

CXXIX.—*The Introduction of the Triphenylmethyl Group into Phenols. Part II.*

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It has previously been shown that the Baeyer-Villiger reaction may be utilised in order to condense triphenylcarbinol with phenol and anisole (Baeyer and Villiger, *Ber.*, 1902, **35**, 3018), pyrocatechol (Zincke and Wugk, *Annalen*, 1908, **363**, 284), *o*-cresol, *o*-tolyl methyl ether, and *m*-cresol (Schorigin, *Ber.*, 1927, **60**, 2373; Part I, Boyd and Hardy, *J.*, 1928, 630). Moreover, the failure of the

reaction has been observed with *p*-cresol (Schorigin, *loc. cit.*) and with methyl salicylate (Part I), but whereas the latter is quite unreactive, the former induces a novel reaction in which the triphenylcarbinol is reduced to triphenylmethane and the *p*-cresol is oxidised to a product for which the constitution of a highly polymerised *p*-quinomethane has been suggested. With a view to elucidate the factors which determine this variation in behaviour, an extended study of the Baeyer-Villiger reaction has been undertaken.

According to their behaviour towards an acetic-sulphuric acid solution of triphenylcarbinol, phenols and phenolic ethers fall naturally into three groups, *viz.*, those which undergo condensation (group I), those under whose influence the carbinol is reduced to triphenylmethane (group II), and those which are unreactive (group III).

Group I: Phenol, anisole, phenetole, *o*-cresol, *o*-tolyl methyl ether, *o*-tolyl ethyl ether, *m*-cresol, pyrocatechol, guaiacol, veratrole, resorcinol and its dimethyl ether, quinol, pyrogallol and its trimethyl ether, thymol, α - and β -naphthols, *o*-chlorophenol,* and *o*-bromophenol.*

Group II: *p*-Cresol, *p*-tolyl methyl and ethyl ethers, *o*-,* *m*-, and *p*-chlorophenols, *o*-bromophenol,* and quinol dimethyl ether.

Group III: *o*- and *p*-Nitrophenols, picric acid, *o*- and *p*-nitroanisoles, salicylic acid and its methyl ester, trichlorophenol, trichloroanisole, and tribromophenol.

The addition of any member of groups I and II to an acetic-sulphuric acid solution of triphenylcarbinol causes the production of a deep brown colour, but the members of group III produce no appreciable alteration in the reddish-orange colour of the carbinol solution. These and previous results permit three deductions, namely, (1) the deep brown colours indicate the formation of intermediate compounds, (2) the formation of these intermediate compounds is essential to reaction, and (3) the primary reaction takes place between the ions of triphenylmethyl sulphate (compare Part I) and the undissociated phenol—since the phenolic ethers react similarly to the phenols.

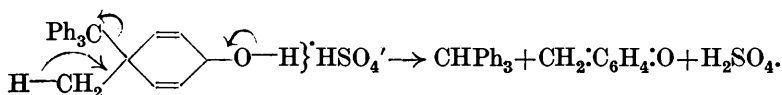
As applied to members of group I, the Baeyer-Villiger reaction serves, in general, to introduce one triphenylmethyl group into the nucleus, but, contrary to a statement by Schorigin (*Ber.*, 1928, 61, 2517) that "Es tritt bekanntlich in den Kern eines Phenols stets nur ein Triphenylmethyl-Rest ein, . . ." di-triphenylmethylation has been observed with α -naphthol and with 1:3-dimethoxybenzene.

* In the reactions with *o*-chlorophenol and with *o*-bromophenol condensation and formation of triphenylmethane occur simultaneously.

The available data indicate that, although the triphenylmethyl group usually enters the nucleus para to hydroxyl, methoxyl, etc., ortho-substitution occasionally occurs.

Reaction with members of group II involves the oxidation of the phenol or phenolic ether, a process which in some cases can only be realised by removal of nuclear hydrogen and in others probably follows the lines indicated by the researches of Pummerer, Goldschmidt, Hunter, and others (see Davis and Hill, *J. Amer. Chem. Soc.*, 1929, 51, 493). The oxidation products are usually intractable oils or resins, but from *p*-cresol two amorphous solids have been isolated, viz., (A) a red substance of high melting point, believed to be a highly polymerised *p*-quinomethane, which was obtained by Schorigin (*loc. cit.*) on carrying out the reaction at 100°; and (B) a yellowish-brown substance of comparatively low melting point which has now been isolated by working at room temperature. It has been suggested that A is formed by the dehydration of *p*-toluquinol, a compound which, together with three amorphous substances, was isolated by Bamberger (*Ber.*, 1903, 36, 2030) by oxidising *p*-cresol with Caro's acid. The properties of B are closely in agreement with those of one (C₁₄H₁₀O₃) of Bamberger's amorphous substances.

In Part I of this investigation, a mechanism of the Baeyer-Villiger reaction was suggested which, when generalised, assumes (i) nuclear attack by the triphenylmethyl cation, and (ii) that the formation of triphenylmethane is preceded by the elimination of the triphenylmethyl anion from the complex :



An alternative mechanism has been suggested by van Alphen (*Rec. trav. chim.*, 1927, 46, 799) for the analogous reaction between triphenylmethyl chloride and phenol. This assumes the formation of an oxonium intermediate which, under the influence of an alkaline medium, e.g., pyridine, loses hydrogen chloride to form phenyl triphenylmethyl ether (compare Helferich, *Ber.*, 1925, 58, 882), whereas under acid conditions it undergoes intramolecular rearrangement, the triphenylmethyl group migrating to the *p*-position of the nucleus :



On these assumptions also must the triphenylmethyl anion play an essential part in the reaction, for not only must it be eliminated

E X P E R I M E N T A L.

The Action of Triphenylcarbinol upon Phenols and Phenolic Ethers in the Presence of Sulphuric Acid.—Except where otherwise stated, the reaction mixtures were prepared by dissolving triphenylcarbinol (6 g.) and the phenol or phenolic ether (6 g.) in acetic acid (60 c.c.) by warming, and adding sulphuric acid (10 g.) to the warm solution.

(1) *Phenetole*. After standing for a week, the crystalline condensation product was collected, washed with dilute acetic acid, and dried (3.8 g.); a further quantity (2.58 g.) was obtained by diluting the mother-liquor. It was twice recrystallised from benzene-alcohol and then formed a colourless powder, m. p. 191° (Found : C, 88.7; H, 6.8. $C_{27}H_{24}O$ requires C, 89.0; H, 6.6%).

4-Ethoxytetraphenylmethane is difficultly soluble in acetic acid and in alcohol and easily soluble in benzene. When boiled with a mixture of acetic and hydriodic acids, it was converted into 4-hydroxytetraphenylmethane.

(2) *Pyrocatechol*. The 3 : 4-dihydroxytetraphenylmethane (8.10 g.) was collected after 10 minutes, washed, dried, and recrystallised from acetone or from toluene. It formed colourless needles which became brown at 260°, and melted at 262° as recorded by Zincke and Wugk (*loc. cit.*).

(3) *Guaiacol*. The washed (with alcohol) and dried product (8.2 g.), which was collected after 24 hours, was repeatedly crystallised from acetic acid and also from benzene-petrol, but a fraction of definite melting point could not be obtained. On boiling with a mixture of hydriodic and acetic acids it was converted into 3 : 4-dihydroxytetraphenylmethane, m. p. and mixed m. p. with an authentic specimen, 262°. The product consisted, therefore, of a mixture of 4-hydroxy-3-methoxy- and 3-hydroxy-4-methoxy-tetraphenylmethane.

(4) *Veratrole*. 7.62 G. of product were obtained as under (3) and consisted of almost pure 3 : 4-dimethoxytetraphenylmethane. Dilution of the reaction mixture furnished a further quantity. The substance formed colourless prisms, m. p. 170° after recrystallisation from acetic acid, as recorded by Gomberg and Forrester (*J. Amer. Chem. Soc.*, 1925, **47**, 2389) for the compound obtained by treating 3 : 4-dimethoxytriphenylmethyl chloride with magnesium phenyl bromide. By treatment with a mixture of hydriodic and acetic acids the substance was converted into 3 : 4-dihydroxytetraphenylmethane.

(5) *Resorcinol*. Sulphuric acid (5 g.) was added to a solution of triphenylcarbinol (4 g.) and resorcinol (4 g.) in acetic acid (30 c.c.) and as soon as the mixture was cold the crude 2 : 4-dihydroxytetra-

phenylmethane was collected, washed with alcohol, and dried (4.04 g.). After recrystallisation from toluene and then from acetone it formed colourless crystals, m. p. about 268° with previous shrinkage and decomposition. The compound has also been prepared by E. von Meyer (*J. pr. Chem.*, 1910, **82**, 521) from resorcinol and triphenylmethyl chloride, the melting point being given as 268° . The true melting point of 2:4-dihydroxytetraphenylmethane appears to be considerably higher, for if placed in a bath at 250° and rapidly heated, it does not melt until about 280° .

(6) *Resorcinol dimethyl ether*. 7.50 G. of the condensation product were collected after 15 minutes, and a further quantity (0.5 g.) was obtained by diluting the mother-liquor. The product was extracted with a large volume of boiling acetic acid, and the insoluble material collected. The acetic acid solution deposited crystals, m. p. 180° after recrystallisation from benzene-alcohol. Its properties are in agreement with those of 2:4-dimethoxytetraphenylmethane, which was prepared by Gomberg and Forrester (*loc. cit.*) from 2:4-dimethoxytriphenylmethyl chloride and magnesium phenyl bromide.

The material insoluble in acetic acid separated from benzene-alcohol in colourless crystals (1.1 g.), m. p. 271° (Found: C, 88.45; H, 6.6. $C_{46}H_{38}O_2$ requires C, 88.7; H, 6.15%). 1:3-Dimethoxy-4:6-bistriphenylmethylbenzene is difficultly soluble in most of the common organic solvents but moderately easily soluble in benzene.

(7) *Pyrogallol*. A solution of triphenylcarbinol (6 g.) in acetic acid (50 c.c.) and sulphuric acid (10 g.) was mixed with a solution of pyrogallol (6 g.) in acetic acid (10 c.c.), and after an hour the crystalline product was washed (dilute alcohol) and dried (7.99 g.). Purification of the product was complicated by the presence of another substance (in all probability formed by the di-triphenylmethylation of pyrogallol) whose removal was very difficult, as was shown by the high carbon content of the various preparations. After many recrystallisations from acetone, 3:4:5-trihydroxy-tetraphenylmethane was obtained as efflorescent colourless prisms which contained two molecules of acetone (Found: loss on heating at 80° in a vacuum, 21.4. $C_{25}H_{20}O_3 \cdot 2Me_2CO$ requires loss, 24.0%). The pure substance darkens at about 230° and melts with much decomposition at about 255° , the melt being black (Found: C, 81.0; H, 5.5. $C_{25}H_{20}O_3$ requires C, 81.5; H, 5.5%). 3:4:5-Trihydroxy-tetraphenylmethane is difficultly soluble in alcohol, benzene, and acetic acid but easily soluble in hot acetone.

(8) *Pyrogallol trimethyl ether*. At the end of a week the 3:4:5-trimethoxytetraphenylmethane (7.87 g.) was collected, washed (dilute alcohol), dried, and recrystallised from acetic acid; it then formed

colourless needles, m. p. 178° (Found : C, 81.6; H, 6.3. $C_{28}H_{26}O_3$ requires C, 81.9; H, 6.4%).

(9) α -Naphthol. 7.25 G. of the reaction product were obtained as in (3). It was boiled with alcohol and the solution, after filtration from an insoluble residue (0.80 g.), deposited colourless clusters of prisms which contained one molecule of alcohol (Found : loss on heating at 80° in a vacuum, 10.5. $C_{29}H_{22}O, EtOH$ requires loss, 10.7%). The pure 4-triphenylmethyl-1-naphthol melted at 204—204.5° (Found : C, 89.9; H, 5.8; *M*, 359. $C_{29}H_{22}O$ requires C, 90.1; H, 5.7%; *M*, 386).

The material insoluble in alcohol was crystallised from acetic acid and recrystallised from aqueous acetone, after which it formed a white powder (Found : C, 91.45; H, 6.1; *M*, 617, 605, 598. $C_{48}H_{36}O$ requires C, 91.7; H, 5.8%; *M*, 628). 2 : 4-Bistriphenylmethyl-1-naphthol melts at 235—236°.

(10) β -Naphthol. The reaction mixture slowly deposited crystals of 1-triphenylmethyl-2-naphthol, which were collected at the end of a month, washed with dilute alcohol, dried (6.4 g.), and recrystallised from alcohol; m. p. 228° (Found : C, 89.9; H, 5.85. $C_{29}H_{22}O$ requires C, 90.1; H, 5.7%).

(11) Thymol. The deep brown reaction mixture was left until the next day; the colour had then faded to light brown. It was poured into water, the mixture boiled, and the resulting oil digested with sodium hydroxide solution, after which it solidified on cooling. It was taken up in ether, and the solution shaken with sodium hydroxide solution and dried over sodium sulphate. After removal of ether, the residue crystallised from methyl alcohol in colourless needles which, after drying in a vacuum over sulphuric acid for 24 hours, melted at 106—107°. At a higher temperature the melt resolidified, and a second and sharp melting occurred at 157°. The low-melting material was heated in a vacuum at 80° (5 hours), then at 110° (4 hours), and finally at 148° (5 hours), a treatment which failed to bring about either an appreciable loss in weight or fusion of the substance. The dried material melted at 157°, and after recrystallisation from methyl alcohol was converted into the lower-melting form. 4-Hydroxy-2-methyl-5-isopropyltetraphenylmethane exists, therefore, in two crystalline modifications melting at 106—107° and 157° (Found in higher-melting form : C, 88.5; H, 7.5. $C_{29}H_{28}O$ requires C, 88.7; H, 7.2%). It is easily soluble in all organic solvents with the exception of cold methyl alcohol.

(12) *o*-Chlorophenol. At the end of 2 months the crude 3-chloro-4-hydroxytetraphenylmethane was collected, washed (dilute acetic acid), dried (2.1 g.), and recrystallised first from alcohol and then from ether-petrol; it then formed colourless silky needles, m. p.

193.5° (Found : Cl, 9.6. $C_{25}H_{19}OCl$ requires Cl, 9.6%). It is easily soluble in alcohol, benzene, and acetic acid but difficultly soluble in petrol and ether. It is stable towards a boiling mixture of hydriodic and acetic acids (see Part I).

The acetic-sulphuric acid mother-liquor was poured into water and the resulting oil was digested with sodium hydroxide solution, after which it solidified on cooling. The well-washed and dried solid was dissolved in the minimum quantity of benzene, and on addition of alcohol gave colourless crystals of the benzene compound of triphenylmethane, m. p. 78°, which after loss of benzene melted at 93° and weighed 1.66 g. Evaporation of the mother-liquor gave an intractable oil.

(13) *m-Chlorophenol*. The reaction mixture was set aside for a month and was then heated on a boiling water-bath until the deep brown colour had faded. It was then poured into water, and the product worked up as under (12). 1.68 G. of triphenylmethane were isolated.

(14) *p-Chlorophenol*. This experiment was conducted exactly as under (13). 2.4 G. of triphenylmethane (m. p. and mixed m. p. with an authentic specimen, 93°) were isolated, together with an uncrystallisable oil.

(15) *o-Bromophenol*. This experiment was similar to (12) with the exception that the reaction mixture was worked up after one month. The crude 3-bromo-4-hydroxytetraphenylmethane (1.68 g.) was recrystallised from alcohol, and formed a white crystalline powder, m. p. 186—187° with previous shrinkage (Found : Br, 19.5. $C_{25}H_{19}OBr$ requires Br, 19.3%). From the acetic-sulphuric acid solution triphenylmethane (1.56 g.) was isolated.

(16) *p-Cresol*. *p*-Cresol (3 g.) was added to a cold solution of triphenylcarbinol (3 g.) in acetic acid (30 c.c.) and sulphuric acid (5 g.). The next day the deep brown solution was full of crystals, and at the end of another day the solution was fuchsine-coloured. The crystals (2.43 g.) after recrystallisation from alcohol melted at 93° alone or mixed with triphenylmethane. On working up the acetic-sulphuric acid solution as previously described, a further 0.40 g. of triphenylmethane was obtained. Acidification of the sodium hydroxide extract produced a yellowish-brown precipitate of an amorphous substance (1.45 g.) which was easily soluble in alcohol, acetone, and acetic acid, but difficultly soluble in benzene, petrol, and chloroform. It dissolved in concentrated sulphuric acid to give a fuchsine-coloured solution. The substance shrinks at about 85° and melts between 100° and 110° with evolution of gas.

(17) *p-Tolyl methyl ether*. Sulphuric acid (13 g.) was added to a

solution of triphenylcarbinol (13 g.) and *p*-tolyl methyl ether (6.1 g.; 1 equiv.) in acetic acid (80 c.c.). After a month the mixture was heated on a boiling water-bath for 2 hours, and on cooling deposited almost pure triphenylmethane (10.05 g.). The mother-liquor was worked up as usual and gave a further quantity of triphenylmethane (1.98 g., making in all 12.03 g., *i.e.*, 98.4% of the theoretical yield) together with a fuchsine-coloured resin which was insoluble in sodium hydroxide solution.

(18) *p*-Tolyl ethyl ether. The reaction mixture was warmed at 75° for several hours, and on cooling, triphenylmethane (3.13 g.) separated. A further quantity (1.95 g.) was obtained from the mother-liquor, together with a brown, uncrystallisable oil.

(19) *Quinol dimethyl ether*. This experiment was conducted as described under (13), triphenylmethane (2.76 g.) and an oil being the only products.

(20) *Methyl salicylate*. The orange-red solution was set aside for a month and then poured into water, and the mixture boiled until the precipitated oil had completely changed into a crystalline mass (5.76 g.), m. p. 159°, of almost pure triphenylcarbinol.

The experiments with other members of group III were carried out in like fashion, the recovered triphenylcarbinol being always in almost theoretical yield.

(21) *o*-Tolyl ethyl ether. Crude 4-ethoxy-3-methyltetraphenylmethane (6.06 g.) was isolated as under (3), and after recrystallisation from benzene-alcohol formed colourless prisms, m. p. 144°. The substance is difficultly soluble in alcohol and acetic acid and easily soluble in benzene.

By the condensation of triphenylcarbinol with *o*-toluidine, van Alphen (*Rec. trav. chim.*, 1927, 46, 501) obtained a base the diazonium sulphate of which furnished a compound (m. p. 143°) when boiled with alcohol. Although no analysis was given, the compound was suggested to be α -2-ethoxyphenyl- $\beta\beta\beta$ -triphenylethane. In view of the revision of the structure of the original base (see Part I) it seemed desirable to re-open the investigation of this derivative.

4-Amino-3-methyltetraphenylmethane.—A mixture of triphenylcarbinol (20 g.), *o*-toluidine (16 g.), concentrated hydrochloric acid (10 c.c.), and acetic acid (40 c.c.) was heated under reflux for an hour. The crystalline hydrochloride of the base which separated (26.8 g.) was boiled with a solution of sodium hydroxide (5 g.) in 60% alcohol (150 c.c.) for 2 hours, and the insoluble amine was collected, washed thoroughly with water, and dried (24 g.). After crystallisation from carbon tetrachloride it formed a white powder, m. p. 216—217°. It was diazotised (4 g.) in a mixture of acetic acid (15

c.c.) and sulphuric acid (2 g.) at 30° with amyl nitrite (4 c.c.). After standing for several hours in a warm place (25—28°) the solution was diluted with a considerable volume of ether; the precipitated diazonium sulphate, after being washed with ether and dried in a vacuum, melted at 106—107° with vigorous decomposition.

4-Ethoxy-3-methyltetraphenylmethane.—The diazonium sulphate (4 g.) was added in small portions to boiling absolute alcohol (60 c.c.) and after partial evaporation of the alcoholic solution, somewhat brownish crystals were deposited (1.4 g.). These, after recrystallisation from acetic acid and then from alcohol, were colourless, m. p. 143° (Found: C, 88.4; H, 7.1. $C_{28}H_{26}O$ requires C, 88.8; H, 6.9%). A mixed melting-point determination with the compound prepared from *o*-tolyl ethyl ether and triphenylcarbinol showed no depression.

4-Chloro-3-methyltetraphenylmethane.—4-Amino-3-methyltetraphenylmethane (15 g.) was diazotised as above, and the diazo-solution poured into boiling cuprous chloride-hydrochloric acid. The mixture was then poured into water, and the precipitated oil extracted with benzene, shaken repeatedly with water, and dried over sodium sulphate. Light petroleum (b. p. 60—80°) was added to the concentrated benzene solution, and the sandy crystals (9.4 g.) which separated were recrystallised repeatedly from acetic acid. *4-Chloro-3-methyltetraphenylmethane* forms somewhat brownish crystals, m. p. 160° (Found: Cl, 8.6, 8.7.* $C_{26}H_{21}Cl$ requires Cl, 9.6%). It is stable towards both sulphuric acid and a mixture of hydriodic and acetic acids.



—*o*-Diphenylenephénylcarbinol was condensed with phenol as described by Ullmann and Wursterberger (*Ber.*, 1904, **37**, 73). On boiling the *o*-diphenylene-4-hydroxydiphenylmethane with a mixture of hydriodic and acetic acids it was converted into *o*-diphenylene-phenylmethane, m. p. 145° after crystallisation from alcohol.

Diphenyl-4-hydroxytriphenylmethane, $C_6H_5 \cdot C_6H_4 \cdot CPh_2 \cdot C_6H_4 \cdot OH.$
—Diphenyldiphenylcarbinol (Schlenk, Herzenstein, and Weickel, *Annalen*, 1910, **372**, 18) (1.5 g.) and phenol (1.5 g.) were dissolved in acetic acid (15 c.c.), and sulphuric acid (2.5 g.) added. The fuchsine-coloured solution was set aside for a week, and the condensation product was then collected, washed (dilute alcohol), dried, and recrystallised three times from acetic acid, *diphenyl-4-hydroxytriphenylmethane* being obtained as white aggregates,

* The low values obtained (by the method of Carius) are probably due to the fact that even after prolonged heating at 320° some substance remained unoxidised.

m. p. 183° (Found : C, 90.15; H, 6.2. $C_{31}H_{24}O$ requires C, 90.25; H, 5.9%).

The same substance was obtained when diphenyldiphenylmethyl chloride (1 g.) was boiled with phenol (3 g.). The cherry-red solution gave off hydrogen chloride and eventually became almost colourless. The melt was digested with sodium hydroxide solution, and the residue (1.15 g.) crystallised from acetic acid; the product then melted at 183°, alone or when mixed with the previously prepared substance.

Diphenyl-4-hydroxytriphenylmethane is stable towards a mixture of hydriodic and acetic acids.

The Decomposition of Tetra-arylmethane Derivatives.—Further investigation of the stability of the tetra-arylmethane derivatives has shown that fission of the types mentioned in Part I is fairly general. The following table is a summary of some further results in that connexion (compare Part I, pp. 634, 638).

	Action of sulphuric acid.			Yield of $CPh_3 \cdot OH$.	Action of hydriodic-acetic acid.
	Wt. (g.).	Temp.	Time (mins.).		
3 : 4-Dihydroxytetraphenylmethane	0.5	50°	30	0.03	Stable.
3 : 4-Dimethoxytetraphenylmethane	0.5	40	20	0.132	Demethylated.
2 : 4-Dihydroxytetraphenylmethane	0.5	40	5	0.144	$CHPh_3$.
2 : 4-Dimethoxytetraphenylmethane	{ 0.5	25	5	0.027	"
	{ 0.5	25	5	0.022	
3 : 4 : 5-Trihydroxytetraphenylmethane	0.5	40	15	0.083	"
3 : 4 : 5-Trimethoxytetraphenylmethane	{ 0.5	40	5	0.072	"
	{ 1.0	22	20	0.146	
4-Hydroxy-2-methyl-5-isopropyltetraphenylmethane	0.5	40	15	0.058	"
3 : 5-Dibromo-4-hydroxytetraphenylmethane		Stable.			Stable.
1-Triphenylmethyl-2-naphthol	1.0	60	20	Nil.	"
4-Triphenylmethyl-1-naphthol	1.0	18	16	0.41	$CHPh_3$.

These decompositions are analogous to those of 2-hydroxytriphenylmethane (Schmidt, *Diss.*, Heidelberg, 1898, p. 26) and of the hexamethyl ether of phloroglucinolphthalein (Lund, J., 1928, 1569). The new data with regard to the decomposition by means of sulphuric acid form additional evidence that the Baeyer-Villiger reaction is reversible.

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