LXXXVI.—*The Introduction of the Triphenylmethyl Group into Phenols.*

By David Runciman Boyd and Douglas Vernon Nelmar Hardy.

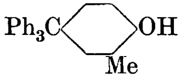
Baeyer and Villiger (*Ber.*, 1902, **35**, 3018) found that phenol and anisole, in the presence of acetic and sulphuric acids, condense with triphenylcarbinol at the ordinary temperature to give 4-hydroxy- and 4-methoxy-tetraphenylmethane respectively. It was afterwards shown by Baeyer (*Ber.*, 1909, **42**, 2624) that 4-hydroxytetraphenylmethane is also formed on warming the deep brown solution which results on dissolving triphenylchloromethane in molten phenol, but that the phenyl ether of triphenylcarbinol is obtained when triphenylchloromethane reacts with potassium phenoxide in the presence of excess of phenol. Gomberg and Kamm (*J. Amer. Chem. Soc.*, 1917, **39**, 2009) have proved that relatively small amounts of hydrogen chloride or of sulphuric acid are sufficient to effect the condensation of triphenylcarbinol with phenol, so that the action of the acids appears to be catalytic.

In studying the properties of triphenylmethoxyphosphorus dichloride (Boyd and Chignell, J., 1923, **123**, 813; Boyd and Smith, J., 1924, **125**, 1477) we observed some time ago that this compound can be used in place of triphenylchloromethane for the preparation of 4-hydroxytetraphenylmethane. Further investigation showed, however, that the reaction has only a limited application as a means of introducing the triphenylmethyl group into phenols. Thus, on heating with *p*-cresol, triphenylmethoxyphosphorus dichloride is converted mainly into triphenylmethane, and on heating with methyl salicylate it yields derivatives of triphenylmethylphosphorous acid. With methyl salicylate the Baeyer–Villiger method also fails, but we have found that condensation in this case can be effected by merely boiling a solution of the carbinol in the ester.

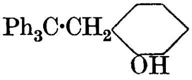
Reaction takes place in the complete absence of any catalytic agency other than the excess of methyl salicylate :

$$Ph_3C{\cdot}OH + C_6H_4(OH){\cdot}CO_2Me = Ph_3C{\cdot}C_6H_3(OH){\cdot}CO_2Me + H_2O.$$

Triphenylcarbinol condenses, under the same conditions, with phenol, but not with *o*-cresol, *m*-cresol, anisole, or *o*-chlorophenol. In the course of our experiments we employed the Baeyer–Villiger method, in a modified form, to condense *o*-cresol with triphenylcarbinol. The product of the reaction was identical with a substance previously obtained by Schorigin (*Ber.*, 1926, **59**, 2502) by heating triphenylchloromethane with a mixture of *o*-cresol and sodium *o*-tolyloxide. On grounds which appear to us to be inadequate, Schorigin regards this compound, not as 4-hydroxy-3-methyltetraphenylmethane (I), but as ααα-triphenyl-β-2-hydroxyphenylethane (II). In a more recent paper (*Ber.*, 1927, **60**, 2373) Schorigin describes experiments on the condensation of triphenylcarbinol with cresols by the Baeyer–Villiger method. In this way he has prepared from triphenylcarbinol and *m*-cresol a condensation compound which he considers to be a tetraphenylmethane derivative (III or IV). With *p*-cresol, in the presence of acetic and sulphuric acids, triphenylcarbinol is converted into triphenylmethane; but a condensation product, to which he assigns formula (V), has been obtained by Schorigin by heating triphenylchloromethane with sodium *p*-tolyloxide and *p*-cresol.



(I.)



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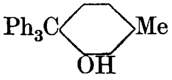

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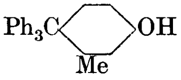

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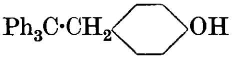

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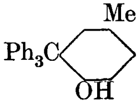


(VI.)

Schorigin bases his formulæ for the *o*- and *p*-cresol condensation products mainly on the fact that, whereas he was able to obtain triphenylcarbinol in small quantity on oxidising the *o*- and *p*-cresol derivatives with chromic anhydride, no triphenylcarbinol could be isolated on treating either the *m*-cresol derivative or 4-hydroxytetraphenylmethane with the same oxidising agent. Since Gomberg and Cone (*Ber.*, 1906, **39**, 1464) have shown that unsymmetrical tetraphenylethane gives triphenylcarbinol on oxidation with chromic anhydride, it is argued that the *o*- and *p*-cresol condensation compounds are derivatives of this hydrocarbon, and that the *m*-cresol compound is derived from tetraphenylmethane.

Several observations which we have made are, however, opposed to the view that the *o*- and *p*-cresol compounds differ in type from the *m*-cresol derivative and 4-hydroxytetraphenylmethane :

(1) The four compounds behave similarly on distillation with soda-lime ; each gives triphenylmethane.

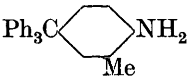
(2) From their behaviour on heating with a mixture of hydriodic and acetic acids they fall into two groups, but not the groups which are to be expected on the basis of Schorigin's views. The *o*- and *m*-cresol compounds behave similarly, yielding triphenylmethane, whereas the *p*-cresol derivative and 4-hydroxytetraphenylmethane are both stable towards this reducing agent.

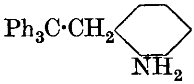
(3) Although on oxidising with chromic anhydride, Schorigin failed to obtain triphenylcarbinol from 4-hydroxytetraphenylmethane and its homologue derived from *m*-cresol, we have found that the carbinol can be obtained from each of the four compounds by merely warming with sulphuric acid.

The weight of evidence appears to us, therefore, to be against the view that the *o*- and *p*-cresol derivatives differ fundamentally in constitution from the *m*-cresol derivative and the unsubstituted hydroxytetraphenylmethane, and we consider that, until definite proof to the contrary has been brought forward, the *o*- and *p*-cresol compounds should be represented by formulæ (I) and (VI) respectively.

The adoption of formula (I) for the *o*-cresol derivative of triphenylcarbinol necessitates a corresponding alteration in the formula of the condensation product obtained from triphenylcarbinol and *o*-toluidine hydrochloride (van Alphen, *Rec. trav. chim.*, 1927, **46**, 501). Since the *o*-toluidine derivative can be converted into compound (I) by diazotisation, it follows that formula (VII) must be assigned to it ; and not, as van Alphen suggests, formula (VIII) :

(VII.)



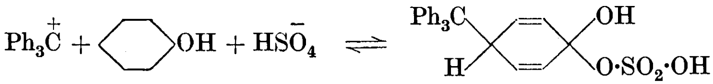


(VIII.)

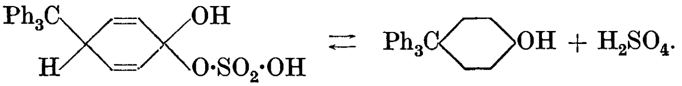
Our observations on the action of sulphuric acid upon 4-hydroxytetraphenylmethane and its derivatives show that the Baeyer–Villiger reaction is reversible ; and in this connexion it is of interest to consider the mechanism of the process. An acetic–sulphuric acid solution of triphenylcarbinol is orange-red, and doubtless contains triphenylmethyl sulphate, ionised to a certain extent :

$$Ph_3C{\cdot}OH + H_2SO_4 \longrightarrow Ph_3C{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftarrows Ph_3\overset{+}{C} + SO_4\overset{-}{H}.$$

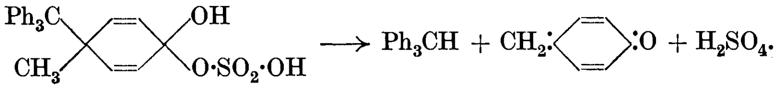
If to this orange solution a phenol, or its methyl ether, is added, a deep brown colour is immediately produced. This we attribute to the formation of a quinonoid addition compound, the ions of triphenylmethyl sulphate being added to the 1 : 4-positions of the phenolic nucleus :



In the normal reaction this complex gradually breaks up into sulphuric acid and the tetraphenylmethane derivative :



This hypothesis explains the rôle of the sulphuric acid, and the reversibility of the reaction. With *p*-cresol, however, the decomposition of the complex cannot proceed in the way indicated in the above equation, owing to the blocking of the position para to the hydroxyl group. In place of a condensation compound, triphenylmethane is formed; the other product being not improbably, as Schorigin has suggested, a polymerised form of *p*-quinomethane :



The action of phenols upon triphenylchloromethane and upon triphenylmethoxyphosphorus dichloride may be explained in a similar fashion (compare Busch and Knoll, *Ber.*, 1927, **60**, 2243). But whereas in the Baeyer–Villiger reaction the dissociating solvent is the mixture of acetic and sulphuric acids, here it is the phenol itself which performs this function. It follows that where the phenol has a low ionising power no ionisation may result and therefore no colour be developed, *e.g.*, with methyl salicylate and guaiacol. The appearance of a brown colour, and the accompanying acceleration of the reaction, which Baeyer observed (*loc. cit.*) on adding stannic chloride to the colourless solution of triphenylchloromethane in guaiacol, are doubtless due to the formation of the double salt $Ph_3CCl,SnCl_4$, which readily dissociates into ions, thus enabling the quinonoid complex to be formed.

The data recorded in the following table show that the stability of the tetraphenylmethane molecule towards reagents, such as sulphuric and hydriodic acids, which promote fission, is altered markedly by the presence of substituent groups, and that the influence of a substituent is dependent both on its chemical nature and on its position in the molecule.

Tetraphenylmethane Derivatives.

	Action of sulphuric acid.				
	Wt. (g.).	Temp.	Time (mins.).	Yield of $Ph_3C{\cdot}OH$.	Action of hydriodic–acetic acid.
4-Hydroxy-	2	60°	30	0·1	Stable.
4-Methoxy-	1	50	15	0·22	4-Hydroxytetraphenylmethane.
4-Hydroxy-3-methyl-	1	40	10	0·26	Ph_3CH.
4-Methoxy-3-methyl-	2	40	5	1·15	,,
4(2)-Hydroxy-2(4)-methyl-	1	50	30	0·05	,,
2-Hydroxy-5-methyl-	1	40	30	0·05	Stable.
4-Hydroxy-3-carboxy-	1	40	10	Nil	,,

The study of the tetra-arylmethane group of compounds from this point of view is being continued.

EXPERIMENTAL.

The Direct Action of Triphenylcarbinol upon Phenols.—4 G. of triphenylcarbinol and 5 g. of phenol were heated to boiling for about an hour, the mixture becoming almost completely solid. After cooling, the mass was boiled with dilute caustic soda solution to remove the excess of phenol, and the solid 4-hydroxytetraphenylmethane filtered off. After washing and drying, it crystallised from acetic acid in white flakes, m. p. 282°. The yield was 5·0 g., 97% of the theoretical. The compound was identified by the melting point of a mixture with an authentic specimen and by conversion into its acetyl derivative, m. p. 175°, as recorded by Baeyer.

4-*Hydroxytetraphenylmethane*-3-*carboxylic Acid*,

$$CPh_3{\cdot}C_6H_3(OH){\cdot}CO_2H.$$—

4 G. of triphenylcarbinol and 5 g. of methyl salicylate were gently boiled under reflux. Water vapour was continuously evolved for about an hour; the mixture was then allowed to cool. The excess of methyl salicylate was hydrolysed by boiling with 40 c.c. of alcohol and 3 g. of caustic potash for 2 hours under reflux. The alcohol was then evaporated, the residue boiled with water, and the insoluble matter filtered off. After drying, the product (5·2 g.) was boiled with a mixture of 20 c.c. of acetic acid and 5 c.c. of hydriodic acid for 2 hours. On cooling, almost colourless crystals of the carboxylic acid separated together with some triphenylmethane. The crystals were collected and washed with sulphurous acid to remove iodine. The dried material crystallised from petroleum (b. p. 100—120°) in colourless needles, m. p. 232°. The yield was 1·9 g. (Found: C, 82·2; H, 5·5. $C_{26}H_{20}O_3$ requires C, 82·0; H, 5·3%).

When the acid was heated above its melting point, carbon dioxide was evolved and a white sublimate obtained, which was identified as

4-hydroxytetraphenylmethane by its melting point (276—282°), mixed-melting point (278—282°), and by conversion into 4-acetoxytetraphenylmethane (m. p. 173—175°). 4-Hydroxytetraphenylmethane-3-carboxylic acid is insoluble in aqueous alkalis; with an alcoholic solution of sodium hydroxide it gives a sodium salt.

4-*Acetoxytetraphenylmethane*-3-*carboxylic Acid*, $CPh_3{\cdot}C_6H_3(OAc){\cdot}CO_2H$.—1 G. of the hydroxy-acid was boiled with 10 c.c. of acetic anhydride and 3 g. of anhydrous sodium acetate for 2 hours. The solid left after the mixture had been diluted with water and boiled was filtered off, washed, and dried. It crystallised from acetone–light petroleum as a white powder, m. p. 210° (Found: C, 79·5; H, 5·5. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·25%). The acid is insoluble in aqueous alkalis.

5-*Bromo*-4-*hydroxytetraphenylmethane*-3-*carboxylic Acid*, $CPh_3{\cdot}C_6H_2Br(OH){\cdot}CO_2H$.—2 G. of the hydroxy-acid, 1 g. of bromine, and 15 c.c. of acetic acid were boiled under reflux until evolution of hydrogen bromide ceased. On cooling, the *bromo*-compound separated in colourless prisms, m. p. 239° after recrystallisation from acetic acid (Found: Br, 17·2. $C_{26}H_{19}O_3Br$ requires Br, 17·4%). Like the parent substance, the bromo-acid is insoluble in aqueous alkalis.

5-*Nitro*-4-*hydroxytetraphenylmethane*-3-*carboxylic Acid*, $CPh_3{\cdot}C_6H_2(NO_2)(OH){\cdot}CO_2H$.—2 C.c. of nitric acid were added to a mixture of 2 g. of the hydroxy-acid and 50 c. c. of acetic acid, and the whole kept for 24 hours with frequent shaking. All the hydroxy-acid had then dissolved. The solution was poured into water and the resulting yellow precipitate was collected and dried. After crystallisation from light petroleum and then from benzene, the substance formed light yellow needles, m. p. 226° (Found: N, 3·2, 3·6. $C_{26}H_{19}O_5N$ requires N, 3·3%). The nitro-acid dissolves readily in dilute caustic soda solution, from which it is precipitated on acidification.

The Action of Triphenylmethoxyphosphorus Dichloride upon Phenols.—(1) *Phenol.* 5 G. of triphenylmethoxyphosphorus dichloride were added to 5 g. of molten phenol. The dichloride dissolved slowly with production of an intense red-brown colour, and at the same time hydrogen chloride was evolved. After standing for 20 minutes with stirring, the mixture was heated to 120°. The colour then rapidly faded, and after heating for 30 minutes the product consisted of a light brown solid. When cold, this was boiled with dilute caustic soda solution, and the insoluble material was collected, washed, and dried. After crystallisation from alcohol it melted at 282°. The yield was 3·5 g. (87%). The identity of the product as 4-hydroxytetraphenylmethane was shown by a mixed melting point determination and by acetylation. On acidifying the caustic soda solution, 0·18 g. of a phosphorus-containing acid was obtained.

(2) m-*Cresol.* A mixture of 2 g. of the phosphorus dichloride and 2 g. of *m*-cresol was gradually warmed in an oil-bath. A brown colour developed slowly, and faded to a pale brown when the temperature was raised to 120°. After cooling, the excess of *m*-cresol was removed by treatment with caustic soda, and the residue was dissolved in ether and shaken with caustic soda. The resulting white gelatinous precipitate was washed with ether and boiled with hydrochloric acid. The product, after crystallisation from acetic acid, melted at 213° and weighed 0·44 g. Mixed with 4(2)-hydroxy-2(4)-methyltetraphenylmethane, it melted also at 213°. From the ethereal solution there were obtained a phosphorus-containing oil and 0·32 g. of triphenylmethane, identified by a mixed melting point determination and by conversion into the benzene compound (m. p. 78°).

(3) p-*Cresol.* 5 G. of the phosphorus dichloride and 5 g. of *p*-cresol were heated together in an oil-bath. The mixture gradually became brown and hydrogen chloride was evolved. The temperature was maintained at 100° and the colour changed to wine-red. When cold, the unchanged *p*-cresol was removed in the usual manner with caustic soda; on acidification of the alkaline filtrate a very small amount of a phosphorus-containing acid, mixed with a little red, amorphous colouring matter, was precipitated. The insoluble portion was crystallised from alcohol. After 2·45 g. of triphenylmethane had separated, the mother-liquor deposited 0·5 g. of a phosphorus-containing substance. This crystallised from alcohol in colourless prisms, m. p. 179—180°, and from its analysis appeared to be the *di*-p-*tolyl ester* of *triphenylmethylphosphorous acid* (Found : C, 78·6; H, 6·1; P, 6·0. $C_{33}H_{29}O_3P$ requires C, 78·55; H, 5·8; P, 6·2%).

The Action of Triphenylcarbinol upon Phenols in the Presence of Sulphuric Acid.—In carrying out these experiments the amounts of acetic and sulphuric acids employed were considerably less than those used by Baeyer and Villiger. As a result the products were more readily isolated.

(1) o-*Cresol.* 6 G. of triphenylcarbinol and 6 g. of *o*-cresol were dissolved in 60 c.c. of acetic acid by warming, and 10 g. of pure sulphuric acid were then added. The intense brown solution was kept until the following day; the colour had then faded to a pale red-brown. The solution was poured into water, and the precipitated material boiled with caustic soda solution. After drying, the

product was crystallised by dissolving it in a little benzene and adding hot methyl alcohol to the filtered solution. White, powdery crystals separated, m. p. 180—181°. The yield was 8·1 g. By dissolution in Claisen's solution (*Annalen*, 1919, **418**, 96) and subsequent crystallisation, the melting point was raised to 183° (Schorigin originally gave 183°, but in his most recent paper gives 186°). Mixed with a specimen of Schorigin's "cryptophenol," prepared from sodium *o*-tolyloxide and triphenylchloromethane, it melted also at 183°. Further evidence of identity was obtained by converting the two products into their acetyl derivatives.

4-*Acetoxy*-3-*methyltetraphenylmethane*, $CPh_3{\cdot}C_6H_3Me{\cdot}OAc$.—1 G. of 4-hydroxy-3-methyltetraphenylmethane, 1 g. of anhydrous sodium acetate, and 10 c.c. of acetic anhydride were refluxed together for 2 hours. The mixture was poured into water and the precipitated solid was collected, dried, and crystallised from benzene and methyl alcohol. The substance forms colourless prisms, m. p. 150°. The yield was 0·8 g. (Found: C, 85·7; H, 6·3. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%).

4-*Methoxy*-3-*methyltetraphenylmethane*, $CPh_3{\cdot}C_6H_3Me{\cdot}OMe$.—The methyl *o*-tolyl ether required for this preparation was made by warming 11 g. of *o*-cresol in a solution of caustic soda (16 g. in 20 c.c. of water) to 40°, and adding 25 g. of methyl sulphate in small portions, the mixture being well shaken after each addition. The oil was extracted with ether, shaken with caustic soda, and dried over sodium sulphate. After removal of the ether and distillation, 8·8 g. of the pure substance were obtained.

9 G. of methyl *o*-tolyl ether and 6 g. of triphenylcarbinol were dissolved in 60 c.c. of acetic acid, and 12 g. of pure sulphuric acid were added. The dark brown solution, after 24 hours, deposited a considerable amount of crystals, which were filtered off after 48 hours and washed, first with acetic acid and then with alcohol. The yield was 8·56 g. (The mother-liquor may be used for a second preparation by merely dissolving a further quantity of triphenylcarbinol in it.) The compound crystallises from acetic acid or acetone in white, spherical aggregates, m. p. 165°. Its constitution was established by analysis (Found: C, 88·9; H, 6·4. $C_{27}H_{24}O$ requires C, 89·0; H, 6·6%), and by its preparation by direct methylation of 4-hydroxy-3-methyltetraphenylmethane. 2 G. of 4-hydroxy-3-methyltetraphenylmethane were dissolved in 20 c.c. of benzene, and shaken with 50 c.c. of Claisen's solution. To this mixture, 2 g. of methyl sulphate were added, and the whole was well shaken for 15 minutes. The benzene layer was separated, washed with a little of Claisen's solution and then with water, and evaporated to a small bulk. The addition of alcohol caused the separation of

brownish crystals, m. p. 162—165°. On recrystallisation the product melted at 165°, and gave the same melting point when mixed with some of the previously prepared material.

3-*Bromo*-4-*methoxy*-5-*methyltetraphenylmethane*, $CPh_3{\cdot}C_6H_2MeBr{\cdot}OMe$.—2 G. of 4-methoxy-3-methyltetraphenylmethane were boiled with 20 c.c. of acetic acid and 1 g. of bromine until evolution of hydrogen bromide ceased. On cooling, 2·2 g. of colourless crystals separated. These crystallised from acetic acid in prisms, m. p. 180°, with a little previous shrinkage (Found: Br, 18·15. $C_{27}H_{23}OBr$ requires Br, 18·0%).

(2) m-*Cresol*. 6 G. of triphenylcarbinol and 6 g. of *m*-cresol were dissolved in 60 c.c. of acetic acid, and 10 g. of sulphuric acid were added. After standing 24 hours, 5·0 g. of the condensation product were filtered off, and several days later a further quantity, 2·3 g., was obtained. The melting point after two recrystallisations from acetic acid was 213—214° as recorded by Schorigin.

The Action of Hydriodic Acid upon 4-*Hydroxytetraphenylmethane and its Derivatives*.—0·5 G. of each compound was boiled with a mixture of 4 c.c. of hydriodic acid and 8 c.c. of acetic acid for 3 hours. In those cases where fission occurred, the substance dissolved fairly rapidly and triphenylmethane separated as an oil on the surface of the liquid, the action being completed in 30 minutes. The yield of triphenylmethane was practically theoretical. Where the tetraphenylmethane compound was stable, the material never passed completely into solution, and on cooling and filtering, almost the whole amount was recovered unchanged. The acetic acid filtrate was poured into water and the minute amount of material precipitated was carefully examined, but no trace of triphenylmethane could be detected.

The Action of Sulphuric Acid upon 4-*Hydroxytetraphenylmethane and its Derivatives*.—A mixture of the substance with pure sulphuric acid (10 c.c. for 1 g.) was gently warmed as recorded in the table on p. 634. At the end of the time practically all (in most cases all) the substance had dissolved and the solution was coloured orange. The white precipitate produced on pouring this solution into water was extracted with benzene, the benzene layer washed with dilute caustic soda solution and with water, and the benzene evaporated. The residue was weighed after recrystallisation from light petroleum. It was identified as triphenylcarbinol by its melting point and by a mixed melting point determination.

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