

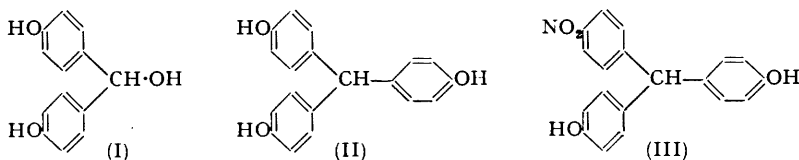
*The Condensation of Phenols with Nitrobenzaldehydes.*

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Triphenylmethane derivatives have been isolated (some in high yield) from the products of condensation of phenols with *o*-, *m*-, and *p*-nitrobenzaldehydes. Many of them form molecular compounds with hydrocarbon solvents.

It has been shown (Driver and Sousa, *J.*, 1954, 985) that if phenols are condensed with hydroxybenzaldehydes at a sufficiently low temperature and in a suitable medium trihydroxytriarylmethanes can be isolated, though usually only in small yield, from the resinous products. The first reaction (as established in a typical case) leads to the formation of a dihydroxydiarylmethanol (as I), which gives the triarylmethane compound (as II) by the preferred *para*-condensation. Resinification may be the result of formation of large molecules by repeated electrophilic attack at positions *ortho* to hydroxyl groups in these and later products.



The use of a deactivated aromatic aldehyde would be expected to make the resulting di- or tri-arylmethane derivatives more easily isolable, since one nucleus in the intermediate methanol, and in the triarylmethane product, would then not be susceptible to further attack by the aldehyde; and further the lower rate of *ortho*-condensation by the less easily protonated aldehyde might be more significant than any reduction in rate of the faster *para*-condensations. The nitrobenzaldehydes were therefore selected for study.

de Varda and Zenoni (*Gazzetta*, 1891, 21, 174) condensed phenol with *m*-nitrobenzaldehyde and obtained an amorphous product, m. p. 59–60°, which they recorded as 4 : 4'-dihydroxy-3''-nitrotriphenylmethane; from the present work it was clearly a resinous mixture. Chlorine-containing substances were obtained by Guyot and Haller (*Bull. Soc. chim. France*, 1904, 31, 530) and Zincke and Siebert (*Ber.*, 1906, 39, 1930) by condensation of phenol with *o*-nitrobenzaldehyde in presence of hydrochloric-acetic acid. Danckwortt (*Ber.*, 1909, 42, 4163) obtained from phenol and *p*-nitrobenzaldehyde a red resin having a nitrogen content corresponding to a 2 : 1-molecular condensation. King and Lowy (*J. Amer. Chem. Soc.*, 1924, 46, 760) obtained from the same reactants a yellow, amorphous product from which they prepared a crystalline tetrabromo-derivative; from *p*-nitrobenzaldehyde and other phenols they also obtained only amorphous products. All these experiments were done under what appear to be unfavourable conditions.

It is now shown that crystalline dihydroxynitrotriarylmethanes can be readily prepared by condensing various simple phenols with *o*-, *m*-, and *p*-nitrobenzaldehydes by means of sulphuric acid in cold, acetic acid solution. By reduction they yield the corresponding aminodihydroxy-compounds. The *para*-orientation of a typical compound (III; from

phenol and *p*-nitrobenzaldehyde) has been proved by its reduction to the amine and conversion of this into leucaurin (II).

To demonstrate that resin formation in these reactions results from successive condensations at activated positions, 2 : 6-xylene-1-ol was condensed with *m*-nitrobenzaldehyde. The product, 4 : 4'-dihydroxy-3 : 3' : 5 : 5'-tetramethyl-3''-nitrotriphenylmethane, which has no positions open to electrophilic attack, was formed in very high yield and unaccompanied by any significant amount of resin.

Many of the dihydroxynitrotriarylmethanes and the corresponding amines form molecular compounds with aromatic hydrocarbons, usually in stoichiometric proportions (see Table). Most of these solvated compounds lose solvent freely only above their m. p.s. at ordinary rates of heating.

*Molecular compounds of substituted triphenylmethanes with aromatic hydrocarbons.*

4 : 4'-Dihydroxytriphenylmethane (A)	Solvent (B)	A : B (mols.)	Solvent-free compd. from :
3''-Nitro- .....	Benzene	1 : 2	<i>p</i> -Xylene
	Toluene	1 : 1	—
2 : 2'-Dimethyl-3''-nitro- .....	Benzene	1 : 2	—
3 : 3'-Dimethyl-3''-nitro- .....	Benzene	1 : 1	—
4''-Nitro- .....	Benzene	1 : 2	—
	Toluene	1 : 1	—
2 : 2'-Dimethyl-4''-nitro- .....	Benzene	1 : 2	—
2''-Nitro- .....	Benzene	1 : 1	Toluene
3 : 3'-Dimethyl-2''-nitro- .....	Benzene	2 : 1	—
	Toluene	2 : 1	—
3 : 5 : 3' : 5'-Tetramethyl-3''-nitro- .....	Benzene	3 : 2	—
	Toluene	3 : 2	—
	<i>p</i> -Xylene	3 : 2	—
3''-Amino- .....	Benzene	1 : 1	—
	Toluene	1 : 1	—

### EXPERIMENTAL

Sulphuric acid and acetic acid used were 99%.

Microanalyses are by Dr. Zimmermann, Melbourne.

*Condensation of Phenol and m-Nitrobenzaldehyde.*—A solution of *m*-nitrobenzaldehyde (7.6 g.) and phenol (9.4 g.) in acetic acid (35 ml.) was cooled to 3—4°, and sulphuric acid (3 ml.) in acetic acid (15 ml.) was added dropwise with stirring. The mixture, which turned orange, was kept at 0—5° for 48 hr., and was then stirred into crushed ice. The resin which separated was washed until free from acid, and freed from adhering water. The solution in hot benzene deposited some red resin on cooling, followed by yellow crystals of the *benzene* compound (10.7 g., 45%) which after recrystallization melted at 72°, solidified with slowly continued rise in temperature, and melted again at 156—157° (Found : C, 78.4; H, 5.8; N, 3.1; loss at 100°/25 mm., 32.3. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>C<sub>6</sub>H<sub>6</sub> requires C, 78.0; H, 5.7; N, 2.9; C<sub>6</sub>H<sub>6</sub>, 32.7%). Unsolvated 4 : 4'-*dihydroxy-3''-nitrotriphenylmethane* separated from aqueous alcohol, ether-light petroleum, *p*-xylene, or chlorobenzene in crystals, m. p. 158.5° (Found : C, 71.3; H, 4.8 N, 4.3%; *M*, 321. C<sub>18</sub>H<sub>15</sub>O<sub>4</sub>N requires C, 71.0; H, 4.7; N, 4.4%; *M*, 321). The *toluene* compound formed crystals, m. p. 150—157.5° with loss of solvent (Found : loss at 100°/3 mm., 22.0. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>C<sub>7</sub>H<sub>8</sub> requires C<sub>7</sub>H<sub>8</sub>, 22.3%). The *diacetyl* derivative separated from ethyl alcohol in needles, m. p. 98.5° (Found : C, 68.4; H, 4.9; N, 3.7; Ac, 20.9. C<sub>23</sub>H<sub>19</sub>O<sub>6</sub>N requires C, 68.2; H, 4.7; N, 3.5; Ac, 21.2%). The *dibenzoyl* derivative crystallized from light petroleum or carbon tetrachloride and had m. p. 145—146° (Found : C, 75.0; H, 4.5; N, 2.2. C<sub>33</sub>H<sub>23</sub>O<sub>6</sub>N requires C, 74.9; H, 4.35; N, 2.6%).

3-Amino-4' : 4''-*dihydroxytriphenylmethane*. (a) The nitro-compound (20 g.) in alcohol (100 ml.) was reduced by hydrogen in presence of Adams's catalyst. Absorption of hydrogen (3200 c.c.) was complete in 30 min. The solution was filtered through kieselguhr and the alcohol removed. Extraction of the remaining glue with benzene yielded prisms (2.2 g.) of the amine (as below).

(b) Reduction in acid media gave red resins. The nitro-compound (15 g.) in ethyl alcohol (50 ml.) was treated with 12% ammonia solution (10 ml.), and the solution was added to a boiling solution of ferrous sulphate (61.5 g., 7 mols.) in water (150 ml.). After addition of excess of ammonia the mixture was boiled with stirring for 10—15 min., and filtered. The

filtrate and the black residue were extracted with ether. Removal of solvent left a brown residue which was crystallized from benzene to yield the *benzene* compound (6.8 g.) which melted at about 110° with evolution of solvent, solidified thereafter, and melted again at 168° (Found: C, 81.3; H, 6.2; N, 3.9; loss at 116°/25 mm., 21.3.  $C_{19}H_{17}O_2N_2C_6H_6$  requires C, 81.3; H, 6.2; N, 3.8;  $C_6H_6$ , 21.1%. Found for the desolvated compound: C, 78.4; H, 5.9; N, 3.9%; *M*, 488.  $C_{19}H_{17}O_2N$  requires C, 78.3; H, 5.8; N, 4.8%; *M*, 291).

Unsolvated *3-amino-4': 4"-dihydroxytriphenylmethane* crystallized from aqueous alcohol and had m. p. 168°. It was not easily soluble in dilute acid, but dissolved freely in aqueous sodium hydroxide. A suspension of the amine in hydrochloric acid was diazotized and coupled with  $\beta$ -naphthol in sodium carbonate-hydrogen carbonate buffer to give a bright-red *dye* which separated as an amorphous solid from glacial acetic acid (Found: N, 6.4.  $C_{29}H_{22}O_3N_3$  requires N, 6.3%). The *toluene* compound sintered at 80–90°, solidified again, and melted at 166–168° (Found: C, 81.6; H, 6.6; N, 3.5; loss at 116°/25 mm., 23.4.  $C_{19}H_{17}O_2N_2C_7H_8$  requires C, 81.5; H, 6.5; N, 3.65;  $C_7H_8$ , 24.0%). Attempts to deaminate the amine, or to methylate it with a view to subsequent oxidation, failed.

*Condensation of m-Cresol and m-Nitrobenzaldehyde*.—A yield of only 17% by a procedure similar to that used for phenol (time, 7 hr.) was increased to 44% as follows. A solution of *m*-nitrobenzaldehyde (20 g.) and *m*-cresol (30 g.) in acetic acid (50 ml.) was cooled to 0°, and sulphuric acid (2.5 ml.) in acetic acid (15 ml.) was added dropwise with stirring to the crystalline mass. The mixture was kept at 0–5° for 8 hr. and stirred into ice-water, and the product was washed free from acid. The hard resin by crystallization from benzene yielded the *benzene* compound (29 g., 44%) which melted at 85–90° with loss of solvent, then solidified, and melted again at 169–171° (Found: C, 78.2; H, 6.15; N, 2.9; loss at 154°/25 mm., 30.1.  $C_{21}H_{19}O_4N_2C_6H_6$  requires C, 78.4; H, 6.2; N, 2.8;  $C_6H_6$ , 30.9%). From aqueous alcohol what appeared to be a *hemihydrate* crystallized which melted at 140°, resolidified, and melted again (Found, in the substance dried at 100°/25 mm.: C, 70.8; H, 5.7; N, 4.0; loss at 154°/25 mm., 2.9.  $C_{21}H_{19}O_4N_2\frac{1}{2}H_2O$  requires C, 70.4; H, 5.6; N, 3.9;  $H_2O$ , 2.5%). Unsolvated *4': 4"-dihydroxy-2': 2"-dimethyl-3"-nitrotriphenylmethane* had m. p. 171–172° (Found: C, 72.4; H, 5.6; N, 3.6%; *M*, 330.  $C_{21}H_{19}O_4N$  requires C, 72.2; H, 5.5; N, 4.0%; *M*, 349). The *diacetyl* derivative, crystallized from ethyl alcohol, had m. p. 156° (Found: C, 69.7; H, 5.4; N, 3.4; Ac, 19.6.  $C_{25}H_{23}O_6N$  requires C, 69.3; H, 5.35; N, 3.2; Ac, 19.9%). The *dibenzoyl* derivative, crystallized from light petroleum, had m. p. 173.5–175° (Found: C, 75.7; H, 5.1; N, 2.8.  $C_{25}H_{27}O_6N$  requires C, 75.4; H, 4.9; N, 2.5%).

*3-Amino-4': 4"-dihydroxy-2': 2"-dimethyltriphenylmethane*. The solvated nitro-compound (10 g.) in ethyl alcohol (35 ml.) and 12% ammonia solution (6 ml.) was added with stirring to ferrous sulphate crystals (40 g.) in boiling water (100 ml.). Ammonia was added portionwise until the liquid was alkaline, and the mixture was boiled and stirred for 15 min. and filtered. Extraction of the residue and filtrate with ether yielded a viscous liquid which by crystallization from benzene yielded a buff, crystalline powder with a benzene content (7.8–9.8%) which varied with different samples. Crystallization from aqueous alcohol yielded unsolvated *3-amino-4': 4"-dihydroxy-2': 2"-dimethyltriphenylmethane*, m. p. 245–247° (Found: C, 78.2; H, 6.8; N, 4.3%; *M*, 337.  $C_{21}H_{21}O_2N$  requires C, 78.9; H, 6.6; N, 4.4%; *M*, 319).

*Condensation of o-Cresol and m-Nitrobenzaldehyde*.—Many condensations under varied conditions yielded orange-red resins from which no crystalline product could be obtained by various methods of separation which included molecular distillation and chromatography. After having been kept for 4 months the resins had partly crystallized, and thereafter the crystalline compound was readily prepared. A solution of *o*-cresol (pure, for cineole determination; 10.8 g.) and *m*-nitrobenzaldehyde (7.55 g.) in acetic acid (40 ml.) was cooled to 4°. To the resulting soft, crystalline mass sulphuric acid (2 ml.) in acetic acid (10 ml.) was added with stirring. After being kept below 0° for 24 hr. the mixture was stirred into ice-water. From the solid product the *benzene* compound (12 g.; 70%) was obtained in yellow crystals, m. p. 63–68° (Found: C, 75.8; H, 5.7; N, 2.5; loss at 132°/2–5 mm., 17.4.  $C_{21}H_{19}O_4N_2C_6H_6$  requires C, 75.7; H, 5.8; N, 3.3;  $C_6H_6$ , 18.3%). Desolvated *4': 4"-dihydroxy-3': 3"-dimethyl-3"-nitrotriphenylmethane* sintered at 63° but the m. p. was indefinite; it did not crystallize from solvents other than benzene (Found: C, 71.4; H, 5.65; N, 3.2.  $C_{21}H_{19}O_4N$  requires C, 72.2; H, 5.5; N, 4.0%). The *diacetyl* derivative crystallized from ethyl alcohol in needles, m. p. 163° (Found: C, 69.5; H, 5.55; N, 3.1; Ac, 20.8.  $C_{25}H_{23}O_6N$  requires C, 69.3; H, 5.35; N, 3.2; Ac, 19.9%).

*Condensation of p-Cresol and m-Nitrobenzaldehyde*.—A solution of *p*-cresol (5.4 g.) and *m*-nitrobenzaldehyde (3.78 g.) in acetic acid (20 ml.) was cooled to 3–4°, and sulphuric acid

(2 ml.) in acetic acid (5 ml.) was dropped in with stirring. After 44 hr. at *ca.* 0° the product was isolated as before. 2:2'-Dihydroxy-5:5'-dimethyl-3"-nitrotriphenylmethane was very soluble in most common organic solvents but crystallized from light petroleum (b. p. 80—100°), or a mixture of this with benzene, in clusters of yellow needles, m. p. 144° (Found: C, 72.4; H, 5.55; N, 3.9%; *M*, 336. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0%; *M*, 349). The diacetyl derivative, crystallized from ethyl or methyl alcohol, had m. p. 131° (Found: C, 69.6; H, 5.2; N, 3.3; Ac, 18.0. C<sub>25</sub>H<sub>23</sub>O<sub>6</sub>N requires C, 69.3; H, 5.35; N, 3.2; Ac, 19.9%).

*Condensation of Phenol and p-Nitrobenzaldehyde.*—Phenol (9.4 g.) in acetic acid (50 ml.) was added to *p*-nitrobenzaldehyde (7.55 g.) in acetic acid (200 ml.), and the mixture was cooled slowly to 7° with stirring, the hard deposit being continuously broken up. Sulphuric acid (10 ml.) in acetic acid (30 ml.) was added slowly, drop by drop, with cooling, and the mixture kept at between -2° and 0° for 18 hr. The product separated from benzene partly as resin and partly as large, pale yellow prisms of the benzene compound (8.5 g., 36%), m. p. 49—57° (Found: loss at 100°/2—5 mm., 32.6. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N, 2C<sub>6</sub>H<sub>6</sub> requires C<sub>6</sub>H<sub>6</sub>, 32.7%). The toluene compound melted at 45—50° (Found: loss at 100°/3 mm., 19.4. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N, C<sub>7</sub>H<sub>8</sub> requires C<sub>7</sub>H<sub>8</sub>, 22.3%). Unsolvated 4:4'-dihydroxy-4"-nitrotriphenylmethane, made by removal of benzene from the solvated compound, melted at 86—87° with previous sintering, but did not crystallize from solvents (Found: C, 70.0; H, 4.9; N, 4.1%; *M*, 278. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N requires C, 71.0; H, 4.7; N, 4.4%; *M*, 321). The tetrabromo-derivative, made by brominating the compound in acetic acid, separated from acetic acid in yellow crystals, m. p. 211° [King and Lowy (*loc. cit.*) give m. p. 215° for the tetrabromo-derivative prepared from their amorphous product] (Found: C, 36.4; H, 1.9; N, 2.3; Br, 50.7. Calc. for C<sub>19</sub>H<sub>11</sub>O<sub>4</sub>NBr<sub>4</sub>: C, 35.8; H, 1.7; N, 2.2; Br, 50.2%).

4-Amino-4':4"-dihydroxytriphenylmethane. The nitro-compound (3 g.) was reduced by ferrous sulphate and ammonia as described in the first example. The amine crystallized from aqueous alcohol or benzene in unsolvated needles, m. p. 219—221°, with a pink tinge (Found: C, 77.8; H, 5.75; N, 4.8%; *M*, 291. C<sub>19</sub>H<sub>17</sub>O<sub>2</sub>N requires C, 78.3; H, 5.8; N, 4.8%; *M*, 291).

*Leucaurin.* Sodium nitrite (0.15 g.) was added to ice-cold sulphuric acid (1.2 ml.); the mixture was warmed slightly to give a solution, and cooled to 0°. The amine (0.3 g.) in acetic acid (4 ml.) was added dropwise very slowly, the temperature being kept below 10°. The solution was stirred into 40 ml. of boiling water, and boiling was continued until gas ceased to be evolved. The mixture was cooled and extracted with ether. The solid left by evaporation of the ether was crystallized from aqueous alcohol (charcoal) to give long needles of leucaurin, m. p. and mixed m. p. with an authentic sample, 233—235°.

*Condensation of m-Cresol and p-Nitrobenzaldehyde.*—*m*-Cresol (2.16 g.) and *p*-nitrobenzaldehyde (1.51 g.) were condensed in acetic acid solution, and the product isolated, as in the first example. The benzene compound formed pale yellow crystals which melted at 88—94° with evolution of benzene; the melt resolidified at 100—110° (Found: C, 77.8; H, 6.05; N, 2.9; loss at 132°/3—6 mm., 30.1. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N, 2C<sub>6</sub>H<sub>6</sub> requires C, 78.4; H, 6.2; N, 2.8; C<sub>6</sub>H<sub>6</sub>, 30.9%). Unsolvated 4:4'-dihydroxy-2:2'-dimethyl-4"-nitrotriphenylmethane separated from aqueous alcohol in pale yellow needles, m. p. 203.5—204.5° (Found: C, 72.1; H, 5.6; N, 3.7%; *M*, 380. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0%; *M*, 349).

*Condensation of p- and o-Cresols and p-Nitrobenzaldehyde.*—The yellow product from *p*-cresol was obtained in doubtfully crystalline form, m. p. *ca.* 210—220°, after several separations from cyclohexane. It was not analyzed.

No crystalline product was obtained from *o*-cresol and *p*-nitrobenzaldehyde.

*Condensation of Phenol and o-Nitrobenzaldehyde.*—Phenol (1.88 g.) and *o*-nitrobenzaldehyde (1.51 g.) were condensed and the product isolated as in the first example. The benzene compound (yield, 2.0 g., 50%) formed crystals, m. p. 162—163° (Found: loss at 183°/3—4 mm., 19.2. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N, C<sub>6</sub>H<sub>6</sub> requires C<sub>6</sub>H<sub>6</sub>, 19.55%). 4:4'-Dihydroxy-2"-nitrotriphenylmethane separated in unsolvated, pale yellow prisms, m. p. 163°, from alcohol, toluene, or chlorobenzene (Found: C, 71.3; H, 4.8; N, 4.1%; *M*, 651. C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>N requires C, 71.0; H, 4.7; N, 4.4%; *M*, 321).

*Condensation of m-Cresol and o-Nitrobenzaldehyde.*—*m*-Cresol (5.4 g.) and *o*-nitrobenzaldehyde (3.8 g.) were condensed as in the first example (time, 42 hr.). The product, 4:4'-dihydroxy-2:2'-dimethyl-2"-nitrotriphenylmethane, separated from benzene in unsolvated yellow needles, m. p. 236—238°; it was also crystallized from light petroleum, cyclohexane, and ethyl alcohol, but from all solvents many recrystallizations (charcoal) were necessary to free it from resin (Found: C, 71.6; H, 5.7; N, 4.3. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0%).

*Condensation of p-Cresol and o-Nitrobenzaldehyde.*—*p*-Cresol (5.4 g.) and *o*-nitrobenzaldehyde (3.8 g.) were condensed as in the first example (time, 24 hr.). The product crystallized readily

from benzene, toluene, aqueous alcohol, or light petroleum (yield, 5.1 g., 66%); the crystals from all these retained small proportions of solvent which lowered the m. p. by several degrees. 2 : 2'-Dihydroxy-5 : 5'-dimethyl-2"-nitrotriphenylmethane, dried at 160°/3 mm., had m. p. 176—177° (Found : C, 72.5; H, 5.75; N, 4.0%; M, 337. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0%; M, 349).

*Condensation of o-Cresol and o-Nitrobenzaldehyde.*—*o*-Cresol (10.8 g.) and *o*-nitrobenzaldehyde (7.55 g.) were condensed as in the first example (time, 24 hr.). The orange-red product yielded stout, yellow prisms of the benzene compound, m. p. 100—110° (indefinite) (yield, 7.5 g., 50%), and some dark red resin (Found : loss at 116°/3—5 mm., 10.5. 2C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N, C<sub>6</sub>H<sub>6</sub> requires C<sub>6</sub>H<sub>6</sub>, 10.1%). The toluene compound melted at 95—110° (Found : loss at 116°/3—5 mm., 12.05. 2C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N, C<sub>7</sub>H<sub>8</sub> requires C<sub>7</sub>H<sub>8</sub>, 11.6%). The chlorobenzene compound melted at 85—100° (Found : loss at 116°/3—5 mm., 21.7. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N, C<sub>6</sub>H<sub>5</sub>Cl requires C<sub>6</sub>H<sub>5</sub>Cl, 24.4%). Unsolvated 4 : 4'-dihydroxy-3 : 3'-dimethyl-2"-nitrotriphenylmethane had m. p. 138—139°; crystals from aqueous alcohol retained a little solvent which was lost at 100°/3—5 mm. (Found : C, 72.1; H, 5.5; N, 4.0%; M, 352. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0%; M, 349).

*Condensation of Anisole and m-Nitrobenzaldehyde.*—Condensations with 2 : 1 molar quantities, under varied conditions, yielded resins which failed to crystallize; crystallization could however be induced by seeding solutions of the resins with the compound which was readily prepared with excess of anisole, as follows. A solution of anisole (8.65 g., 4 mols.) and *m*-nitrobenzaldehyde (3.0 g., 1 mol.) in acetic acid (20 ml.) was cooled to 2°, and sulphuric acid (8 ml.) in acetic acid (12 ml.) was added dropwise. After a day the mixture had separated into two layers. It was kept for 4 days at 0° with occasional shaking, and then poured into ice-water. The oil was extracted with ether, and the solution washed with sodium hydroxide solution and dried (CaCl<sub>2</sub>). Ether was removed, and the excess of anisole distilled off at 6—8 mm. The remaining viscous oil crystallized readily in unsolvated form from ethyl alcohol, methyl alcohol, light petroleum, or cyclohexane. 4 : 4'-Dimethoxy-3"-nitrotriphenylmethane, large, stout prisms from light petroleum (b. p. 60—80°) (3.85 g., 55%), had m. p. 73—75° (Found : C, 72.0; H, 5.1; N, 4.0; OMe, 17.7%; M, 405. C<sub>21</sub>H<sub>19</sub>O<sub>4</sub>N requires C, 72.2; H, 5.5; N, 4.0; OMe, 17.8%; M, 349). The same compound (m. p. and mixed m. p.) was prepared by methylating 4 : 4'-dihydroxy-3"-nitrotriphenylmethane with methyl sulphate and potassium hydroxide.

3-Amino-4' : 4'-dimethoxytriphenylmethane. Ferrous sulphate and ammonia failed to reduce the nitro-compound, which was recovered. Acid reducing agents were also unsuccessful. The nitro-compound (1.05 g.) was reduced with hydrogen in ethyl alcoholic solution in the presence of Adams's catalyst (absorption 214 ml.; calc., 201 ml.). The product was an oil which was repeatedly extracted with hot 18% hydrochloric acid; the crystals of 3-amino-4' : 4'-dimethoxytriphenylmethane hydrochloride, washed with 18% hydrochloric acid and dried, had m. p. ca. 120° (Found : C, 69.1; H, 6.3; N, 3.9; Cl, 10.0; OMe 16.8. C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>NCl requires C, 70.9; H, 6.2; N, 3.9; Cl, 10.0; OMe, 17.4%).

No crystalline product was isolated from condensations of anisole with *o*- or *p*-nitrobenzaldehyde.

*Condensation of 2 : 6-Xylen-1-ol and m-Nitrobenzaldehyde.*—2 : 6-Xylen-1-ol (6.1 g.) and *m*-nitrobenzaldehyde (3.775 g.) were condensed as in the first example (time, 31 hr.). The product was a readily powdered solid, free from obvious resin, which by crystallization from light petroleum or aqueous alcohol yielded 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyl-3"-nitrotriphenylmethane (8.0 g., 85%), m. p. 146°. The benzene compound crystallised in pale yellow rods which melted at ca. 100°, resolidified, and melted again at 146° (Found : loss at 116°/5 mm., 13.1. 3C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>N, 2C<sub>6</sub>H<sub>6</sub> requires O<sub>6</sub>H<sub>6</sub>, 12.1%. Found for the desolvated compound : C, 73.1; H, 6.4; N, 3.7. C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>N requires C, 73.2; H, 6.1; N, 3.7%). The *p*-xylene compound melted at 104°, resolidified, and melted again at 144—145° (Found : loss at 116°/5 mm., 15.5. 3C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>N, 2C<sub>8</sub>H<sub>10</sub> requires C<sub>8</sub>H<sub>10</sub>, 15.8%). The toluene compound melted at ca. 100°, resolidified, and melted again at 143° (Found : loss at 116°/5 mm., 15.5. 3C<sub>23</sub>H<sub>23</sub>O<sub>4</sub>N, 2C<sub>7</sub>H<sub>8</sub> requires C<sub>7</sub>H<sub>8</sub>, 14.0%).

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