

Condensation of *p*-Cresol with Carbon Tetrachloride

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p-Cresol has been condensed with carbon tetrachloride in the presence of anhydrous zinc chloride as catalyst. The products were di-*p*-tolyl carbonate, *p*-tolyl 2-hydroxy-5-methylbenzoate, 2,7-dimethylxanthone, 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane, and 2,2',2''-trihydroxy-5,5',5''-trimethyltriphenylmethane. The predicted dihydroxydimethylbenzophenone was not isolable, but a considerable amount of its reduction product, dihydroxydimethyldiphenylmethane was obtained. The latter, homologues of which have not been previously isolated from similar condensations, was also prepared by the reaction of *p*-cresol with chloroform in the presence of zinc chloride.

GOMBERG and SNOW¹ devised a scheme for the metal halide-catalysed condensation of phenol with carbon tetrachloride, based on the numerous isolable products. Gomberg also studied the similar condensation of *o*-cresol,² which presents complications as great. But as far as we are aware, nothing has been done with *p*-cresol, which because of the limitation to *ortho* substitutions, should present a more straightforward problem, comparable to that of the xylenols with a methyl group in the 4-position studied by Driver and Lai,³ but giving products whose constitutions should be more easily determined.

As in previous condensations, the reaction was carried out with 3.5 mol. of *p*-cresol and 1 mol. of carbon tetrachloride. Although in some previous cases, aluminium chloride was found to be preferable as a condensing agent, it could not be used with *p*-cresol, as the reaction mixture completely solidified with evolution of hydrogen chloride and the extent of condensation, if any, was slight. However with a large excess of carbon tetrachloride at 100° a reaction took place leading to the formation of 1-methyl-1-trichloromethylcyclohexa-2,5-dien-4-one. This product was further characterised by its oxime, thus confirming the classical reaction reported by Zincke and Suhl.⁴ With zinc chloride as a catalyst, the usual condensation of *p*-cresol with carbon tetrachloride took place smoothly, but longer reaction times greatly encouraged the formation of resins. Isolated compounds from this condensation were di-*p*-tolyl carbonate (I), *p*-tolyl 2-hydroxy-5-methylbenzoate (II), 2,7-dimethylxanthone (III), 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane (IV), and 2,2',2''-trihydroxy-5,5',5''-trimethyltriphenylmethane (V). These can all be traced from the hypothetical di-*p*-cresoxydichloro- and tri-*p*-cresoxychloro-methanes, and, because of the symmetry of *p*-cresol, the assignment of their constitutions appears unambiguous. The first stage in the reaction involves the condensation of two molecules of *p*-cresol with one of carbon tetrachloride to form the hypothetical di-*p*-cresoxydichloromethane, which may be consumed in three days. First, it may be hydrolysed to (I). Secondly, it may undergo an intramolecular rearrangement in the presence of hydrogen chloride to give either *p*-cresyl-*p*-cresoxydichloromethane or di-*p*-cresyldichloromethane. Hydrolysis of the former yields (II),

while that of the latter yields the benzophenone (VI) which can be either condensed to (III) or else reduced to (IV). Finally, it may be further condensed with another molecule of *p*-cresol and the resulting tri-*p*-cresoxychloromethane undergoes rearrangement and then reduction to (V).

The condensation of *p*-cresol with carbon tetrachloride differs from those of other phenols in that the predicted 2,2'-dihydroxy-5,5'-dimethylbenzophenone (VI) could not be isolated. Presumably, here there is a greater tendency of reduction so that, in place of the benzophenone (VI), the diphenylmethane (IV) is obtained instead. Another point of interest about the present condensation is that highly coloured *o*-quinonoid products corresponding to the *p*-quinonoid aurin dyes are not formed. Although there is a reference⁵ in the classical organic literature to a "kresolaurin" made from what appears from the context to be *p*-cresol by heating it with formic acid and zinc chloride, this is probably a misconception due to the use of an impure cresol. *o*-Cresol, on the other hand, with both *ortho* and *para* positions available for substitution, forms a *p*-quinonoid type of aurin dye.²

Compound (I) was insoluble in cold sodium hydroxide solution, indicating the absence of phenolic groups. However, on boiling with sodium hydroxide it dissolves, and the resulting solution gave carbon dioxide and *p*-cresol on acidification with dilute hydrochloric acid. It was further identified by conversion into carbanilide. For identification purposes, the ester (II) was hydrolysed and the resulting benzoic acid isolated and then acetylated; the xanthone (III) was converted into the corresponding dioxanthylene,⁶ while compounds (IV) and (V) were acetylated. Theoretically, it should be possible to obtain the two last compounds by condensation of *p*-cresol with chloroform, but experiments indicated that only (IV) could be isolated. No reaction was observed when methylene chloride was used.

EXPERIMENTAL

p-Cresol was extra pure and distilled within 1°. Carbon tetrachloride and chloroform were AnalaR. Light petroleum had b. p. 60–80° and crystallisations of crude products were carried out with charcoal. Microanalyses were by Dr. Zimmermann, Melbourne.

¹ J. E. Driver and T. F. Lai, *J. Chem. Soc.*, 1958, 3009.

² T. Zincke and R. S. Suhl, *Ber.*, 1906, **39**, 4148.

³ M. Nencki, *J. prakt. Chem.*, 1882, [2], **25**, 275.

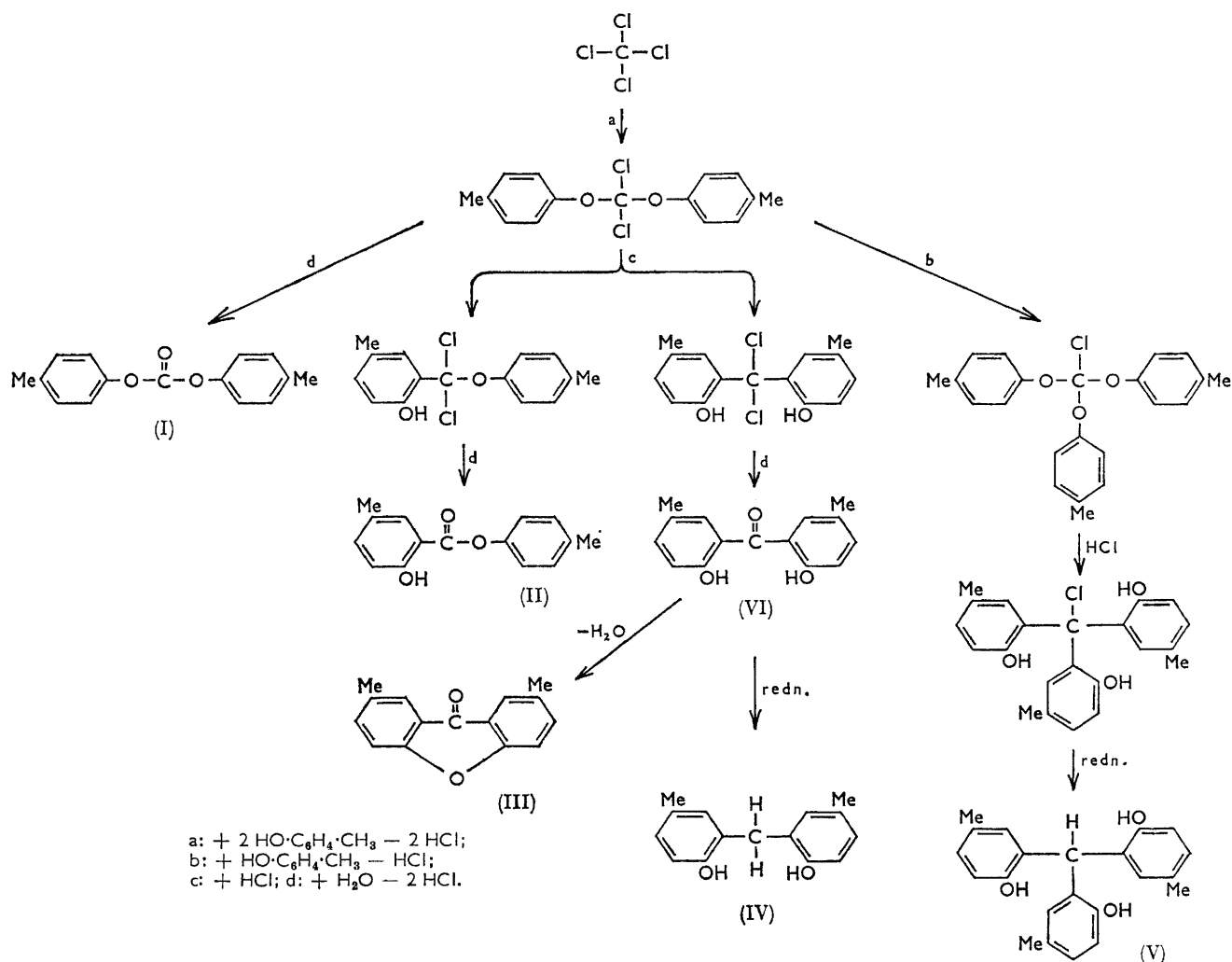
⁴ G. Gurgenjanz and S. Kostanecki, *Ber.*, 1895, **28**, 2311.

¹ M. Gomberg and H. R. Snow, *J. Amer. Chem. Soc.*, 1925, **47**, 198.

² M. Gomberg and L. C. Anderson, *J. Amer. Chem. Soc.*, 1925, **47**, 2022.

Condensation of p-Cresol with Carbon Tetrachloride in the Presence of Anhydrous Zinc Chloride.—36 g. of *p*-cresol and 30 g. of anhydrous zinc chloride in a flask with reflux condenser and calcium chloride tube were heated to 125° and carbon tetrachloride (16 g.) was added dropwise. The contents were kept at 125° for 3 hr. After cooling, the excess of *p*-cresol and carbon tetrachloride were steam-distilled out. The residue (10 g.) was collected, washed, and dried. (If the condensation was carried out for 22½ hr.,

ammonia was washed with water and extracted four times with 4% sodium hydroxide solution. Acidification with dilute acetic acid gave, after three days, a precipitate which was filtered off, washed, dried, and crystallised from carbon tetrachloride. Crystals of 2,2',2''-trihydroxy-5,5',5''-trimethyltriphenylmethane were obtained which darkened at 145° and melted with complete charring at 158° (Found: C, 79.4; H, 6.3. C₂₂H₂₂O₃ requires C, 79.0; H, 6.6%).



the yield of the residue was 22 g., but consisted largely of resins from which no crystalline substance could be isolated.)

The crude product was dissolved in light petroleum and the solution extracted three times with 2.8% aqueous ammonia. Acidification with dilute acetic acid gave, after standing for three days, a solid which was filtered off, washed, dried, and crystallised from light petroleum three times, giving 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane, m. p. 125–125.5° (lit.,⁷ 126°) (Found: C, 79.2; H, 7.0. Calc. for C₁₅H₁₆O₂: C, 79.0; H, 7.0%).

The light petroleum solution after extraction with aqueous

The light petroleum solution after extraction with aqueous sodium hydroxide was washed with water and dried (Na₂SO₄). It was concentrated and allowed to crystallise. Four recrystallisations from the same solvent gave colourless needles of di-*p*-tolyl carbonate, m. p. 112.5–113° (lit.,⁸ 113°). The mother-liquor was further concentrated and allowed to stand. The solid was filtered off and recrystallised twice from light petroleum. Colourless crystals of *p*-tolyl 2-hydroxy-5-methylbenzoate were obtained, m. p. 74–75° (lit.,⁹ 74–75°).

The residual mother-liquor contained 2,7-dimethyl-xanthone mixed with di-*p*-tolyl carbonate and *p*-tolyl

⁷ Beilsteins Handbuch der Organischen Chemie, Vierte Auflage, Erstes Ergänzungswerk, Sechster Band, Verlag von Julius Springer, Berlin, 1931, p. 493.

⁸ A. F. Holleman and J. M. A. Hoefflake, *Rec. Trav. chim.*, 1916, **36**, 272.

⁹ Ref. 7, Zehnter Band, 1924, p. 229.

2-hydroxy-5-methylbenzoate, but it was not possible to isolate the first *pure* by fractional crystallisation. Consequently the condensation of *p*-cresol and carbon tetrachloride with zinc chloride was repeated at 125° for 4 hr. The residue (15 g.), after removal of excess of *p*-cresol and carbon tetrachloride, was digested for 1 hr. with 200 ml. of 5% aqueous sodium hydroxide in which the 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane and 2,2',2''-trihydroxy-5,5',5''-trimethyltriphenylmethane were soluble. In this process the di-*p*-tolyl carbonate was converted into *p*-cresol and carbon dioxide, while the *p*-tolyl 2-hydroxy-5-methylbenzoate was hydrolysed to *p*-cresol and the appropriate benzoic acid, all products being soluble in sodium hydroxide. The insoluble tar (5 g.) was washed with water, dried, and extracted with light petroleum (Soxhlet) giving a red solution, which was chromatographed on alumina (350 g.). Portions (500 ml.) of the eluate were collected, the eluents being in order: (1) light petroleum, (2) 33% benzene–67% light petroleum, (3) 67% benzene–33% light petroleum, (4) benzene, (5) ethyl acetate. From the third group of eluates, yellowish needles of 2,7-dimethylxanthone were obtained, m. p. 142–143° (lit.,¹⁰ 143°).

Identification of Condensation Products.—(a) *Acetylation of 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane and 2,2',2''-trihydroxy-5,5',5''-trimethyltriphenylmethane.* The acetylation was carried out using a mixture of anhydrous sodium acetate and acetic anhydride at 100°. Pure crystals, respectively, of 2,2'-diacetoxy-5,5'-dimethyldiphenylmethane, m. p. 108–109° (Found: C, 73.0; H, 6.3. Calc. for C₁₉H₂₀O₄: C, 72.8; H, 6.4%) and 2,2',2''-triacetoxy-5,5',5''-trimethyltriphenylmethane, m. p. 194–194.5° (slight charring) (Found: C, 73.3; H, 6.0. Calc. for C₂₈H₂₈O₆: C, 73.0; H, 6.1%) were obtained.

(b) *Preparation of carbanilide from di-*p*-tolyl carbonate.* A little of the substance (1 mol.) was heated with aniline (2 mol.) and a little copper powder in a sealed tube at 150–180° for 3 hr. The brown residue was washed with dilute hydrochloric acid, and a phenolic smell was noticed. It was washed with dilute sodium hydroxide, filtered, washed with water, and crystallised from 95% alcohol. Colourless needles of carbanilide separated, m. p. 237–238° (lit.,¹¹ 238–239°).

(c) *Hydrolysis of *p*-tolyl 2-hydroxy-5-methylbenzoate.* The hydrolysis was carried out by refluxing with 2*N*-sodium hydroxide for 1½ hr. The resulting 2-hydroxy-5-methylbenzoic acid after being crystallised from hot water, had m. p. 151–151.5° (lit.,¹² 151°). The acetyl derivative of the acid, after being crystallised from glacial acetic acid, had m. p. 142.5–143.5° (lit.,¹³ 142–143°).

(d) *Conversion of 2,7-dimethylxanthone into 2,7,2',7'-tetramethyldixanthylene.* The xanthone was dissolved in acetic acid and zinc dust was added, together with a drop of hydrochloric acid from time to time. The mixture was heated to boiling and when the reduction was complete the dixanthylene was filtered off and dissolved in boiling xylene. Hot alcohol was added to the solution, when

almost white needles were obtained, m. p. 275–276° (lit.,⁹ 275–277°).

*Condensation of *p*-Cresol with Chloroform in the Presence of Anhydrous Zinc Chloride.*—36 g. of *p*-cresol and 20 g. of zinc chloride in a dry flask with a reflux condenser and calcium chloride tube were heated to 135° and chloroform (13 g.) was added dropwise whereupon a pink colour developed. The contents were kept at this temperature for 7 hr., cooled, and steam-distilled to remove the unchanged *p*-cresol and chloroform. The residue (7 g.) was collected, washed, dried, and extracted (Soxhlet) with light petroleum. The resulting pink solution was extracted with 4% aqueous sodium hydroxide solution which was then acidified with dilute acetic acid. The precipitate was filtered off, washed, dried, and crystallised three times from light petroleum. The crystals had m. p. 125° (not depressed on admixture with a sample of 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane).

*Attempted Condensation of *p*-Cresol with Methylene Chloride in the Presence of Anhydrous Zinc Chloride.*—*p*-Cresol (36 g.), methylene chloride (13 g.), and zinc chloride (20 g.) were heated at 135° for 24 hr. No apparent reaction took place and the contents remained colourless. Steam distillation gave no solid residue.

*Attempted Condensation of *p*-Cresol with Carbon Tetrachloride in the Presence of Anhydrous Aluminium Chloride.*—*p*-Cresol (36 g.) and aluminium chloride (30 g.) were put in a flask fitted with a reflux condenser and a calcium chloride tube. Hydrogen chloride was evolved and the contents solidified. Carbon tetrachloride (16 g.) was added dropwise while the contents were warmed on a steam-bath. The contents were kept at 100° for 10 hr. Water (200 ml.) was added and the excess of *p*-cresol and carbon tetrachloride were removed by steam-distillation. Only resin separated when attempts were made to isolate crystalline substances from the residue (6 g.).

*Reaction of *p*-Cresol with Excess of Carbon Tetrachloride in the Presence of Aluminium Chloride.*—*p*-Cresol (25 g.) was dissolved in carbon tetrachloride (125 g.) and the solution was warmed on a boiling-water bath under a reflux condenser and calcium chloride tube. Anhydrous aluminium chloride (30 g.) was added in small portions and the contents kept at 100° for 2 hr. The excess of carbon tetrachloride was distilled off and the black solid residue treated with dilute hydrochloric acid. This was steam-distilled and when all the *p*-cresol had been removed, a white solid began to distil which was separately collected. The dried product crystallised from light petroleum as large colourless prisms of 1-methyl-1-trichloromethylcyclohexa-2,5-dien-4-one, m. p. 104–105° (lit.,⁴ 105°). A sample of this ketone was converted into its oxime which was crystallised from light petroleum and then had m. p. 132° (lit.,⁴ 134°).

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¹⁰ A. Schönberg and W. Asker, *J. Chem. Soc.*, 1946, 609.

¹¹ I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," vol. 1, Eyre and Spottiswoode, London, 1953, p. 426.

¹² Ref. 9, p. 227.

¹³ Ref. 9, p. 228.