1207), sodium reacts with a boiling toluene solution of triphenylcarbinol to produce sodium triphenylmethoxide, but Schlenk and Mair (*Ber.*, 1911, **44**, 1169) found little if any reaction between the materials in boiling xylene. They prepared the substance from the molten carbinol and sodium at 180—190°. We find that xylene or diphenyl solutions of the carbinol react smoothly with sodium to produce the desired methoxide.

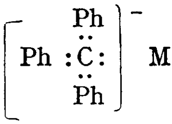
Lithium and rubidium triphenylmethoxides may be obtained by methods similar to that employed by Blicke (*J. Amer. Chem. Soc.*, 1923, **45**, 1965) for the preparation of the potassium derivative. *Lithium triphenylmethoxide*, like its sodium analogue, is a white microcrystalline powder of no definite melting point, but sintering with decomposition at a high temperature. Metallic rubidium reacts less readily than potassium, but *rubidium triphenylmethoxide* is deposited from xylene solution in large white crystals resembling the potassium derivative. Calcium is without action on the carbinol in boiling xylene.

The formation of the triphenylmethoxyl radical, CPh_3O–, has been postulated by Walden ("Chemie der freien Radikale," Leipzig, 1924, p. 90) and by Wieland (*Ber.*, 1911, **44**, 2551) to account for certain properties of triphenylmethyl peroxide. Cryoscopic measurements show, however, that its stability is of very low order, and it was of interest therefore to compare the reactions of compounds containing this radical with those containing triphenylmethyl, which is considerably more stable in the free state. Although the alkali-metal triphenylmethides are readily relieved of alkali metal on treatment with mercury even at room temperature, we find that a xylene solution of potassium triphenylmethoxide can be boiled with mercury for prolonged periods without losing a trace of potassium.

This difference in behaviour is consistent with the electronic structures (I) and (II) for the methide and methoxide respectively. Although there is a fundamental difference in the character of the link between metal and radical, the reactivity of the metal atom of the methoxide is apparent in its reactions with alkyl halides, carbonyl chloride, and methyl sulphate.

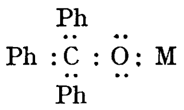
The analogous function of the univalent magnesium halide radical, –MgX, and the alkali metals in the methides led us to compare the behaviour of potassium triphenylmethoxide and the corresponding magnesium bromide derivative, CPh$_3$·OMgBr. This does not produce the methyl and benzyl ethers of triphenylcarbinol on treatment with the corresponding halides, although these ethers are readily prepared from potassium triphenylmethoxide. Both methoxides react slowly in the cold with an ethereal solution of triphenylmethyl bromide, but triphenylmethyl oxide cannot be isolated. Moreover, the combination of radicals which occurs when Grignard reagents are treated with anhydrous cupric chloride does not take place to any appreciable extent in the case of triphenylmethoxymagnesium bromide.

(I.)



$$\left[\begin{array}{c}\mathrm{Ph}\\ \mathrm{Ph}:\ddot{\underset{\cdot\cdot}{\mathrm{C}}}:\\ \mathrm{Ph}\end{array}\right]^{-}\mathrm{M}^{+}$$

(II.)



$$\begin{array}{c}\mathrm{Ph}\\ \mathrm{Ph}:\ddot{\underset{\cdot\cdot}{\mathrm{C}}}:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{M}\\ \mathrm{Ph}\end{array}$$

Acetyl chloride reacts with the last-named compound to form triphenylmethyl chloride: $\mathrm{CPh_3{\cdot}OMgBr + CH_3{\cdot}COCl \longrightarrow CH_3{\cdot}CO_2CPh_3 + MgBrCl}$; $\mathrm{CH_3{\cdot}CO_2CPh_3 + CH_3{\cdot}COCl \longrightarrow CPh_3Cl + (CH_3{\cdot}CO)_2O}$, and the same substance is produced by the action of carbonyl chloride, owing to the thermal instability of the intermediate chloroformate. In this connexion, the reaction of phenoxymagnesium bromide, which is readily obtained by adding phenol to phenylmagnesium bromide, with carbonyl chloride to give a good yield of phenyl carbonate is of interest as providing a possible general method for synthesising carbonates, for it may be applied in those cases where the usual procedure is not feasible.

EXPERIMENTAL.

Preparation of Methoxides.—Lithium triphenylmethoxide. On account of the comparatively low reactivity and high m. p. of lithium, this preparation presents several difficulties. The following methods were investigated.

(*a*) Schlenk and Mair's method (*loc. cit.*) for preparing sodium triphenylmethoxide was modified as follows. Pure triphenylcarbinol (6 g.) was distilled into a Pyrex reaction tube provided with a stirring device and an inlet tube for the admission of pure, dry nitrogen. Thin shavings of metallic lithium (0·025 g.), held in the crook of the stirrer, were lowered into the molten carbinol. At 280°, a slow evolution of hydrogen and precipitation of the white lithium derivative occurred. Apart from the slowness of the reaction, the difficulty of removing the excess of carbinol from the methoxide renders this method unsuitable.

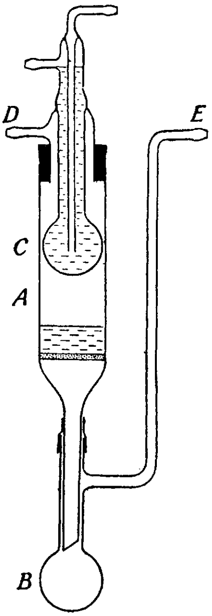
(*b*) A solution of the carbinol in diphenyl was boiled with metallic lithium, but again reaction was very slow. Unexpectedly, however, the use of the lower-boiling xylene as solvent proved satisfactory. The carbinol (3 g.), dry sulphur-free xylene (20 c.c.), and very thin shavings of lithium (0·8 g.; 10 atom-equivs.) were heated in a reflux apparatus provided with a mercury seal. Although there was no visible evolution of hydrogen at the surface of the metal, the separation of the lithium derivative began after 5 hours and was complete after a further 12 hours. The cold mixture was diluted with dry benzene (25 c.c.), and the excess of metal removed under a stream of nitrogen by means of a hat-pin. The solid was collected on a sintered-glass filter, washed repeatedly with low-boiling light petroleum, and dried *in situ* under reduced pressure in a slow current of nitrogen (Found: Li, 2·6. $\mathrm{C_{19}H_{15}OLi}$ requires Li, 2·6%). The *compound* was a white, very finely divided powder, insoluble in benzene, xylene, and ligroin. It decomposed without previous melting in a sealed tube above 360° and was immediately hydrolysed to the carbinol and lithium hydroxide on contact with moist air.

The peculiar influence of the presumably inert solvent in these experiments is further illustrated by the fact that use of benzene instead of xylene yields no trace of the methoxide even after 120 hours' boiling.

Sodium triphenylmethoxide. The method described in the literature for the preparation of this compound is unsuitable (see Blicke, *loc. cit.*) and we studied the action of sodium on the carbinol in various solvents with a view to find a better one, since the compound offers possibilities as a synthetic agent. The following methods proved to be entirely satisfactory.

(*a*) The apparatus consisted of a 100-c.c. Pyrex flask (with a side-tube situated below the neck) provided with a reflux condenser and an inlet tube for admission of nitrogen. A solution of the carbinol (3·0 g.) in xylene (30 c.c.) was boiled under nitrogen with sodium (1·7 g.) for 24 hours. The excess of metal was removed from the cold mixture, and the methoxide collected on a sintered-glass filter attached to the side-tube of the flask. The methoxide was washed with light petroleum and dried on the filter by means of a current of nitrogen (Found: Na, 8·6. Calc. for $C_{19}H_{15}ONa$: Na, 8·15%); yield, 2·5 g. (75%).

(*b*) Preliminary experiments showed that sodium began to attack triphenylcarbinol in diphenyl when the solution reached 80° but that reaction was comparatively slow even at 180°. In a Kjeldahl flask, fitted with an air-condenser and a delivery tube for admission of nitrogen, a mixture of diphenyl (40 c.c.), triphenylcarbinol (10 g.), and sodium (0·5 g.) was brought to its b. p. Owing to interfacial tension, the metal broke up into numerous globules, thus accelerating the reaction. The metal dissolved in 3 hours. After the mixture had been cooled to about 75°, benzene was added to dissolve the diphenyl and unchanged carbinol. The residual sodium triphenylmethoxide was dried as described above (Found: Na, 8·4%). This method is very suitable for the rapid preparation of the compound in good yield.



Rubidium triphenylmethoxide. In a preliminary experiment on the action of rubidium on the carbinol in xylene hydrogen was generated in the cold, but the reaction took place very slowly even at 100°, the metal being less reactive than potassium at this temperature.

The preparation of the compound was carried out on a micro-scale in the apparatus shown in the diagram. It consisted essentially of a sintered-glass filter *A* (7 × 2 cm.) attached to a small receiver *B* provided with a side-tube *E*. The filter was closed with a rubber stopper carrying the internal condenser *C* and the exit tube *D*. With a slow stream of nitrogen passing upwards through the filter, a mixture of pure triphenylcarbinol (0·2 g.), potassium-dried xylene (1 c.c.), and rubidium (0·033 g.) was heated in *A* by immersing the apparatus for 4 hours in an oil-bath at 130°. During this process *rubidium triphenylmethoxide* was deposited in large white crystals. After the whole had been cooled to room temperature, nitrogen was admitted through *D*, and the solution filtered by applying gentle suction at *E*. The material was washed with benzene and light petroleum, and dried *in situ* at 140°/50 mm. for 3 hours in a slow up current of nitrogen. The crystals disintegrated into a white powder, m. p. 235° (decomp.) (Found: Rb, 26·7, 26·75. $C_{19}H_{15}ORb$ requires Rb, 24·5%). The compound was insoluble in cold xylene, burned with a yellow flame, and was hydrolysed very readily in the air to form the carbinol and rubidium hydroxide.

Similar experiments showed that calcium is entirely without action on a boiling solution of triphenylcarbinol in xylene, although Kraus and Kawamura (*J. Amer. Chem. Soc.*, 1923, **45**, 779) reported the formation of calcium triphenylmethide by treatment of triphenylmethyl chloride with calcium in liquid ammonia.

Triphenylmethoxymagnesium bromide. This compound was prepared by treating phenylmagnesium bromide with an ethereal solution of triphenylcarbinol or benzophenone: the latter reagent is preferable, because its higher solubility facilitates purification of the methoxide. The required compound separated from solution in white crystals, which were pure after being washed. Its solutions were prone to exhibit super-saturation.

Reactions of Methoxides.—Potassium triphenylmethoxide and benzyl bromide. The potassium derivative, prepared from the carbinol (11·5 g.) and excess of potassium (Blicke, *loc. cit.*), was heated with a solution of benzyl bromide (5·6 g.) in benzene (30 c.c.) for 2 hours. The clear solution was siphoned from the gelatinous potassium bromide and allowed to evaporate spontaneously. The residue was washed with water and dissolved in the minimum amount of alcohol, from which triphenylmethyl benzyl ether separated in long needles (10 g.), m. p. 106°.

Potassium triphenylmethoxide and methyl sulphate. To the potassium derivative prepared from 10 g. of the carbinol, a solution of freshly distilled methyl sulphate (2·4 g.) in benzene (20 c.c.) was added in small portions during ½ hour. The exothermic reaction was accompanied by formation of colloidal potassium methyl sulphate, and in the later stages by the production of a yellow colour, which disappeared on shaking. After an hour, the solution was siphoned off, combined with benzene extracts of the residue, and allowed to evaporate spontaneously. The residue was extracted with light petroleum; the first crop of crystals was triphenylcarbinol, but the second crop was triphenylmethyl methyl ether (3·6 g.), m. p. 83—84°. 2·2 G. of potassium methyl sulphate were obtained.

Potassium triphenylmethoxide and mercury. The potassium derivative, dissolved in toluene and xylene, was boiled with a large excess of pure mercury for several hours in an atmosphere of nitrogen. The mercury was washed with toluene but gave a negative test for potassium, and the whole of the methoxide was recovered as triphenylcarbinol after hydrolysis.

Triphenylmethoxymagnesium bromide and alkyl halides. A solution of methyl iodide in benzene was boiled with the bromide for 2 hours, but the expected methyl ether was not produced. A similar negative result was obtained with benzyl bromide. Triphenylmethoxymagnesium bromide, prepared from benzophenone (2·9 g.) and phenylmagnesium bromide, was shaken for 2 days in a sealed vessel in the dark with a solution of freshly prepared triphenylmethyl bromide (5·2 g.) in benzene (20 c.c.) at room temperature. The solution became yellowish-red, and after a further 2 days it was treated with water, but no trace of triphenylmethyl oxide was obtained, the product consisting largely of triphenylcarbinol. [Schlenk (*Annalen*, 1912, **394**, 178) obtained triphenylcarbinol and resinous substances by treating sodium triphenylmethoxide with triphenylmethyl chloride, and Blicke (*loc. cit.*) obtained similar results with the potassium derivative.]

Triphenylmethoxymagnesium bromide and cupric chloride. Finely powdered anhydrous cupric chloride was heated with a benzene–ether solution of the bromide for 7 hours (cf. Krizewsky and Turner, J., 1919, **115**, 560; Bowden, J., 1931, 1113). The mixture was decomposed with ice and hydrochloric acid, and the non-aqueous layer dried with sodium sulphate and allowed to evaporate. Triphenylcarbinol alone remained, and triphenylmethyl peroxide or its decomposition products could not be detected.

Triphenylmethoxymagnesium bromide and acid chlorides. The methoxide, prepared from phenylmagnesium bromide and benzophenone (5·8 g.), was treated with a solution of freshly distilled acetyl chloride (6·3 g.; 2·5 mols.) in dry benzene (20 c.c.). A yellow colour was immediately developed, and this increased in intensity on standing. After an hour's gentle heating, the liquid was filtered in the absence of moisture, and dry air passed through it at 60° to remove the excess of acetyl chloride. The solution was diluted with benzene and shaken with mercury in a sealed vessel for several hours. Air was passed through the filtrate until oxidation of the radical was complete; 2·13 g. of triphenylmethyl peroxide (m. p. 180—182°) were obtained. Under these conditions, therefore, the conversion of methoxide into triphenylmethyl chloride occurred to the extent of 37%.

To the bromide prepared as above, a solution of carbonyl chloride (3·2 g.) in toluene (25 c.c.) was added in small quantities. Very little heat was generated during the reaction, but the solution rapidly became yellow. After 24 hours, the supernatant solution was decanted, and the excess of carbonyl chloride removed in a current of dry air. The solution was reduced by means of mercury, and the free radical oxidised by air to the peroxide; after being washed with ether, this weighed 0·75 g., m. p. 179—180°. Accordingly, the yield of triphenylmethyl chloride, based on the amount of peroxide, was 14% of the theoretical.

Triphenylmethoxymagnesium bromide and carbonyl chloride. To a filtered solution of phenylmagnesium bromide (magnesium, 3·3 g.; bromobenzene, 20 g.; ether, 30 c.c.), freshly distilled phenol (11·8 g.) in ether (25 c.c.) was added in small portions, the strongly exothermic reaction being moderated by frequent cooling in water. The phenoxide was deposited as a greyish-white solid, and the reaction was completed by 2 hours' gentle heating. The supernatant solution was decanted through the side-tube of the reaction flask, and the residual phenoxide cooled to 0° and slowly treated with a solution of carbonyl chloride (6·2 g.) in toluene (30 c.c.). Reaction took place rapidly, with formation of a white gelatinous precipitate. After some hours, the toluene solution was filtered, and the excess of carbonyl chloride removed in a stream of air. Spontaneous evaporation of the solution yielded a white solid, which was washed with water, dried, and crystallised from ligroin. Phenyl carbonate was thus obtained in large, well-formed crystals, m. p. 79—81°, not depressed by an authentic specimen. The yield (9 g.; 66%) compares favourably with that obtained in the interaction of carbonyl chloride with the alkali phenoxides.

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF. [*Received, November* 30*th*, 1938.]