

(excess) sulfur, which proceeded smoothly at 250° provided an extremely high yield of the cyclic monosulfide (CF₂)₄S, thiaperfluorocyclopentane.^{3a} This compound, owing to its "globular" shape and weak intermolecular forces, resembles cyclohexane and perfluorocyclohexane in having a relatively high freezing point (-6.5°) and a very low entropy of fusion (*ca.* 2 e.u.), which corresponds to very little inhibition of motion in the crystal. At -127.2° there is a solid state transition with an entropy change of 18 e.u., a more nearly "normal" value for the immobilizing of fluorocarbons.⁴

EXPERIMENTAL

Thiaperfluorocyclopentane. Into each of five 30-ml. heavy-walled borosilicate glass ampoules was placed 7.0 g. of 1,4-diiodoperfluorobutane,⁵ n_D^{25} 1.4265, (total 0.077 mole) and 1.0 g. of sulfur (total 0.156 g.-atom). These were sealed *in vacuo*, heated for 20 hr. at 250° in a rocking tube-oven, then chilled in liquid air, opened cautiously, and warmed to room temperature. The crude liquid reaction product, decanted from the solid lumps of iodine and unchanged sulfur, weighed 17.0 g. A portion, 11.7 g., was distilled in an efficient 10-cm. packed⁶ fractionating column, and from it there was obtained 9.8 g. of thiaperfluorocyclopentane, (CF₂)₄S, (0.042 mole), corresponding to a yield of 79% from the diiodide.

*Anal.*⁷ Calcd. for C₄F₈S; C, 20.70; S, 13.82. Found: C, 20.8; S, 13.9.

Thiaperfluorocyclopentane has b.p. 40.7°, n_D^{25} 1.3052, d_4^{25} 1.6339 ± .0003, f.p.^{4,8,9} -6.5°, and solid state transition point,^{4,9} -127.2°. The heat of fusion was estimated as 0.5 kcal./mole (entropy of fusion *ca.* 2 e.u.) and the heat of transition as approximately 2.6 kcal./mole (entropy of transition *ca.* 18 e.u.) by the relative area method,⁹ the equipment having been calibrated with cyclohexane, toluene, and other similar materials. The observed molar refraction, 26.92 cc., leads¹⁰ to an atomic refraction of 7.40 for sulfur, a value lower than the usual Eisenlohr values due to electron withdrawal by the perfluorinated group. The strongest bands in the infrared spectrum of the vapor are at 7.42, 7.76, 8.22, 8.75, and 10.10 microns.

The ultraviolet spectrum (0.1% in isoctane) shows a single band having $\lambda_{max} = 2211 \text{ \AA.}$, $\epsilon_{max} = 50$, and width at half-height $W_{1/2} = 6920 \text{ cm.}^{-1}$

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and especially for the development of a modified procedure for compounds of this type⁷; and Dr. J. J. McBrady for infrared spectroscopy.

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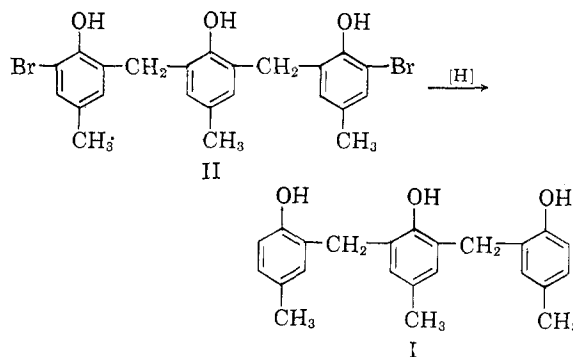
Phenol-Formaldehyde Condensations

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The condensation of 2,6-dihydroxymethyl-*p*-cresol with excess *p*-cresol gives a well defined crystalline product, m.p. 215°.¹⁻³ The structure of this compound has been in some doubt since both a linear "tri-nuclear" dibenzylphenol structure^{1,3} and a cyclic "tetra-nuclear" structure² have been suggested. Very recently, Hayes and Hunter⁴ presented good evidence for the linear "tri-nuclear" structure.

We have confirmed the findings of Hayes and Hunter by the unambiguous synthesis of 2,6-bis-(2-hydroxy-5-methylbenzyl)-*p*-cresol, I, *via* debromination of 2,6-bis(2-hydroxy-3-bromo-5-methylbenzyl)-*p*-cresol, II.



The condensation product of 2,6-dihydroxymethyl-*p*-cresol and excess *p*-cresol was identical by microanalysis, melting point, mixed melting point, and infrared absorption spectrum with I.

As supporting evidence for the "tetra-nuclear," 2:2 (2,6-dihydroxymethyl-*p*-cresol:*p*-cresol) structure, Niederl and McCoy² reported that the equimolar condensation of 2,6-dihydroxymethyl-*p*-cresol with *p*-cresol yielded a crystalline, well defined product. We attempted to repeat this experiment, although we could not reproduce the

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(2) J. B. Niederl and J. S. McCoy, *J. Am. Chem. Soc.*, **65**, 629 (1943).

(3) S. R. Finn and G. J. Lewis, *J. Soc. Chem. Ind. (London)*, **69**, 132 (1950).

(4) B. T. Hayes and R. F. Hunter, *J. Appl. Chem.*, **8**, 743 (1958).

(3a) ADDED IN PROOF: This compound was recently claimed in U.S. Patent 2,931,803 (C. G. Krespan, to the Du Pont Co.), and was made by the thermal reaction of tetrafluoroethylene with sulfur.

(4) L. L. Burger and G. H. Cady, *J. Am. Chem. Soc.*, **73**, 4243 (1951); also V. E. Stiles and G. H. Cady, *J. Am. Chem. Soc.*, **74**, 3771 (1952).

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(7) H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27**, 146 (1955). Furnace temp. 1200°.

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experimental conditions exactly, and obtained only resinous material.

On the other hand, condensation of 2,6-dihydroxymethyl-*p*-chlorophenol with excess *p*-cresol proceeded in a completely analogous manner as when 2,6-dihydroxymethyl-*p*-cresol was condensed with excess *p*-cresol. A well defined, crystalline product, m.p. 222–223°, was obtained. Because of the presence of chlorine, microanalyses clearly permitted a choice in favor of the "tri-nuclear," 1:2 (2,6-dihydroxymethyl-*p*-chlorophenol:*p*-cresol) condensation product, 2,6-bis(2-hydroxy-5-methylbenzyl)-*p*-chlorophenol; a "tetra-nuclear," 2:2 condensation product is clearly ruled out. Similarly, condensation of 2,6-dihydroxymethyl-*p*-cresol with either *p*-chlorophenol or *p*-bromophenol gave in each case, the "tri-nuclear," 1:2 (2,6-dihydroxymethyl-*p*-cresol:*p*-halophenol) condensation product, characterized as such by microanalysis.

EXPERIMENTAL⁵

*2,6-Bis(2-hydroxy-3-bromo-5-methylbenzyl)-p-cresol.*³ A mixture of 8.4 g. (0.05 mole) of recrystallized 2,6-dihydroxymethyl-*p*-cresol and 65 g. (large excess) of 2-bromo-*p*-cresol was warmed on the steam bath until nearly all the dihydroxymethyl derivative had dissolved. The mixture was cooled to 40°, and treated with 1 ml. of concd. hydrochloric acid. After a short time, the mixture was treated with 50 ml. of petroleum ether (b.p. 30–60°) and permitted to stand.

After a week, the reaction mixture was diluted with 100 ml. of petroleum ether, the solid product was filtered and washed copiously with petroleum ether.

The solid was recrystallized from alcohol-water, acetic acid-water (several times) and finally from acetic acid to give a colorless, microcrystalline product, m.p. 175–177°; lit., m.p. 176°.

2,6-Bis(2-hydroxy-5-methylbenzyl)-p-cresol. A sample of the dibromo compound (1.8 g., 0.0035 mole) was dissolved in 50 ml. of 95% ethanol and 4 ml. of 10% sodium hydroxide. The solution was further treated with 0.1 g. of palladium-carbon catalyst and hydrogenated in a Parr apparatus for several days. The catalyst was then filtered, and the clear filtrate diluted with an equal volume of water. The solution was then neutralized with several drops of concentrated hydrochloric acid and the now cloudy solution concentrated on the steam bath. The solid which separated from solution was filtered and recrystallized from acetic acid. The crystalline solid, still moist with acetic acid, was digested with boiling benzene for several minutes, filtered, washed copiously with petroleum ether, and dried to give a very pure sample, m.p. 215–217°.

Anal. Calcd. for C₂₂H₂₄O₃: C, 79.28; H, 6.94; mol. wt., 348. Found: C, 79.45; H, 7.17; mol. wt.,⁶ 331 ± 10.

A sample of the condensation product of the dihydroxymethyl-*p*-cresol with a large excess of *p*-cresol,² purified as above, melted at 215–217°, also; mixed m.p. 214–216°.

Anal. Calcd. for C₂₂H₂₄O₃ ("tri-nuclear" product): C, 79.28; H, 6.94; mol. wt., 348. Calcd. for C₃₂H₃₂O₄ ("tetra-nuclear" product): C, 79.97; H, 6.71; mol. wt., 481. Found: C, 79.09; H, 6.91; mol. wt.,⁶ 298 ± 10.

Comparison of the infrared absorption spectra of the two samples furnished additional evidence of their identity.

*Equimolar condensation of 2,6-dihydroxymethyl-*p*-cresol and *p*-cresol.* A mixture of 8.4 g. (0.05 mole) of recrystallized 2,6-dihydroxymethyl-*p*-cresol, 5.4 g. (0.05 mole) *p*-cresol, and 50 ml. of glacial acetic acid was warmed on the steam bath to give a clear solution (a solution did not form at room temperature), chilled in ice, and the slurry saturated with anhydrous hydrogen chloride during cooling in ice water. The solution which formed was permitted to stand at room temperature. After 1 week, the solid product which had separated from solution was filtered and drained with suction. The solid was nonhomogeneous and could be separated into three fractions: soluble in cold acetic acid, soluble in hot acetic acid, and insoluble in acetic acid. All three fractions melted over wide ranges and could not be recrystallized from acetic acid, aqueous acetic acid, alcohol or aqueous alcohol.

*2,6-Dihydroxymethyl-*p*-chlorophenol.* A solution of 28 g. (0.25 mole) of *p*-chlorophenol, 12.5 g. of sodium hydroxide and 15 ml. of water was cooled to about 15° and treated with 55 ml. of 37% formalin solution. The mixture was permitted to stand at room temperature. After several days the reaction mixture had set to a very stiff paste. The mixture was diluted with 60 ml. of 15% brine solution and was stirred until fairly uniform. The solid was filtered, washed with 40 ml. of 15% brine solution, and drained with suction. After neutralization of an aqueous solution of the sodium salt with dilute acetic acid, the product was dissolved in methanol, a small amount of acetic acid was added, the solution was clarified and poured into a large volume of water. The nearly colorless product was filtered, washed with water, drained with suction, and dried at 55°. The yield of pure product was 10.8 g., m.p. 162–163°C.; lit.,⁷ m.p. 165°.

*2,6-Bis(2-hydroxy-5-methylbenzyl)-*p*-chlorophenol.* To a mixture of 4.8 g. (0.025 mole) of 2,6-dihydroxymethyl-*p*-chlorophenol and 30 ml. (large excess) of *p*-cresol was added 10 drops of concd. hydrochloric acid. No visible reaction occurred. The mixture was treated with 25 ml. of petroleum ether (b.p. 30–60°), warmed gently on the steam bath until all the petroleum ether had been evaporated and again treated with 25 ml. of petroleum ether. The reaction mixture was permitted to stand at room temperature. After several days, the reaction mixture had completely solidified. The solid mass was triturated with 50 ml. of petroleum ether, the slurry stirred until uniform, and the solid filtered. The solid was washed with petroleum ether, and drained dry with suction. A sample was twice recrystallized from glacial acetic acid, m.p. 220–222°. The sample appeared to be partially solvated.

Anal. Calcd. for C₂₂H₂₁ClO₃·1/3 CH₃CO₂H: C, 70.00; H, 5.79; Cl, 9.12. Found: C, 70.00; H, 6.47; Cl, 8.99.

The sample was desolvated by digestion with boiling benzene, followed by digestion and washing with boiling hexane; m.p. 222–223°.

Anal. Calcd. for C₂₂H₂₁ClO₃: C, 71.63; H, 5.74; Cl, 9.61. Found: C, 71.88; H, 5.656; Cl, 9.34.

The benzene extract from above was permitted to cool yielding a small amount of colorless needles. After another recrystallization from benzene and washing with hexane the sample melted at 222–224°.

Anal. Calcd. for C₂₂H₂₁ClO₃: Cl, 9.61. Found: Cl, 9.82.

*2,6-Bis(2-hydroxy-5-chlorobenzyl)-*p*-cresol.* Recrystallized 2,6-dihydroxymethyl-*p*-cresol (4.2 g., 0.025 mole) was dissolved in 35 g. (large excess) of previously melted *p*-chlorophenol. A few milliliters of hexane were added to prevent crystallization of the starting materials, and the mixture further treated with 10 drops of concd. hydrochloric acid. The reaction mixture which became milky was heated on the steam bath for a short time and then permitted to stand at room temperature. The gummy, semi-solid product was

(5) All melting points are uncorrected. Microanalyses were obtained by the late Mr. O. E. Sundberg and associates.

(6) Abraham Wilson, Louis Bini, and Robert Hofstader, *Anal. Chem.*, **33**, 135 (1961).

(7) M. Weiler and K. Berres, German Patent 510,447 (1930).

filtered and washed with a little benzene. The still gummy material was suspended in cold benzene, the slurry stirred until uniform, and the solid filtered. The more granular product was then digested with boiling benzene. The quite pure product was easily recrystallized from glacial acetic acid (twice) and then digested with boiling benzene. The product was subsequently washed with benzene and hexane, m.p. 242–244°; lit.,³ m.p. 239–240°. At this stage, microanalyses indicated that the sample was partially solvated with benzene. The sample was desolvated by digestion with boiling hexane and drying at 55° in vacuum for several days.

Anal. Calcd. for $C_{21}H_{13}Cl_2O_3$: C, 64.79; H, 4.66; Cl, 18.22. Found: C, 65.18; H, 4.45; Cl, 18.41.

Another sample was recrystallized from acetic acid. After preliminary drying at 50° for several days the sample was further dried in vacuum at 100° for 24 hr.

Anal. Calcd. for $C_{21}H_{13}Cl_2O_3$: C, 64.79; H, 4.65; Cl, 18.22. Found: C, 64.65; H, 4.87; Cl, 17.84, 17.79.

2,6-Bis(2-hydroxy-5-bromobenzyl)-p-cresol. To a partial solution of 35 g. (large excess) of *p*-bromophenol and 35 ml. of hexane at steam-bath temperature, was added 4.2 g. (0.025 mole) of recrystallized 2,6-dihydroxymethyl-*p*-cresol. The mixture was then treated with 10 drops of coned. hydrochloric acid, whereupon a vigorous exothermic reaction ensued. A dense, semi-solid mass separated from the reaction mixture. The supernatant was decanted and the residue treated with benzene. This treatment promoted rapid crystallization of the product. The product was filtered and washed with benzene. Then it was suspended in cold benzene, filtered, and digested with boiling benzene. Finally, the product was recrystallized from acetic acid (twice) followed by digestion with boiling benzene. The sample was washed with benzene and hexane and dried, m.p. 231–232° dec., with prior sintering and discoloration beginning at 215°. The sample appeared to be partially solvated with benzene. The sample was desolvated by digestion with hexane, followed by drying at 100° in vacuum for 24 hr.

Anal. Calcd. for $C_{21}H_{13}Br_2O_3$: C, 52.74; H, 3.79; Br, 33.43. Found: C, 52.59; H 3.88; Br, 33.24.

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Reactions of Antimony Pentachloride and Ferric Chloride with Deactivated Aromatic Compounds¹

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Earlier publications in this series have dealt with the interaction of antimony pentachloride³ and ferric chloride⁴ with simple alkyl- and halo-benzenes. This investigation is concerned with the scope of the reaction of these metal halides with deactivated aromatic compounds. Benzotrifluoride,

nitrobenzene and benzaldehyde were selected for study.

Benzotrifluoride. Products obtained from anti-mony pentachloride and benzotrifluoride included *m*-chloro- α,α,α -trifluorotoluene,⁵ *m*-benzoyl- α,α,α -trifluorotoluene, benzoic acid and tarry polymer. The compounds derived from side-chain attack might arise from precursors^{6–10} such as $C_6H_5CX_2^+$ ($X = F$ or Cl). It is presumed that *m*-benzoyl- α,α,α -trifluorotoluene is formed by hydrolysis¹¹ of the intermediate *m*- $C_6H_5CX_2C_6H_4CF_3$ ($X = F$ or Cl). Similar condensations of benzotrichloride with itself,¹² phenols^{13,14} and benzene¹⁵ have been reported.

On the other hand, ferric chloride reacted exclusively with the trifluoromethyl group of benzotrifluoride, yielding *m*-benzoyl- α,α,α -trifluorotoluene and benzoic acid as the only isolable products after hydrolysis, in addition to tar.

Nitrobenzene. Antimony pentachloride combined with nitrobenzene at 103–118° to give a 64% yield of chloronitrobenzene (predominantly *meta*).

In contrast, ferric chloride exhibited a quite different mode of reaction. Chloronitrobenzene, *p*-chloroaniline, 2,4,6-trichloroaniline, and chloranil were isolated in low yields. It seems reasonable that the amines rose *via* reduction of nitrobenzene by ferrous chloride. Robertson and Evans have discussed¹⁶ the relationship between the nature of the reducing system and chloroaniline formation in the reduction of nitrobenzene. The generation of chloranil is somewhat reminiscent of conversion of a *p*-aminophenol to a chloroquinone by oxidation with ferric chloride.^{17–19} Although the reaction sequences leading to the various products are un-

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(17) J. Cason, *Org. Reactions*, **4**, 311 (1948).

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(1) Part X of a series on *Reactions of Metal Halides with Organic Compounds*; from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

(2) Allied Chemical Corp. Fellow, 1958–1960.

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(4) P. Kovacic, C. Wu and R. W. Stewart, *J. Am. Chem. Soc.*, **82**, 1917 (1960); P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).