101. *The Methylation of Triphenylcarbinol.*

By H. H. Hatt.

Triphenylcarbinol is methylated by methyl alcohol in presence of hydrogen chloride, but not by the pure alcohol alone. An addition *compound* of the carbinol and alcohol is described. Triphenylmethyl methyl ether is dimorphous.

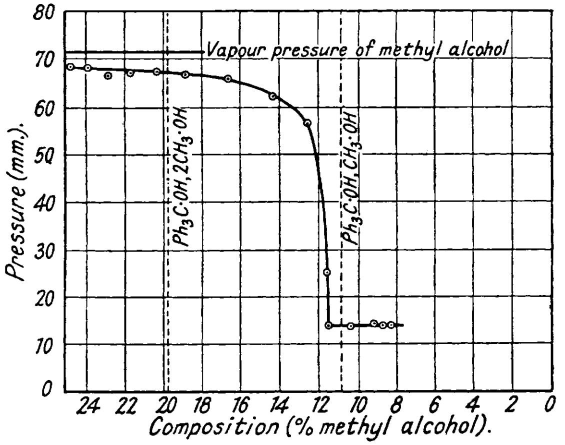
Strauss and Hüssy (*Ber.*, 1909, **42**, 2177) reported that triphenylcarbinol is methylated by boiling with methyl alcohol. In syntheses of tertiary carbinols where a Grignard reagent has been used, the part formation of the methyl or ethyl ether has been sometimes reported (Haller and Guyot, *Bull. Soc. chim.*, 1904, **31**, 979; Thiele and Balhorn, *Ber.*, 1904, **37**, 1463; Stadnikoff, *Ber.*, 1924, **57**, 5). Ether formation may have been due in such cases to subsequent use of an alcohol as a solvent for the carbinol (compare Boyd and Hatt, J., 1927, 904). In the one case of triphenylcarbinol the conditions under which methyl alcohol can effect methylation have now been more exactly determined.

Triphenylcarbinol was crystallised repeatedly from benzene. The methyl alcohol used was freed from acetone with iodine and alkali, dried with sodium, fractionated repeatedly through a Clarke and Rahrs column (*Ind. Eng. Chem.*, 1923, **15**, 401), and fractionally distilled from sulphanilic acid in a Pyrex apparatus. This alcohol did not methylate triphenylcarbinol. After a solution of the carbinol in methyl alcohol had been refluxed for 100 hours, methylation did not exceed 0·4% (the experimental limit). Methylation also did not occur when the carbinol (1 g.) was refluxed for 5 hours with 0·00001M-methyl-alcoholic hydrogen chloride (10 c.c.), but like treatment with a 0·0001M-hydrogen chloride brought about 83—85% methylation. (This is the equilibrium value reached when these quantities of carbinol and alcohol are used with the hydrogen chloride from 0·0001 to 1·0M:

$$CPh_3\cdot OH + CH_3\cdot OH \rightleftharpoons CPh_3\cdot O\cdot CH_3 + H_2O$$

The same equilibrium position is reached by refluxing together corresponding quantities of triphenylmethyl methyl ether, methyl alcohol, and water in presence of hydrogen chloride.) The methylations were carried out in Pyrex apparatus. When the methyl alcohol was not distilled from sulphanilic acid, or was stored in soft-glass containers, the catalytic effect of the hydrogen chloride could not be detected below a molarity of 0·0003. The quantity of hydrogen chloride present remained essentially constant during a methylation if its initial molarity did not exceed 0·005; with greater molarities, losses, probably due to evaporation or methyl chloride formation, became appreciable. The extent of methylation was estimated as follows: The reaction mixture was poured into an excess of water, washed in with pure methyl alcohol, rendered alkaline with baryta water, and evaporated several times with water to expel the alcohol. The residues were extracted in benzene, the solvent removed on a water-bath under reduced pressure, and the methoxyl content of the residues estimated by the Zeisel method.

Triphenylcarbinol and methyl alcohol form an addition *compound*, which separates from methyl alcohol in large (1 cm.) colourless rhombs (Found: CH_4O, 10·8. $C_{19}H_{16}O,CH_4O$ requires CH_4O, 10·9%). The alcohol is lost rapidly at 100°. The results of vapour-pressure measurements of triphenylcarbinol–methyl alcohol mixtures at 15° are shown in the figure.



Vapour Pressures of Methyl Alcohol–Triphenylcarbinol Mixtures at 15°.

Clearly, only one addition compound is formed. Its free energy of formation at 15° from solid triphenylcarbinol and liquid methyl alcohol, calculated from its vapour pressure (14 mm.) and that of methyl alcohol (71·3 mm.), is about 930 cals. Thus the hydrogen bridges which here presumably unite the two alcohols possess a considerable stability.

The experience of Norris and Cresswell (*J. Amer. Chem. Soc.*, 1933, **55**, 4946) concerning triphenylmethyl methyl ether has been confirmed. At first this ether was obtained melting at 82·5—83°. In later preparations it was obtained in colourless plates, m. p. 96·0—96·5° (Found: $O{\cdot}CH_3$, 11·3. Calc. for $C_{19}H_{15}{\cdot}O{\cdot}CH_3$: $O{\cdot}CH_3$, 11·3%). All my previous preparations now had this melting point and the lower-melting form could not be obtained. Mr. A. Pilgrim obtained the low-melting form again by working in another laboratory and it was found to change rapidly into the high-melting form upon inoculation. Triphenylmethyl methyl ether is therefore dimorphous, the form of m. p. 83° most frequently obtained being the less stable.

Although pure methyl alcohol cannot methylate triphenylcarbinol in absence of acid, published evidence indicates that this is possible in the case of malachite-green base (Fischer, *Ber.*, 1900, **33**, 3356; Herzig and Wengraf, *Monatsh.*, 1901, **22**, 601).

THE CENTRAL TECHNICAL COLLEGE, BIRMINGHAM.

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