**Diphenylacetylene** (1.68 g., 10 mmoles) was dissolved in 25 ml. of Freon 11 ($CCl_3F$) and slurried with 2.0 g. of sodium fluoride. The mixture was thoroughly degassed and was equilibrated at −40°. The $OF_2$ was admitted to the reactor and 10 mmoles was consumed within 2 hr. The unchanged $OF_2$ was distilled off at −40° and the sodium fluoride was removed by filtration. Evaporation of the solvent produced 1.9 g. of yellow unstable oil with a very weak band at 5.49 (pH COF) and strong carbonyl absorption at 5.85, which agrees with the literature value[10] of 5.85 μ for α-phenyl-α,α-difluoroacetophenone. The 2,4-DNP prepared directly from this oil and recrystallized from ethanol had m.p. 181–182° (lit.[10] m.p. 180–181°).

**Methylphenylacetylene** (2.5 ml., 20 mmoles) was dissolved in a mixture of 5 ml. of Freon 11 and 5 ml. of diethyl ether. Sodium fluoride (2.0 g., 48 mmoles) was added and the entire mixture was thoroughly degassed. The $OF_2$ (20 mmoles) was passed into the reactor and work-up began at 50% $OF_2$ consumption. This required 70 min. at −78°. The excess $OF_2$ was removed and and the sodium fluoride was separated by filtration. The solvent was fractionated away and the pale yellow unstable oil was analyzed by vapor phase chromatography. The major product (81% yield, internal standard) is assigned the structure α-methyl-α,α-difluoroacetophenone and is accompanied by benzoyl fluoride (18%). The fluoro ketone had a carbonyl band at 5.85 μ and is therefore conjugated and analogous to α-phenyl-α,α-difluoroacetophenone mentioned above. The $F^{19}$ n.m.r. spectrum was a quartet ($J_{FH}$ = 20 c.p.s.) centered at +548 c.p.s. (TFA). The magnitude of the coupling constant is indicative of fluorine coupling with three equivalent protons on an adjacent carbon atom. The proton n.m.r. spectrum showed the nonaromatic protons as a triplet ($J_{FH}$ = 20 c.p.s.) centered at δ 8.6 in a ratio of 3:5 with the aromatic protons.

*Anal.* Calcd. for $C_9H_8F_2O$: C, 63.53; H, 4.74. Found: C, 62.97; H, 5.02.

**Pentyne-2** (3.4 g., 50 mmoles) was dissolved in 25 ml. of a 1:1 mixture of diethyl ether and Freon 11. Sodium fluoride (2.0 g.) was added and the solution was thoroughly degassed and equilibrated at −78°. The $OF_2$ (50 mmoles) was passed into the reactor and work-up began within 2 hr., (>90% consumption of $OF_2$). The unused $OF_2$ was distilled away and the sodium fluoride was separated by filtration. Distillation of the crude solution produced 4.2 g. (69% yield) of colorless liquid, b.p. 64–67° (756 mm.). Analysis by vapor phase chromatography (SF 96 at 52°) showed two products comprising 61 and 39% of the total. Both possessed carbonyl absorption at 5.71 μ ($CF_2\overset{|}{C}{=}O$) and represent the two possible isomeric difluoro ketones in a total yield of 69%. The proton n.m.r. spectrum of the 39% isomer showed a triplet ($J_{FH}$ = 20 c.p.s.) centered at δ 1.68 and represents the ($O{=}\overset{|}{C}{-}CF_2CH_3$) group. The $F^{19}$ n.m.r spectrum showed a quartet ($J_{FH}$ = 20 c.p.s.) at +898 c.p.s. (TFA) thus identifying the 39% compound as 2,2-difluoropentanone-3. The 61% isomer is 3,3-difluoropentanone-2 and showed the fluorine as a triplet centered at +1238 (TFA) ($J_{FH}$ = 16 c.p.s.).

*Anal.* Calcd. for $C_5H_8F_2O$: C, 49.18; H, 6.60. Found: C, 48.96; H, 6.34.

**Pentyne-1** (3.4 g., 50 mmoles) was dissolved in 20 ml. of a 1:1 mixture of Freon 11 and diethyl ether. Sodium fluoride (2.0 g.) was added and the reaction mixture was thoroughly degassed and equilibrated at −78°. After the uptake of 50 mmoles of $OF_2$ the products were distilled under reduced pressure (25°) and the solution was concentrated. Analysis by vapor phase chromatography (SF 96 at 55°) indicated a single major product in 23% yield (internal standard) which had carbonyl absorption at 5.70 ($-CF_2\overset{|}{C}{=}O$), and C–F absorption at 8.1 and 9.0–9.5 μ. The proton n.m.r. spectrum showed a single proton as a triplet at δ 5.68 ($J_{FH}$ = 54 c.p.s.) which is indicative of a ($O{=}\overset{|}{C}{-}CF_2H$) group. The fluorine n.m.r. spectrum was a doublet ($J_{FH}$ = 52 c.p.s.) centered at +1950 c.p.s. (TFA). No evidence was found for the positional isomer, 2,2-difluoropentanal-1.

*Anal.* Calcd. for $C_5H_8F_2O$: C, 49.18; H, 6.60. Found: C, 49.28; H, 6.94.

**Acknowledgment.**—This work was sponsored under Army Ordnance Contract DA-01-021 ORD-11878. We are grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for n.m.r. spectra.

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(10) J. Bornstein and M. R. Borden, *Chem. Ind.* (London), 441 (1958).

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# Oxidations with Peroxytrifluoroacetic Acid–Boron Fluoride. IV.[1,2] Chloromesitylene

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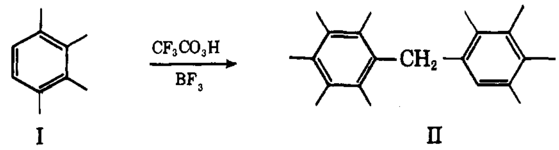
Oxidation of chloromesitylene with peroxytrifluoroacetic acid and boron fluoride gave, in addition to the expected chloromesitol, two diphenylmethane derivatives, 3,3′-dichloro-2,2′,4,4′,6,6′-hexamethyldiphenylmethane (VIII) and 4-(3′-chloro-2′,4′,6′-trimethylbenzyl)-3-chloro-2,6-xylenol (V), the latter being the principal reaction product. The structure of V was deduced largely from the mass-spectral fragmentation pattern and n.m.r. spectrum, and was confirmed by reduction to 4-(2′,4′,6′-trimethylbenzyl)-2,6-xylenol (VI), synthesized also by an independent route. Nitromesitylene gives an analogous oxidation product XI. The products are accounted for by the following reaction sequence: hydroxylation and further oxidation of one molecule of reactant to a benzylic ion, alkylation by this ion of a second molecule of reactant, debenzylation, and alkylation by the new benzylic ion of another molecule of reactant.

When prehnitene (I) was oxidized with peroxytrifluoroacetic acid and boron fluoride,[1a,c] a major product was 2,2′,3,3′,4,4′,5,5′-octamethyl diphenylmethane (II). It was suggested[1c] that II arose from alkylation of I with the appropriate tetramethylbenzyl cation; this, in turn, presumably was produced by debenzylation of III and IV, which were not isolated, but postulated as intermediates. 2,3,5- and 2,3,6-trimethylphenols, the other debenzylation products of III and IV, respec-



I II

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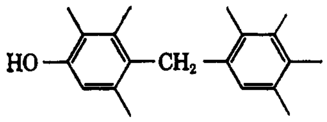
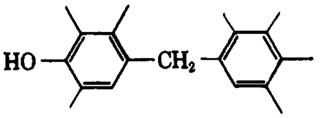
[1] For previous papers, see (a) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963); (b) A. J. Waring and H. Hart, *ibid.*, **86**, 1454 (1964); (c) H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

[2] We are grateful to the National Science Foundation, GP-71, for generous financial support.



III



IV

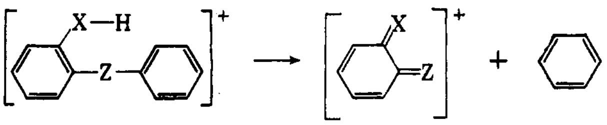
tively, were isolated from the oxidation. Finally, III and IV were assumed to be formed by oxidation of the 4-methyl group of prehnitol or isodurenol (both isolated) to a benzyl cation, followed by alkylation of prehnitene.

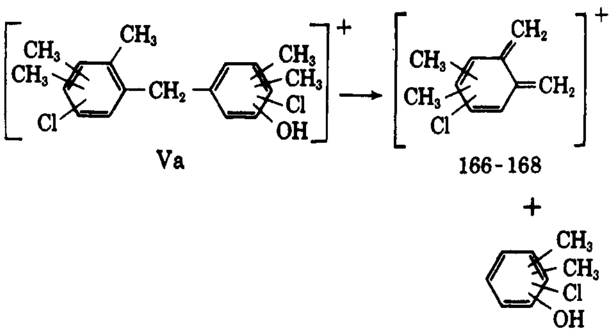
The present paper describes the oxidation of chloromesitylene and gives supporting evidence for the above scheme through the isolation of a product corresponding in structure to intermediate III. The structural determination illustrates the application of a general scheme for the mass-spectral analysis of diarylmethanes and related compounds.[3]

### Results and Discussion

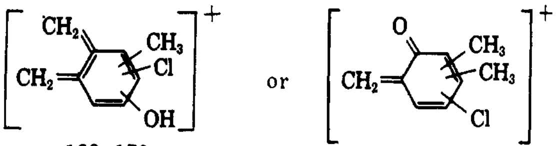
Chloromesitylene was oxidized at 5–7° with peroxytrifluoroacetic acid and boron fluoride in methylene chloride, using 3.4 moles of substrate per mole of oxidant. The oxidation was reasonably efficient, 0.85 mole of chloromesitylene being consumed per mole of peracid. Three crystalline products were isolated; the major one, formed in at least 39% yield, melted at 142.5–143.5°. Elemental analysis showed $C_{18}H_{20}OCl_2$; the parent mass (322 − 4 − 6) in the mass spectrum is consistent with this formula and the isotopic profile confirms the presence of two chlorine atoms. The infrared spectrum shows a hydroxyl group (3533 cm.$^{-1}$), and the n.m.r. spectrum in carbon tetrachloride shows five separate aromatic methyl peaks in the range $\tau$ 7.65–7.97; in addition, sharp singlets occur at 6.09 (2 protons), 3.97 and 3.11 (1 proton each), and a broad band at 5.45 (1 proton). These data are consistent with a dichloromonohydroxypentamethyldiphenylmethane structure. Further, one aromatic proton ($\tau$ 3.97) should be *ortho* to the methylene group.[4]

The mass-spectral decomposition reaction shown has been established for X = $CH_2$ or O and Z = $CH_2$ or O, and probably also applies to other appropriate substitutions, such as NH or S.[3] This generalization was instrumental in establishing the structure of our oxidation product.

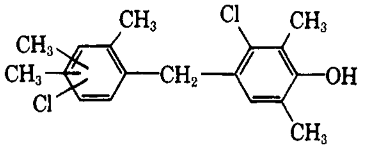




The most abundant ion occurs as a doublet at mass 166–168 (one chlorine atom), establishing the formula Va. If the second aryl ring also contained an *ortho* methyl or hydroxyl group, one would expect a second intense doublet at 168–170 due to the following ion.

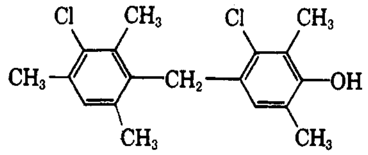


In fact, only a tiny peak appears at 170, ruling out such a structure. This ring must therefore have Cl and H in the *ortho* positions; if the original mesitylene skeleton has not been altered, the partial structure Vb is established.



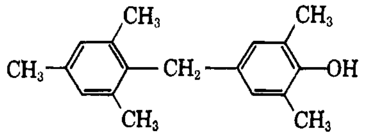
Vb

The remaining *ortho* position in the left ring must be occupied (only one *ortho* H in the n.m.r. spectrum), and if one again assumes no rearrangement of the mesitylene skeleton, the most probable structure for the oxidation product is V.



V

The structure of V was confirmed by reduction with lithium sand in *n*-butyl ether, which led to a dechlorinated product, m.p. 121–123°, shown to be VI. The n.m.r. spectrum of VI is consistent with this structure



VI

(see Experimental); the mass spectrum has a very strong peak at 132 and essentially nothing at 134, showing once again that the left ring has a methyl group *ortho* to the methylene, whereas the right ring can not have methyl or hydroxyl in an *ortho* position. Finally, VI was synthesized independently from chloromethylmesitylene and 2,6-xylenol; the product was identical (melting point, infrared, and n.m.r.) with that from the reduction of V.

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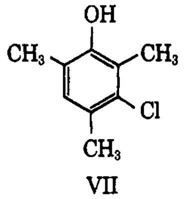
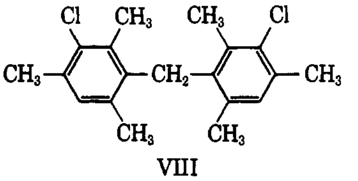
[3] S. Meyerson, H. J. Drews, and E. K. Fields, *J. Am. Chem. Soc.*, **86**, 4964 (1964).

[4] The n.m.r. spectra of numerous diarylmethanes of known structure show similar shielding of the *ortho* proton: C. A. Buehler, Ph.D. Thesis, Michigan State University, 1963.

The other two oxidation products of chloromesitylene were isolated pure in approximately 10% yield each. One of these, m.p. 83–84°, was identical (infrared, n.m.r.) with a sample of 3-chloromesitol (VII) prepared by careful chlorination of mesitol. The other, white prisms, melting at 118–119°, is assigned structure VIII on the basis of elemental analysis and n.m.r. spectrum (sharp singlets at $\tau$ 7.96, 7.85, 7.75, 5.97, and 3.21, with relative areas 3:3:3:1:1).

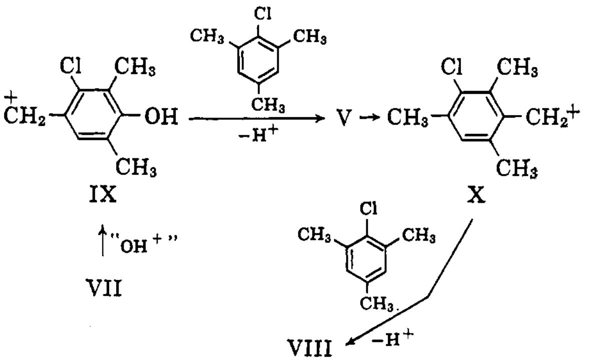


VII



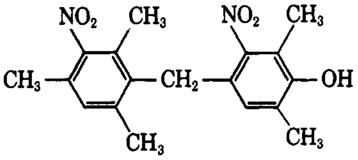
VIII

The three compounds V, VII, and VIII accounted for at least 62% of the oxidation products; these seem to be the major products, and they can be rationalized in terms of the mechanism previously proposed.[1c] Hydroxylation of chloromesitylene first produces chloromesitol (VII), some of which is further oxidized to resonance-stabilized ion IX. This reacts further with a second mole of chloromesitylene, leading to V. V is the major product, but some debenzylation occurs, leading to a small amount of VIII. The other debenzylation product, 3-chloro-2,6-xylenol, was not observed among the reaction products and was either missed or oxidized further. Debenzylation is less important in the chloromesitylene oxidation than in the prehnitene oxidation (*i.e.*, V is less readily debenzylated than III) probably because of the destabilizing influence of the chloro substituent on the intermediate benzyl cation X.



Oxidation of chloromesitylene using an equimolar amount of oxidant (rather than a large excess of aromatic) gave a 25% yield of chloromesitol, but the conversion was low (about 40%), even at 25°. Use of excess aromatic thus favors bimolecular products, as would be expected, but also seems to improve the overall conversion.

Nitromesitylene, oxidized using an excess of aromatic, gave only a single crystalline product, m.p. 244–245°, in 21% yield. The product is assigned structure XI, based on analysis, infrared and n.m.r. spectra, and analogy with V. The low recovery of pure, unchanged nitromesitylene (only about 60% of theory) and formation of considerable amounts of intractable tar suggest that the strongly electron-withdrawing nitro group inhibits the normal electrophilic substitution by "OH+" and favors side reactions.



XI

## Experimental

**Oxidation of Chloromesitylene.**—A methylene chloride solution of peroxytrifluoroacetic acid [prepared from 9.0 g. of trifluoroacetic anhydride, 15 ml. of methylene chloride, and 1.04 ml. (0.0383 mole) of 90% hydrogen peroxide] was added dropwise to a cooled (<7°) solution of 20.0 g. (0.130 mole) of chloromesitylene[5] in 50 ml. of methylene chloride. During the addition, which required 2.5 hr., boron fluoride was bubbled through the reaction mixture. Water (100 ml.) was added, the aqueous layer was salted and extracted with methylene chloride, and the combined organic layers were first washed with 10% solutions of sodium bisulfite and sodium bicarbonate and then dried over anhydrous magnesium sulfate. After the solvent had been removed, distillation of the residue gave 15.0 g. (75%) of v.p.c.-pure chloromesitylene. The residue (4.65 g.) was chromatographed on neutral alumina, using petroleum ether, benzene, and ether in sequence.

The fraction, 0.5 g., m.p. 108–110°, eluted with petroleum ether, was recrystallized from ethanol, giving 0.4 g. of 3,3′-dichloro-2,2′,4,4′,6,6′-hexamethyldiphenylmethane (VIII), white prisms, m.p. 118–119°. (The n.m.r. spectrum is described in the text.)

*Anal.* Calcd. for $C_{19}H_{22}Cl_2$: C, 71.02; H, 6.90; Cl, 22.07. Found: C, 71.14; H, 7.02; Cl, 22.10.

A second fraction, eluted mainly with benzene, weighed 0.5 g., m.p. 157–159°. It proved to be a mixture (primarily V and VII), and no pure compounds were isolated from it.

The major fraction, 3.65 g., m.p. 139–143°, was eluted with ether. This was further purified by rechromatographing on neutral alumina with ether as eluent, ultimately yielding 2.00 g. of white needles, m.p. 142.5–143.5°, on recrystallization from acetic acid-water. This was 4-(3′-chloro-2′,4′,6′-trimethylbenzyl)-3-chloro-2,6-xylenol (V).

*Anal.* Calcd. for $C_{18}H_{20}Cl_2O$: C, 66.87; H, 6.24; Cl, 21.93. Found: C, 66.85; H, 6.25; Cl, 22.02.

The infrared spectrum in carbon tetrachloride shows a sharp hydroxyl band at 3533 cm.$^{-1}$, and the n.m.r. spectrum in the same solvent has singlets at $\tau$ 7.65, 7.69, 7.80, 7.89, and 7.97 (3 protons each), 6.09 (2 protons), 3.97 and 3.11 (1 proton each), and a broad singlet at 5.45 (1 proton). The partial mass spectrum is given in Table I.

The residue from the purification of V contained some tar, from which was sublimed 0.3 g. of white, cotton-like solid, m.p. 83–84°. This material was not analyzed, but was identical (melting point, infrared, and n.m.r.) with an authentic sample of chloromesitol (see below).

**Reduction of V.**—A mixture of 0.069 g. (0.010 g.-atom) of lithium sand, 1.00 g. (0.0031 mole) of V, and 100 ml. of anhydrous ether was refluxed for 12 hr. The solvent was replaced by *n*-butyl ether, and the mixture was refluxed 2 hr. and then cooled to 0° and hydrolyzed with 20 ml. of water, added dropwise. Column (neutral alumina with benzene and ether eluents) and vapor phase (20% SE-30 silicone column, 230°) chromatographic work-up led to the recovery of 0.20 g. of starting material. The major product was 4-(2′,4′,6′-trimethylbenzyl)-2,6-xylennol (VI), m.p. 121–123°, from aqueous acetic acid, identical with an authentic sample (see below). The partial mass spectrum is given in Table I. Also formed was a small amount of a monochloro compound, probably 4-(2′,4′,6′-trimethylbenzyl)-3-chloro-2,6-xylenol, isolated by preparative gas chromatography as above, which shows three aromatic protons in the n.m.r., only one of which occurs at high field ($\tau$ 3.97).

**4-(2′,4′,6′-Trimethylbenzyl)-2,6-xylenol** (VI).—2,6-Xylenol (1.22 g., 0.01 mole) and chloromethylmesitylene[6] (1.68 g., 0.01 mole) were gently fused together in a flask fitted with a drying tube. Addition of a small quantity of anhydrous aluminum

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[5] E. T. McBee and R. E. Leech, *Ind. Eng. Chem.*, **39**, 393 (1947).

[6] A procedure analogous to that described by R. R. Aitken, G. M. Badger, and J. W. Cook, *J. Chem. Soc.*, 331 (1950), for chloromethylation of durene was used.

TABLE I

PARTIAL MASS SPECTRA OF V AND VI

| V | | | VI | | |
|---|---|---|---|---|---|
| Mass | Ion | Relative intensity | Mass | Ion | Relative intensity |
| 326 | | 0.60 | 256 | | 0.91 |
| 325 | | 2.82 | 255 | | 8.73 |
| 324 | | 14.5 | 254 | $C_{18}H_{22}O^+$ | 44.0 |
| 323 | | 4.51 | | | |
| 322 | $C_{18}H_{20}OCl_2^+$ | 22.3 | 240 | | 7.71 |
| | | | 239 | $C_{17}H_{19}O^+$ | 41.4 |
| 311 | | 0.82 | | | |
| 310 | | 0.88 | 137 | | 0.26 |
| 309 | | 4.69 | 136 | | 1.07 |
| 308 | | 1.32 | 135 | | 10.4 |
| 307 | $C_{17}H_{17}OCl_2^+$ | 7.15 | 134 | | 2.79 |
| | | | 133 | | 15.7 |
| 290 | | 0.74 | 132 | $C_{10}H_{12}^+$ | 100.0 |
| 289 | | 3.60 | | | |
| 288 | | 2.23 | 68.6[a] | | 0.12 |
| 287 | $C_{18}H_{20}OCl^+$ | 10.7 | | | |
| 172 | | 0.34 | | | |
| 171 | | 2.85 | | | |
| 170 | | 1.36 | | | |
| 169 | | 12.7 | | | |
| 168 | | 32.9 | | | |
| 167 | | 13.6 | | | |
| 166 | $C_{10}H_{11}Cl^+$ | 100.0 | | | |
| 85.6[b] | | 0.43 | | | |

[a] Metastable peak corresponding to the transition $(254^+) \rightarrow (132^+) + 122$. [b] Metastable peak corresponding to the transition $(322^+) \rightarrow (166^+) + 156$.

chloride initiated the reaction, which was allowed to proceed for 15 minutes at 25°. Petroleum ether (5 ml., b.p. 60–80°) was then added, and the mixture was kept at 60° for 5 hr. Hydrolysis and work-up gave 2.13 g. of recrystallized VI (from aqueous acetic acid), m.p. 121–123°; a second recrystallization raised the melting point to 128–130°.

*Anal.* Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.18; H, 8.72.

The infrared spectrum in carbon tetrachloride shows intense sharp bands at 3620 (hindered phenolic OH) and 1190 cm.$^{-1}$ (phenolic C–O stretch) as well as expected methyl, methylene, and aromatic substitution bands. The n.m.r. spectrum (in carbon tetrachloride) shows singlets at $\tau$ 7.85, 7.78, 7.70, 6.07, 3.33, and 3.02, with relative areas 6:6:3:2:2:2. A mixture melting point with the reduction product of V was undepressed.

**Chloromesitol (VII).**—A solution of chlorine in acetic acid (1 equiv.) was added over a period of 1 hr. to mesitol in the same solvent. The flask was kept at 0° in the dark during addition. Addition of water gave a precipitate, which was dissolved in ether, dried (magnesium sulfate), and evaporated to dryness. Slow vacuum sublimation at 65° removed mesitol, which gradually became richer in chloromesitol. Ultimately only chloromesitol, which was over 99% pure by v.p.c., m.p. 81–83°, sublimed over.[7]

*Anal.* Calcd. for $C_9H_{11}ClO$: C, 63.4; H, 6.51; Cl, 20.8. Found: C, 63.5; H, 6.62; Cl, 20.7.

The infrared spectrum has the expected bands, including those at 3620 (sharp, hindered phenolic OH) and at 1195 and 1175 cm.$^{-1}$ (C–O stretch). The n.m.r. spectrum in carbon tetrachloride has singlets at $\tau$ 7.82, 7.70, 5.60, and 3.15, with relative areas 3:6:1:1.

**Oxidation of Chloromesitylene (1:1 Mole Ratio).**—Chloromesitylene (4.65 g.) in methylene chloride was treated for 3 hr. at 25° with peroxytrifluoroacetic acid (from 4.9 ml. of trifluoroacetic anhydride and 0.82 ml. of 90% hydrogen peroxide) while 1 equiv. of boron fluoride passed through the solution. Work-up gave a yellow oil which was analyzed by v.p.c., showing 0.55 ± 0.02 g. (26.4%) of chloromesitol (VII) and 2.76 ± 0.09 g. (59.3%) of recovered chloromesitylene. The remaining product was tarry and could not be gas chromatographed. A similar run without boron fluoride gave virtually identical results.

**Oxidation of Nitromesitylene.**—Peroxytrifluoroacetic acid (from 4.5 g. of trifluoroacetic anhydride, 0.50 ml. of 90% hydrogen peroxide, and 15 ml. of methylene chloride) was added dropwise to a refluxing solution of 9.4 g. (0.057 mole) of nitromesitylene[8] in 50 ml. of methylene chloride. Boron fluoride was bubbled through the reaction mixture during addition, which required 2.5 hr. Water (100 ml.) was added, and the aqueous layer was salted and extracted with methylene chloride. Combined organic layers were washed with 10% sodium bicarbonate and then extracted with 40 ml. of Claisen's alkali. Work-up of the alkaline extract gave 0.65 g. (21%) of 4-(3′-nitro-2′,4′,6′-trimethylbenzyl)-3-nitro-2,6-xylenol (XI) as yellow platelets from 95% ethanol, m.p. 224–225°.

*Anal.* Calcd. for $C_{18}H_{20}N_2O_5$: C, 62.77; H, 5.85; N, 8.14. Found: C, 62.69; H, 5.71; N, 8.02.

The infrared spectrum shows a sharp hindered phenolic OH band at 3535 cm.$^{-1}$. The n.m.r. spectrum (deuterioacetone) has singlets at $\tau$ 7.92, 7.85, 7.82, 7.75, 6.12, 3.67 and 2.83, with relative areas 3:3:3:6:2:1:1.

**Mass Spectrometry.**—Mass spectra were measured with 70-v. electrons on a modified[9] Consolidated Model 21-103c instrument with the inlet system at 250°.

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[7] A. Siegel and H. Clodi, *Monatsh.*, 92, 914 (1961), give m.p. 84°. The compound was obtained by an indirect route, and the structure was assigned on the basis of analogy with the decomposition of other aryl phosphates.

[8] E. Powell and F. R. Johnson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, 1957, p. 449.

[9] H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Meoller, presented before ASTM Committee E-14, Seventh Annual Conference on Mass Spectrometry, Los Angeles, Calif., May 1959.