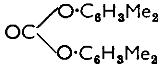
611. *Condensations of the Xylenols with Carbon Tetrahalides.*

By J. E. DRIVER and (MISS) T. F. LAI.

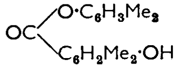
Each of the xylenols has been condensed with carbon tetrachloride by the use of zinc chloride or aluminium chloride as catalyst. Depending on the nuclear positions open to electrophilic attack varying products were obtained, namely xylyl carbonates, xylyl hydroxydimethylbenzoates, dihydroxytetramethylbenzophenones, tetramethylxanthones, aurin-type dyes, and trihydroxytrixylylmethanes. In some reactions the use of carbon tetrabromide gave increased yields of certain products.

THE condensation of phenol with carbon tetrachloride[1] was found by Gomberg and Snow[2] to be complex, giving rise to a variety of products by *ortho*- and *para*-substitutions and by presumed reactions of mutual oxidation and reduction. The xylenols were selected for study because of the varying possibilities of electrophilic attack. Isolated products from xylenols and carbon tetrahalides were xylyl carbonates (I), xylyl hydroxydimethylbenzoates (II), dihydroxytetramethylbenzophenones (III), tetramethylxanthones (IV), aurin-type dyes (V), and trihydroxytrixylylmethanes (VI). These can all be traced from hypothetical dixylyloxydichloro- or trihydroxytrixylylchloro-methanes, and they give a picture of these condensations which is different from, and simpler than, that given by Gomberg and Snow for phenol.[2,3]



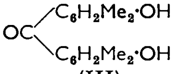
$OC\begin{array}{l}\diagup O\cdot C_6H_3Me_2\\ \diagdown O\cdot C_6H_3Me_2\end{array}$

(I)



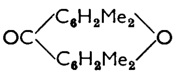
$OC\begin{array}{l}\diagup O\cdot C_6H_3Me_2\\ \diagdown C_6H_2Me_2\cdot OH\end{array}$

(II)



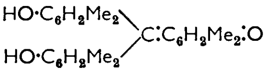
$OC\begin{array}{l}\diagup C_6H_2Me_2\cdot OH\\ \diagdown C_6H_2Me_2\cdot OH\end{array}$

(III)



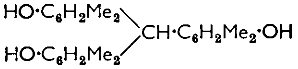
$OC\begin{array}{l}\diagup C_6H_2Me_2\diagdown\\ \diagdown C_6H_2Me_2\diagup\end{array}O$

(IV)



$\begin{array}{r}HO\cdot C_6H_2Me_2\diagdown\\ HO\cdot C_6H_2Me_2\diagup\end{array}C{:}C_6H_2Me_2{:}O$

(V)



$\begin{array}{r}HO\cdot C_6H_2Me_2\diagdown\\ HO\cdot C_6H_2Me_2\diagup\end{array}CH\cdot C_6H_2Me_2\cdot OH$

(VI)

2 : 6-Xylenol, with only the *para*-position open to attack, presents the simplest problem. With carbon tetrachloride it gave deep red 3 : 3′ : 3″ : 5 : 5′ : 5″-hexamethylaurin (VII) in high yield. The aurin gave on acetylation the diacetoxymethylenequinone (VIII) and on benzoylation the corresponding dibenzoyloxy-derivative both of which, with suppressed resonance, are yellow; aurin itself and the homologues previously acylated ("rosolic acid" and "*o*-cresaurin") give only triacyl derivatives of the corresponding carbinols, but 3 : 3′ : 3″ : 5 : 5′ : 5″-hexabromoaurin gives a yellow diacetyl derivative as an intermediate:[4] this is therefore a steric phenomenon. Reduction of the ketone diacetate (VIII) gave the colourless phenolic diacetyl derivative (IX) which was further acetylated to the triacetyl derivative (X); this was also prepared by reduction of the dye to the *leuco*-compound (XI) and subsequent acetylation.

The structure of the aurin (VII) was confirmed by oxidation by hydrogen peroxide to 4 : 4′-dihydroxy-3 : 3′ : 5 : 5′-tetramethylbenzophenone, which by Clemmensen reduction gave the known 4 : 4′-dihydroxy-3 : 3′ : 5 : 5′-dixylylmethane.

2 : 3-Xylenol gave 2 : 2′ : 2″ : 3 : 3′ : 3″-hexamethylaurin, 2 : 3 : 2′ : 3′-dixylyl carbonate, and two yellow dihydroxytetramethylbenzophenones; one of these was shown to be the 2 : 2′-dihydroxy-3 : 3′ : 4 : 4′-tetramethyl compound by an unusual cyclization to 3 : 4 : 5 : 6-tetramethylxanthone by alkali. 2 : 5-Xylenol gave 2 : 2′ : 2″ : 5 : 5′ : 5″-hexamethylaurin [which, like (I), formed a yellow diacetyl derivative] and two crystalline substances—one (from analytical results, probably a dihydroxytetramethylbenzophenone)

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[1] Friedel, *Bull. Soc. chim. France*, 1888, **50**, 2.

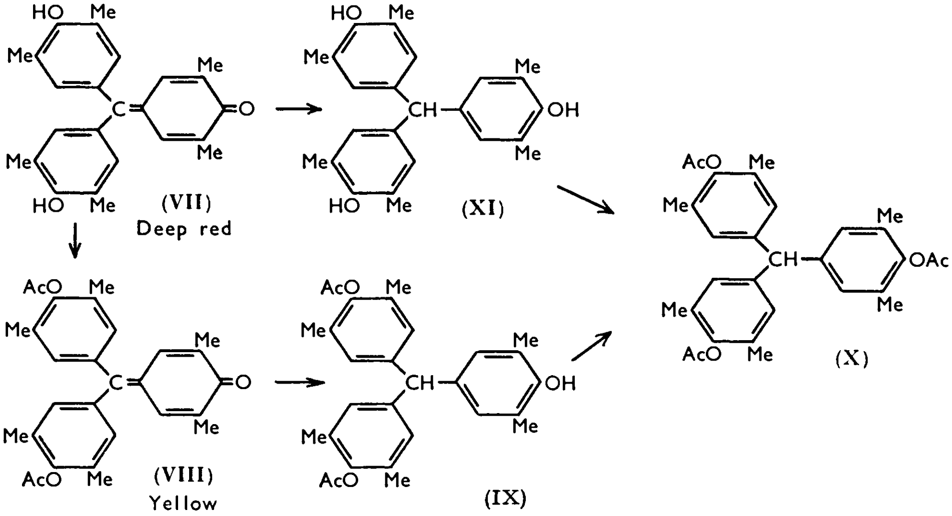
[2] Gomberg and Snow, *J. Amer. Chem. Soc.*, 1925, **47**, 198.

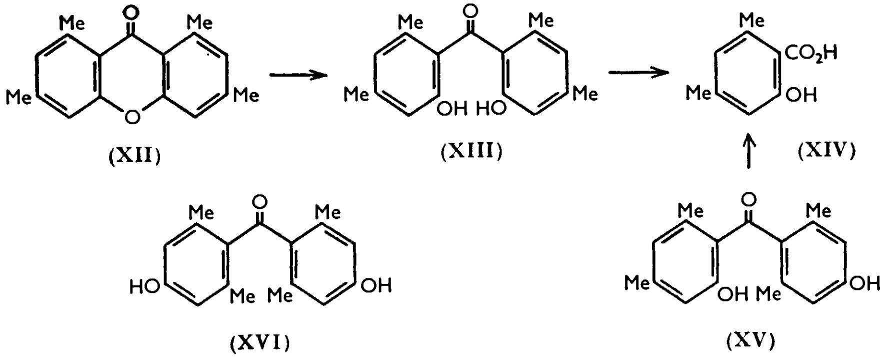
[3] Cf. also Gomberg and Anderson, *ibid.*, p. 2022.

[4] Spiers, *J.*, 1924, **125**, 450.

orange and soluble in 2% ammonia, the other colourless and not soluble—which were not obtained in quantity sufficient for fuller investigation.

It is interesting that 3 : 5-xylenol, which though having a free position *para* to the hydroxyl group is there sterically hindered by the methyl groups, gave no aurin-type dye or other triphenylmethane derivative; the formation of these by the route usually depicted is impossible if formation of $CCl(C_6H_2Me_2{\cdot}OH)_3$ (or the corresponding carbinol) is prevented by steric effects. The yield of crude product in this condensation was markedly improved by the use of carbon tetrabromide, and the isolated products were 3 : 5-xylyl 2-hydroxy-4 : 6-dimethylbenzoate, 1 : 3 : 6 : 8-tetramethylxanthone, 3 : 5 : 3′ : 5′-dixylyl carbonate, and the three possible dihydroxytetramethylbenzophenones; the orientation of one of these last (XIII) was established by its formation as an intermediate degradation product of the xanthone (XII) to 2-hydroxy-4 : 6-dimethylbenzoic acid (XIV), that of another (XV) by formation of the same acid from it, and that of the third (XVI) by elimination (confirmed by the fact that it alone is colourless).





The two xylenols with blocked positions *para* to the hydroxyl group both yielded trihydroxytrixylylmethanes, and the same products were obtained when chloroform was used instead of the carbon tetrahalide. Reactions in which carbon tetrachloride gives the same products as chloroform have long been known.[5] Gomberg and Snow[2] obtained 4 : 4′ : 4″-trihydroxytriphenylmethane (leucaurin) as a by-product of the condensation of

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[5] Ingold and Powell, *J.*, 1921, **119**, 1222.

phenol with carbon tetrachloride, and explained it as resulting from reduction of the intermediate trihydroxytriphenylchloromethane by hydrogen provided by cyclization of a hypothetical *ortho*-substituted intermediate to a fluorone. There is no evidence of any such reactions with the xylenols (in fact, from 2 : 4-xylenol the trihydroxytrixylylmethane was the only crystalline compound isolated), and it would seem more likely that the hydrogen is provided by oxidation of simpler products to resinous complexes. 3 : 4-Xylenol yielded a trihydroxytrixylylmethane, a tetramethylxanthone, 3 : 4 : 3′ : 4′-dixylyl carbonate, and a 2 : 2′-dihydroxytetramethylbenzophenone; the last compound was shown to have methyl groups in the 4 : 6-positions, but an attempted Beckmann rearrangement of its oxime with the idea of orientating the two other methyl groups resulted in cyclization to the oxime of a tetramethylxanthone.*

In most reactions zinc chloride was employed as condensing agent, but in some aluminium chloride was found to be preferable; aluminium chloride could not however be used with 3 : 5-xylenol with which it formed a non-reactive complex. All xylenols isomerize to the 3 : 5-isomer when heated with aluminium chloride (*ca.* 2 mols.):[6] that no isomerization took place under the conditions here used (and always with less than 1 mol. of aluminium chloride) was shown by the distinct nature of the products, the fact that recovered xylenol was always the same as the original, and the results of specific experiments.

The yield of crystalline products was sometimes higher (cf., *e.g.*, above), sometimes much lower, when carbon tetrabromide was used in place of the tetrachloride;[7] it appeared that readier reaction in some cases encouraged the formation of resinous products.

The hexamethylaurins are resistant to air-oxidation in alkaline solution, as contrasted with aurin which gives 4 : 4′-dihydroxybenzophenone with ease: they will be further studied.

EXPERIMENTAL

Xylenols used distilled within 1°. Carbon tetrachloride and chloroform were "AnalaR." Microanalyses are by Dr. Zimmermann, Melbourne.

Condensation of 2 : 6-*Xylenol and Carbon Tetrachloride.*—A mixture of the xylenol (40 g.) and aluminium chloride (25 g.) was heated on a water-bath under reflux, and carbon tetrachloride (15·4 g.) was added dropwise. Hydrogen chloride was evolved and the mixture became red gradually. After 4 hr. water (200 ml.) was added to the viscous mass, and the excess of xylenol was removed in steam. The red solid (30 g.) was collected and washed.

The crude product, which was completely soluble in sodium hydroxide solution, was extracted with 1·5% aqueous ammonia. Acidification of the deep purple extract (temp. 60—70°) with acetic acid gave a bright red precipitate which was collected, washed, dried, and crystallized from 95% ethanol as 3 : 3′ : 3″ : 5 : 5′ : 5″-*hexamethylaurin monoethanolate*, which separated as bright red needles, m. p. 320° (decomp.) *in vacuo* (Found: C, 77·0; H, 7·7; loss at 180°/3 mm., 10·9. $C_{25}H_{26}O_3,C_2H_6O$ requires C, 77·1; H, 7·7; C_2H_6O, 10·9%). Solvent was removed at 180° under reduced pressure to give the *aurin* (Found: C, 79·8; H, 7·0. $C_{25}H_{26}O_3$ requires C, 80·2; H, 7·0%).

The *diacetyl derivative*, prepared by heating the aurin under reflux for 1 hr. with acetic anhydride and sodium acetate, separated from ethyl acetate in yellow needles, m. p. 302—304° (Found: C, 76·2; H, 6·7; Ac, 18·6. $C_{29}H_{30}O_5$ requires C, 76·0; H, 6·6; Ac, 18·8%). It was reduced by zinc and acetic acid to 4 : 4′-*diacetoxy*-4″-*hydroxy*-3 : 3′ : 3″ : 5 : 5′ : 5″-*trixylylmethane*, which separated from 95% ethanol in colourless needles, m. p. 172—174° (Found: C, 75·8; H, 7·0; Ac, 19·2%; *M*, 511. $C_{29}H_{32}O_5$ requires C, 75·6; H, 7·0; Ac, 18·7%; *M*, 461); acetylation of this yielded the triacetyl derivative, which separated from 95% ethanol in colourless, silky needles, m. p. 216—217°, mixed m. p. 217—218° with the triacetyl derivative (m. p. 218—219°) of the *leuco*-compound (below). The aurin could not be benzoylated by

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* The possibility that this compound might have been the isomeric benzoxazole (cf. Meisenheimer, Hanssen, and Wächterowitz, *J. prakt. Chem.*, 1928, **119**, 315) is excluded by its properties.

[6] Baddeley, *J.*, 1943, 527.

[7] Cf. Kishore and Mathur, *J. Indian Chem. Soc.*, 1951, **28**, 72.

the Schotten–Baumann method; it was benzoylated in pyridine, to yield 4 : *4′-dibenzoyl-*3 : 3′ : 3″ : 5 : 5′ : *5″-hexamethylaurin*, which separated from 95% ethanol in yellow prisms. This compound has two melting points; it melts at 169·5° when heated rapidly, and at 245—246° when heated slowly (Found: C, 79 9; H, 5·8. $C_{39}H_{34}O_5$ requires C, 80·4; H, 5·9%).

The crude product could be crystallised directly from 95% ethanol to yield the aurin. The mother-liquor then yielded crystals with a green lustre which changed to the red aurin when heated and were probably its *hydrochloride* (Found: C, 71·9; H, 6·7; Cl, 8·5. $C_{25}H_{27}O_3Cl$ requires C, 73·1; H, 6·6; Cl, 8·6%).

Oxidation. No appreciable reaction took place when oxygen was passed through an alkaline solution of the aurin for 48 hr., but oxidation was readily effected as follows. A solution of the aurin in sodium hydroxide solution was heated on a water-bath, and 3% hydrogen peroxide solution was added portionwise until the solution changed from deep red to yellow (about 3 min.). After being cooled the solution was acidified with acetic acid whereupon colourless, silky needles of 4 : *4′-dihydroxy-*3 : 3′ : 5 : *5′-tetramethylbenzophenone*, m. p. 223° (from aqueous ethanol), separated (Found: C, 75·5; H, 6·6. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). The *diacetyl derivative* separated from 95% ethanol in prisms, m. p. 185—186° (Found: C, 71·3; H, 6·2; Ac, 22·2. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3; Ac, 24·3%). The *dimethyl ether*, prepared by methyl sulphate methylation at water-bath temperature, formed prisms, m. p. 110—111°, from aqueous ethanol (Found: C, 76·2; H, 7·5; OMe, 20·7. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4; OMe, 20·8%). The *oxime* crystallized from aqueous ethanol in prisms, m. p. 230° (decomp.) (Found: C, 71·6; H, 6·7; N, 5·0%; *M*, 277. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%; *M*, 285). Clemmensen reduction of the ketone gave 4 : 4′-dihydroxy-3 : 3′ : 5 : 5′-dixylylmethane, m. p. 173—174° (lit., 175°) (Found: C, 79·7; H, 7·8. Calc. for $C_{17}H_{20}O_2$: C, 79·7; H, 7·9%).

Reduction. The aurin was heated with zinc powder and acetic acid until the solution was almost colourless, and the excess of zinc was then removed. Dilution precipitated 4 : 4′ : *4″-trihydroxy-*3 : 3′ : 3″ : 5 : 5′ : *5″-trixylylmethane*, which crystallized from aqueous ethanol in needles, m. p. 220° (Found: C, 79·8; H, 7·4%; *M*, 363. $C_{25}H_{28}O_3$ requires C, 79·8; H, 7·5%; *M*, 376). The *triacetyl derivative* formed silky needles, m. p. 218—219°, from 95% ethanol (Found: C, 74·0; H, 6·9; Ac, 24·4%; *M*, 519. $C_{31}H_{34}O_6$ requires C, 74·1; H, 6·8; Ac, 25·7%; *M*, 503). The *tribenzoyl derivative*, prepared by the Schotten–Baumann method, formed silky needles, m. p. 190—191°, from 95% ethanol (Found: C, 79·7; H, 6·0. $C_{46}H_{40}O_6$ requires C, 80·2; H, 5·8%).

Condensation of 2 : *6-Xylenol and Carbon Tetrabromide.*—The xylenol (40 g.), carbon tetrabromide (33 g.), and zinc chloride (20 g.) were heated at 100—110° under reflux. Hydrogen bromide was evolved, and after ½ hr. the excess of xylenol was removed in steam. The crude hexamethylaurin (40 g.) was completely soluble in sodium hydroxide solution and was purified as before.

Condensation of 2 : *6-Xylenol and Chloroform.*—The xylenol (15 g.), chloroform (4·5 g.), and aluminium chloride (10 g.) were heated on a water-bath for 3 hr. After removal of xylenol the red, solid product was extracted with ether to yield 4 : 4′ : 4″-trihydroxy-3 : 3′ : 3″ : 5 : 5′ : 5″-trixylylmethane, m. p. 216—218° not depressed on admixture with the reduction product of 3 : 3′ : 3″ : 5 : 5′ : 5″-hexamethylaurin. The triacetyl derivative had m. p. 220—222°, not depressed in admixture with the triacetyl derivative of the reduction product of the aurin.

Condensation of 2 : *3-Xylenol and Carbon Tetrachloride.*—The xylenol (30 g.), carbon tetrachloride (12 g.), and zinc chloride (15 g.) were condensed as in the first example (110—130°, 8 hr.). The crude product, a dark-brown solid (20 g.), was extracted with 5% sodium hydroxide solution; acidification with acetic acid of the deep purple extract precipitated a reddish-brown solid (15 g.) which was collected, washed, dried, and extracted (Soxhlet) with light petroleum (b. p. 60—80°). Evaporation of the extract left 2 : *2′-dihydroxy-*3 : 3′ : 4 : 4′-tetramethyl-*benzophenone* which crystallized from 95% ethanol in yellow needles, m. p. 165—166° (Found: C, 75·5; H, 6·6%; *M*, 283. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270). The *acetyl derivative*, crystallized from aqueous ethanol, had m. p. 129·5—130·5° (Found: C, 73·1; H, 6·5; Ac, 13·7. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·5; Ac, 13·8%). The *oxime*, made by heating the ketone with hydroxylamine hydrochloride, sodium acetate, and aqueous ethanol for 5 hr., crystallized from benzene–light petroleum in prisms which softened at 176° and melted at 180° (Found: C, 71·8; H, 6·4; N, 4·9%; *M*, 272. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%; *M*, 285). The ketone was boiled with 2N-sodium hydroxide for 5 hr. during which 3 : 4 : 5 : 6-*tetramethylxanthone* separated as a white powder which crystallized from ethanol in colourless plates, m. p. 195°, and in sulphuric acid formed a yellow solution with an intense green fluorescence (Found: C, 80·6; H, 6·5%; *M*, 262. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%; *M*, 252).

The mother-liquor after separation of the first crop of yellow hydroxy-compound was concentrated, and addition of water then precipitated crystals which by recrystallization from aqueous ethanol yielded a yellow *dihydroxytetramethylbenzophenone*, m. p. 184—185° (Found: C, 75·6; H, 6·8%; *M*, 270. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270). The *acetyl derivative*, crystallized from aqueous ethanol, had m. p. 127—128°, depressed to below 110° by admixture with the acetyl derivative of the compound of m. p. 165—166° (Found: C, 73·1; H, 6·6; Ac, 13·5%). The ketone did not form an oxime, and was recovered unchanged after having been heated with 2N-sodium hydroxide for 2 hr.

The alkali-soluble product, after extraction with light petroleum, was extracted with 3·5% aqueous ammonia. Acidification of the deep purple solution with acetic acid precipitated 2 : 2′ : 2″ : 3 : 3′ : 3″-*hexamethylaurin* which separated from benzene–methanol in green needles, m. p. 297—298° (decomp.) (Found: C, 80·2; H, 7·1. $C_{25}H_{26}O_3$ requires C, 80·2; H, 7·0%). Hydrogen peroxide in alkaline solution did not oxidize the aurin, but reduction with zinc powder and acetic acid gave a product from which colourless needles (from acetic acid), m. p. 310° (decomp.), were isolated in small quantity. The acetyl derivative was difficult to crystallize and was not obtained pure.

The crude, alkali-insoluble product was extracted with light petroleum (b. p. 60—80°) (Soxhlet). The extract was washed with 5% sodium hydroxide solution, then with water, and dried (Na_2SO_4). Evaporation of solvent left crystals contaminated with resin. Short-path vacuum-distillation and crystallization from 95% ethanol yielded prisms of 2 : 3 : 2′ : 3′-*dixylyl carbonate*, m. p. 99—100·5° (Found: C, 75·5; H, 6·9. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%); this compound did not react with aniline at 150—180°/3 hr. (sealed tube, copper catalyst).

Condensation of 2 : 5-*Xylenol and Carbon Tetrachloride.*—The xylenol (50 g.), carbon tetrachloride (20 g.), and aluminium chloride (30 g.) were condensed as in the first example (120—130°, 5 hr.). From the residue a dark-brown solid (25 g.) was obtained. Extraction of this with 2% aqueous ammonia at 70—80° gave a deep violet solution which by acidification with acetic acid yielded 2 : 2′ : 2″ : 5 : 5′ : 5″-*hexamethylaurin*. This, after separation from the hot solution, crystallized from methanol in stout, red prisms, m. p. 293—295° (decomp.) (Found: C, 79·4; H, 7·1. $C_{25}H_{26}O_3$ requires C, 80·2; H, 7·0%); its alkaline solution showed no appreciable change in colour after being treated with oxygen for 50 hr., and it remained unchanged after being heated with sodium hydroxide solution and hydrogen peroxide for 2 hr. (water-bath). Reduction gave an amorphous product. The *diacetyl derivative* separated from 95% ethanol in yellow plates, m. p. 171—172° (Found: C, 75·8; H, 6·7; Ac, 19·0. $C_{29}H_{30}O_5$ requires C, 76·0; H, 6·6; Ac, 18·8%).

The hot filtrate after acidification of the ammonia extract yielded, on cooling, crystals, probably of a *dihydroxytetramethylbenzophenone*, which crystallized from aqueous ethanol in orange needles, m. p. 234—238° (Found: C, 75·4; H, 6·8. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%).

The crude ammonia-insoluble product yielded colourless rods, m. p. 229—232° (decomp.), after 3 recrystallizations from aqueous ethanol (*ca.* 1 mg.).

Condensation of 3 : 5-*Xylenol and Carbon Tetrabromide.*—The xylenol (61 g.) and zinc chloride (30 g.) were heated at 120—130° under reflux, and carbon tetrabromide (55 g., in pellets) was added in 2 hr. Hydrogen bromide was evolved and the mixture became red. Heating was continued for a further hour, and the excess of xylenol was removed in steam. The mixture was stirred into water (1 l.) containing hydrochloric acid (50 ml.), and the reddish-brown resinous product (40 g.) was collected, washed, and extracted with 5% sodium hydroxide solution. The blue extract, on acidification with acetic acid, yielded a precipitate which settled to a dark resin (20 g.) which was washed and dried.

The alkali-soluble product was extracted with light petroleum (b. p. 60—80°). The hot extract deposited yellow needles when cooled (see later), and the mother-liquor, when evaporated, left a yellow crystalline mass which was recrystallized from aqueous ethanol to yield colourless plates of 3 : 5-*xylyl* 2-*hydroxy*-4 : 6-*dimethylbenzoate*, m. p. 99—100° (Found: C, 75·5; H, 6·8. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). The *acetyl derivative* separated from methanol in hexagonal plates, m. p. 55—56° (Found: C, 73·4; H, 6·7; Ac, 14·4. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·5; Ac, 13·8%). The ester was hydrolysed by sodium hydroxide to 3 : 5-xylenol and 2-hydroxy-4 : 6-dimethylbenzoic acid, m. p. 165—166° (lit., 166°).

The alkali-soluble product after extraction with light petroleum was crystallized from dilute acetic acid (charcoal), to yield yellow crystals, which were extracted with hot benzene (see below). The residue crystallized from acetic acid as prisms, m. p. 256—260° (decomp.), which (being colourless) were 4 : *4′-dihydroxy-*2 : 2′ : 6 : *6′-tetramethylbenzophenone* (Found: C, 75·7; H, 6·8%; *M*, 293. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270). The *diacetyl derivative* separated from light petroleum in prisms, m. p. 116—117° (Found: C, 71·5; H, 6·2; Ac, 24·2. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3; Ac, 24·3%).

The crystals deposited from the petroleum and benzene extracts were combined, and by fractional crystallization from benzene two compounds were obtained. 2 : *2′-Dihydroxy-*4 : 4′ : 6 : *6′-tetramethylbenzophenone*, which was the less soluble in benzene, separated in yellow needles, m. p. 170° (Found: C, 75·5; H, 6·7%; *M*, 288. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270); the *diacetyl derivative* crystallized from light petroleum in stout prisms, m. p. 120° (Found: C, 71·5; H, 6·2; Ac, 22·3. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3; Ac, 24·3%). The ketone reacted with cold sulphuric acid, the solution changing from orange to pale yellow in a few minutes. Dilution then gave a white precipitate and a smell of 3 : 5-xylenol. The precipitate was suspended in sodium carbonate solution; after filtration, acidification precipitated 2-hydroxy-4 : 6-dimethylbenzoic acid which separated from water in needles, m. p. 164—166° undepressed on admixture with the product of hydrolysis of the xylyl 2-hydroxy-3 : 5-dimethylbenzoate. 2 : *4′-Dihydroxy-*4 : 2′ : 6 : *6′-tetramethylbenzophenone* separated from benzene in stout, yellow prisms, m. p. 143·5—145° (Found: C, 75·4; H, 6·7%; *M*, 284); the *diacetyl derivative* crystallized from aqueous ethanol in prisms, m. p. 127—128° (Found: C, 71·1; H, 6·2; Ac, 22·5%); the *dibenzoyl derivative*, prepared by the Schotten–Baumann method, crystallized from 95% ethanol in prisms, m. p. 187° (Found: C, 78·0; H, 5·4%; *M*, 462. $C_{31}H_{26}O_5$ requires C, 77·8; H, 5·5%; *M*, 479). This ketone likewise was decomposed by sulphuric acid with formation of 2-hydroxy-4 : 6-dimethylbenzoic acid, m. p. 164—166°.

The alkali-insoluble part of the condensation product crystallized from aqueous ethanol, to give needles which were a mixture of two compounds: these could be separated by fractional crystallization from ethanol, but were more easily separated as follows. The mixture was shaken with concentrated sulphuric acid and filtered through a sintered-glass crucible, and the filtrate was poured on crushed ice. The precipitate was collected, washed, and crystallized from 95% ethanol, to yield 1 : 3 : 6 : *8-tetramethylxanthone*, which melted at 165—166°; its solution in concentrated sulphuric acid was yellow, with an intense green fluorescence (Found: C, 80·9; H, 6·4%; *M*, 243. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%; *M*, 252). The xanthone was heated with solid potassium hydroxide moistened with water, and the mixture was kept molten for 1 hr., then cooled and extracted with water. Acidification precipitated 2 : 2′-dihydroxy-4 : 4′ : 6 : 6′-tetramethylbenzophenone which crystallized from aqueous ethanol (charcoal) in yellow prisms, m. p. 170° undepressed on admixture with the ketone isolated from the xylenol condensation. The residue insoluble in sulphuric acid crystallized from aqueous ethanol as needles of 3 : 5 : 3′ : *5′-dixylyl carbonate*, m. p. 116—117° (Found: C, 75·7; H, 6·7%; *M*, 246. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270); when heated with aniline (2 mols.) and a little copper powder at 150—180° for 3 hr. (sealed tube) the carbonate yielded carbanilide, m. p. 240—241° (from aqueous ethanol) (not depressed on admixture with an authentic specimen).

Reaction of 3 : *5-Xylenol with Aluminium Chloride.*—The xylenol (50 g.) and aluminium chloride (25 g.) were heated on a water-bath. Some hydrogen chloride was evolved and the mixture became a yellow mass which did not melt at 140°. Carbon tetrachloride was added and the mixture heated at *ca.* 140° for several hours; little reaction took place, and most of the xylenol was recovered.

The xylenol (24 g.) and aluminium chloride (13 g.) were heated in light petroleum (100 ml.) on a water-bath for 6 hr.; the white, solid residue, after being washed with light petroleum and dried, contained 11—12% of aluminium and a variable proportion (15—20%) of chlorine.

Condensation of 2 : *4-Xylenol and Carbon Tetrachloride.*—The xylenol (40 g.), carbon tetrachloride (15·4 g.), and aluminium chloride (35 g.) were condensed as in the first example (5 hr.).

The product isolated was a brown resin (14 g.); this was digested repeatedly with 3·5% ammonia solution on a water-bath. The red ammonia extract was acidified with acetic acid, and the precipitate was washed, dried, and extracted with light petroleum (b. p. 60—80°). Removal of solvent left a yellow mass which was crystallized from aqueous ethanol to yield colourless needles of 2 : 2′ : *2″-trihydroxy-*3 : 3′ : 3″ : 5 : 5′ : *5″-trixylylmethane,* m. p. 145—146° (Found: C, 79·3; H, 7·7. $C_{25}H_{28}O_3$ requires C, 79·8; H, 7·5%). The *triacetyl derivative* separated from aqueous ethanol in needles, m. p. 80—82° (Found: C, 73·8; H, 7·0; Ac, 26·6. $C_{31}H_{34}O_6$ requires C, 74·1; H, 6·8; Ac, 25·7%).

No other crystalline substance was obtained from the condensation product. Condensations of the xylenol and carbon tetrabromide in the presence of aluminium chloride (90—100°, 5 hr.) or zinc chloride (110—130°, 1 hr.) yielded dark products representing up to 80% of the xylenol used, but from them no crystalline substances were isolated.

Condensation of 2 : *4-Xylenol and Chloroform.*—The xylenol (10 g.), aluminium chloride (7 g.), and chloroform (3 g.) were condensed as in the first example (3½ hr.). The grey solid isolated was completely soluble in sodium hydroxide solution; it was soluble in light petroleum (b. p. 60—80°), and crystallized from aqueous ethanol as needles of 2 : 2′ : 2″-trihydroxy-3 : 3′ : 3″ : 5 : 5′ : 5″-trixylylmethane, m. p. 146·5—147°, mixed m. p. 146—147° with that (m. p. 145—146°) obtained in the carbon tetrachloride condensation.

Condensation of 3 : *4-Xylenol and Carbon Tetrachloride.*—(*a*) The xylenol (92 g.), carbon tetrachloride (39 g.), and zinc chloride (20 g.) were heated at 110—130° for 24 hr. After removal of xylenol a dark-brown resin (65 g.) remained. This was extracted with 5% sodium hydroxide solution, the extract was acidified with acetic acid, and the resulting precipitate was washed, dried, and extracted with light petroleum (b. p. 60—80°). Removal of solvent left a yellow solid which separated from acetone in large crystals. These were recrystallized from benzene to yield colourless prisms of a 2 : 2′ : *2″-trihydroxytrixylylmethane,* m. p. 163·5—164·5° (Found: C, 80·0; H, 7·8%; *M*, 371. $C_{25}H_{28}O_3$ requires C, 79·8; H, 7·5%; *M*, 376). The *triacetyl derivative* formed needles, m. p. 107—108°, from ethanol (Found: C, 74·0; H, 7·1; Ac, 25·8. $C_{31}H_{34}O_6$ requires C, 74·1; H, 6·8; Ac, 25·7%).

(*b*) The xylenol (40 g.), carbon tetrachloride (15·4 g.), and zinc chloride (30 g.) were condensed as in (*a*), but for 2½ hr. only, and the crude product (23 g.) was treated as before. The benzene recrystallization gave yellow prisms, m. p. 160—165°, depressed to 140° on admixture with the trihydroxytrixylylmethane obtained as in (*a*). Four recrystallizations from benzene raised the m. p. of this yellow 2 : *2′-dihydroxytetramethylbenzophenone* to 166—167·5° (Found: C, 75·4; H, 6·8%; *M*, 305. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%; *M*, 270). The *diacetyl derivative* separated from 95% ethanol in long needles, m. p. 110·5—111·5° (Found: C, 71·3; H, 6·3; Ac, 23·1%; *M*, 316. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3; Ac, 24·3%; *M*, 354). The *dibenzoyl derivative* separated from 95% ethanol in prisms, m. p. 172—172·5° (Found: C, 77·5; H, 5·4. $C_{31}H_{26}O_5$ requires C, 77·8; H, 5·5%). The *oxime*, prepared by interaction with hydroxylamine hydrochloride in aqueous ethanolic potassium hydroxide (water-bath, 2½ hr.), separated from benzene–light petroleum in prisms, m. p. 165—170° (Found: C, 71·6; H, 6·7; N, 5·3%; *M*, 291. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%; *M*, 285). The ketone was heated with sulphuric acid (water-bath) for several hours; dilution then precipitated 2-hydroxy-4 : 5-dimethylbenzoic acid which crystallized from aqueous ethanol in prisms, m. p. 198—200° (lit., 199°), and gave a deep violet-blue colour with ferric chloride.

To a solution of the above oxime (1 g.) in ether (15 ml.), phosphorus pentachloride (1·5 g.) was added with stirring. Removal of solvent left a brown residue which was washed, dried, and recrystallized from 95% ethanol to yield silky needles of a *tetramethylxanthone oxime,* m. p. 183°; this was insoluble in alkali, but in concentrated sulphuric acid formed a pale yellow solution with a violet-blue fluorescence (Found: C, 75·9; H, 6·4; N, 5·6. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).

The alkali-insoluble part of the condensation product was extracted with light petroleum (b. p. 60—80°) (Soxhlet), and a yellow solution with a green fluorescence was obtained. On evaporation this left a dark resin which solidified. Short-path distillation *in vacuo* at 100—110° gave colourless needles of 3 : 4 : 3′ : *4′-dixylyl carbonate,* which had m. p. 123—124° after recrystallization from 95% ethanol (Found: C, 75·7; H, 6·6. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). By heating the carbonate with aniline (2 mols.) and a little copper powder at 150—180° for 3 hr. (sealed tube), the xylenol and carbanilide (m. p. 240—241°, not depressed on admixture with an authentic sample) were formed.

The residue after sublimation of the carbonate was crystallized from benzene (charcoal), to yield colourless prisms of a *tetramethylxanthone*, m. p. 285—286°, which in concentrated sulphuric acid formed a yellow solution with an intense green fluorescence (Found: C, 81·2; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

Condensation of 3 : 4-*Xylenol and Chloroform.*—The xylenol (8 g.), chloroform (2·6 g.), and zinc chloride (4 g.) were heated at 130—140° for 7 hr. The black solid isolated (2 g.) was extracted with 5% sodium hydroxide solution. Acidification with acetic acid and crystallization from benzene gave prisms of the 2 : 2′ : 2″-trihydroxytrixylylmethane, m. p. 162—164° not depressed on admixture with the compound obtained in the carbon tetrachloride condensation.

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