Formation of δ-Valerolactone (X).[8]—About 0.5 g. of IX is placed in an L-shaped side arm on an ordinary, straight vacuum trap. The outlet of this trap goes to a second trap and thence to a vacuum line. The first trap is provided with a joint so that it can be dismantled in the subsequent operations. The first trap is cooled with Dry Ice and the second with liquid nitrogen, after a pressure of about 0.8 atm. of helium has been introduced. The side arm, containing the betaine, is heated to 225°, and after about 1 min. the helium is slowly bled out of the system *via* the vacuum line. The system is then pumped for about 15 min., during which time trimethylamine collects in the second trap and X distils into the first trap.

δ-Bromovaleric Acid (XI).—X is washed out of the first trap with about 10 ml. of 48% hydrobromic acid and the solution is refluxed overnight.[9] Ether extraction gives XI, m.p. 137–139° (recrystallized from petroleum ether, b.p. 30–60°), in about 10% yield from IX.

Thallium Valerate (VIII).—A solution of 135 mg. of XI in 10 ml. of ethanol is dehalogenated with hydrogen at 1 atm., using 0.5 g. of 5% palladium on calcium carbonate as the catalyst.[10] The calculated amount of hydrogen is taken up in about 10 min., after which the solution is filtered and the ethanol removed under vacuum. The residue is taken up in water, acidified with sulfuric acid, and continuously extracted overnight with ether. A little less than 1 equiv. of an aqueous solution of thallous hydroxide is added to the ether extract and the mixture is stirred vigorously while the base is added to a phenolphthalein end point. This is taken to dryness and the crude XIII is triturated with several milliliters of absolute ethanol (inorganic thallium salts are insoluble). Then about twice the amount of ether is added to the supernatant ethanol and the product is obtained by refrigeration. The yield is about 90%, m.p. 160–164°. This salt can be used directly in running the Schmidt reaction.[12] The subsequent acids, made by the oxidation of the next lower amine (obtained in running the Schmidt reaction), are treated similarly after having been purified by gas chromatography. Each Schmidt reaction, from material based on either pyridone, gives XII representing one specific carbon atom in the original pyridine ring of nicotinic acid. The average activity level from 5 μc. of randomly labeled I is about 0.1 mμc./mg. of carbon.

Peroxytrifluoroacetic Acid–Boron Fluoride as a Source of Positive Hydroxyl[1,2]

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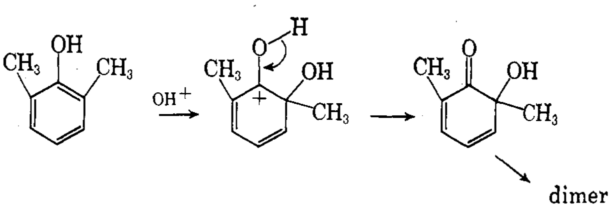
Peroxytrifluoroacetic acid–boron fluoride is shown to be an excellent reagent for effecting electrophilic aromatic hydroxylations with efficient use of the peracid. Mesitylene gave mesitol (88%), isodurene gave isodurenol (65%), but benzene gave only trace amounts of phenol. Prehnitene gave isodurenol, 2,3,5- and 2,3,6-trimethylphenol, 4,5,6,6-tetramethylcyclohexadienone, and 2,2′,3,3′,4,4′,5,5′-octamethyldiphenylmethane in addition to the expected prehnitol. These products can be rationalized by electrophilic attack of positive hydroxyl at substituted, as well as unsubstituted, aromatic carbon atoms, with 1,2-alkyl shifts in the former instance, and by hydride abstraction from methyl groups *para* to a phenolic hydroxyl.

It has long been recognized that organic peracids are sources of electrophilic (positive) hydroxyl in their reactions with the carbon–carbon double bond[4] and with certain aromatic hydrocarbons.[5] The hydroxyl cation was the assumed intermediate in the conversion of mesitylene to mesitol by hydrogen peroxide in acetic–sulfuric acid.[6] A Lewis acid (boron fluoride etherate) has been used in place of mineral acid with hydrogen peroxide to oxidize *m*-xylene, in low yield, to phenols and quinones.[7]

Peroxytrifluoroacetic acid was considered[8] to be an excellent source of positive hydroxyl, because the trifluoroacetate ion is a good leaving group. Using excess peracid, Musgrave, *et al.*, obtained 30–40% conversions of alkylbenzenes to phenols and quinones.[9] The orientation of the xylenols (2,4- and 2,6-) from *m*-xylene supported the contention that the reaction involved positive hydroxyl, rather than hydroxyl radicals.[10] The reaction has been extended to the preparation of *o*- and *p*-methoxyphenols from anisole and analogous phenoxyphenols from diphenyl ether.[11] The products from 2,6-dimethylphenol and peroxytrifluoroacetic acid depend upon reaction conditions; either 2,6-dimethylbenzoquinone or 6-hydroxy-2,6-dimethyl-2,4-cyclohexadienone dimer may predominate, slow addition of peroxide to the phenol favoring the latter (2,6-dimethyl-3-hydroxybenzoquinone is a minor reaction product).[12] Dienone dimer is presumably formed by attack of OH^+[13] at an already substituted position.[14]



It was considered likely that, if a Lewis acid facilitates the cleavage of hydrogen peroxide[7] and of certain diacyl

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support (G-488C).

[2] For a preliminary account, see C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963).

[3] National Science Foundation Cooperative Fellow, 1962–1963.

[4] For a review, see D. Swern, *Org. Reactions*, **7**, 378 (1953).

[5] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949).

[6] D. H. Derbyshire and W. A. Waters, *Nature*, **165**, 401 (1950); no experimental details are given.

[7] J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 24 (1962); this reagent converts aliphatic ketones to esters at room temperature in good yield.

[8] R. D. Chambers, P. Goggin, and W. K. R. Musgrave, *J. Chem. Soc.*, 1804 (1959).

[9] Conversions were calculated on the basis of hydrocarbon consumed: in fact, if calculated on amount of peracid used, they are much lower. The experimental technique described in the present paper (*vide infra*) affords much better conversions than previously reported,[8] even without boron fluoride.

[10] The hydroxyl radical, however, is also electrophilic; see R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc.*, 138 (1962). The question of whether the hydroxyl radical or the cation is involved in certain metal-catalyzed aromatic hydroxylations of biochemical interest is still unsettled; see R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 159; also, G. A. Hamilton and J. P. Friedman, *J. Am. Chem. Soc.*, **85**, 1008 (1963).

[11] J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 627 (1962).

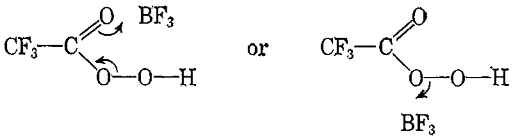
[12] J. D. McClure, *ibid.*, **28**, 69 (1963).

[13] The symbol OH^+ is used for convenience throughout this paper. It is recognized that the precise nature of the positive hydroxyl species is unknown; it may have trifluoroacetate or other ligands attached.

[14] The author[12] prefers a cyclic transition state involving initial hydrogen bonding of peracid to the phenolic hydroxyl, but this does not appear to be required.[15]

[15] A. J. Waring and H. Hart, *J. Am. Chem. Soc.*, **86**, 1454 (1964).

peroxides[16] to furnish positive oxygen fragments, it might also facilitate OH^+ formation from peroxytrifluoroacetic acid. This paper describes the use of $CF_3CO_3H-BF_3$ as a reagent for the oxidation of several methylbenzenes.



Results and Discussion

Addition of peroxytrifluoroacetic acid to a solution of excess mesitylene in methylene chloride, through which boron fluoride was passed, led to an exothermic reaction. The temperature was kept below 7° and an 88% yield of mesitol was obtained.[17] When the boron fluoride was omitted, the yield dropped to 45%. These yields are calculated on the amount of peracid used and represent a considerable improvement over an earlier procedure,[8] wherein the yield based on consumed mesitylene was equally high, but the conversion based on peracid was only 17%. "Aluminum trifluoroacetate," a white solid obtained from reaction of aluminum chloride with trifluoroacetic acid, was not so effective as boron fluoride but did improve the conversion (based on peracid) to 65%. It seems likely, then, that Lewis acids do function as catalysts for the oxidation, facilitating heterolytic cleavage of the O–O bond in the peracid.

Isodurene was readily converted in good yield to isodurenol by a similar one-step oxidation, but, when the reaction was applied to benzene, the yield of phenol was very small and an intractable black solid was obtained. One difficulty which must be overcome for the yield to be high is that the first oxidation product is, in general, more easily oxidized than the starting hydrocarbon. If, however, hydroxylation leads to a phenol in which positions *ortho* and *para* to the entering hydroxyl group are blocked, as in the case of mesitylene and isodurene, further oxidation is sufficiently slow that one can isolate the phenol in good yield. Use of an excess of hydrocarbon over peracid also improves the yield.[18]

The best evidence that the oxidation is the result of electrophilic substitution by OH^+, or some complexed form of it, and is not due to a reaction of hydroxyl radicals comes from a detailed study of the products from the oxidation of prehnitene (I).

Table I summarizes the oxidation products from prehnitene and peroxytrifluoroacetic acid, with and without boron fluoride. The catalytic effect of boron fluoride is again apparent. With it, peracid was used with 86% efficiency; without it, only 30% of the theoretical amount of prehnitene was oxidized. Although oxidized prehnitene was not quantitatively accounted for, the recovery is reasonably satisfactory when one includes the unidentified residues.

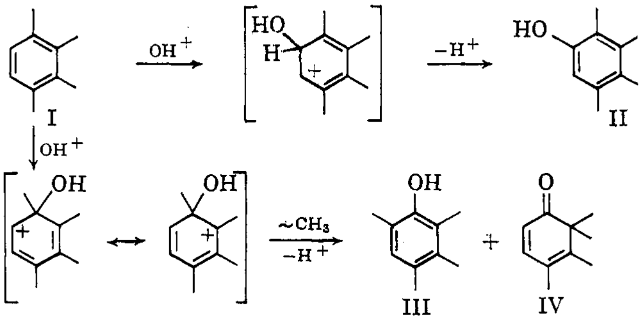
TABLE I

SUMMARY OF THE OXIDATION OF PREHNITENE WITH PEROXYTRIFLUOROACETIC ACID

	With BF_3		Without BF_3	
Prehnitene used (moles)	121.0		121.0	
Peracid used (mmoles)	38.3		38.3	
Prehnitene recovered (mmoles)	87.9		109.4	
Prehnitene oxidized (%)	86.2		30.3	
Products	mmoles	% of prehnitene oxidized	mmoles	% of prehnitene oxidized
Prehnitol (II)	3.0	9.1	2.2	19.0
Isodurenol (III)	1.2	3.6	2.0	17.2
4,5,6,6-Tetramethyl-2,4-cyclohexadienone (IV)	0.58	1.8	1.1	9.5
Unknown, mass 182	. . .	. . .	2.0	17.2
2,3,5-Trimethylphenol (X)	4.8	14.5	0.9	7.8
2,3,6-Trimethylphenol (XII)	1.8	5.4		
2,2′,3,3′,4,4′,5,5′-Octamethyldiphenylmethane (XI)	3.9	23.6	*a*	
Total	15.3	58.0	8.2	70.7
Residue (g.)	1.2		0.8	

[a] This product was present in the residue and identified by n.m.r., but was not isolated or quantitatively determined.

The three C_{10} products obtained with BF_3 can be accounted for by attack of OH^+ at an unsubstituted position, or at C-1 of prehnitene. The same products were obtained in somewhat greater yield (based on prehnitene oxidized) without BF_3; clearly BF_3 either catalyzes further reactions of II–IV, or generates a more reactive form of OH^+ which further oxidized these products.



Isolation of dienone IV constitutes excellent evidence that the hydroxylation involves cationic rather than radical intermediates, since the Wagner–Meerwein rearrangement necessary for its formation is not unusual, whereas a free-radical rearrangement of this type would be exceptional. Musgrave and co-workers[8] isolated a product, 2,3,5-trimethylbenzoquinone, from the oxidation of mesitylene with peroxytrifluoroacetic acid which also arises by a Wagner–Meerwein rearrangement. The structural assignment for IV rests on the following data. It has infrared bands at 1663 and 1630 cm.$^{-1}$ and an ultraviolet spectrum in ethanol, λ_{max} 327 mμ (log ϵ 3.48). These compare favorably with known similarly substituted dienones V[19] [(1667, 1634 cm.$^{-1}$; λ_{max}^{EtOH} 328

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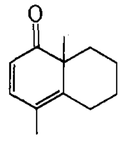
(16) See, for example, J. T. Edward, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962); also D. Z. Denney, T. M. Valega, and D. B. Denney, *J. Am. Chem. Soc.*, **86**, 46 (1964).

(17) Subsequent experiments by A. J. Waring, have shown that the conversion is essentially quantitative at −40°, using 1 mole of boron fluoride per mole of peracid.

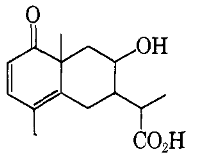
(18) It is perhaps noteworthy that recovered hydrocarbon is not appreciably isomerized.

(19) L. Mandell, D. Caine, and G. E. Kilpatrick, *J. Am. Chem. Soc.*, **83**, 4457 (1961).

mμ (log ε 3.55)] and VI[20] [1663, 1633 cm.$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 320 mμ (log ε 3.69)]. The n.m.r. spectrum of IV showed singlets at τ 8.85 and 8.15 with six protons each (aliphatic and allylic methyls) and doublets at τ 4.19 and 3.26 (J = 9.5 c.p.s.) each corresponding to a single vinyl proton. IV gave a 2,4-dinitrophenylhydrazone with a satisfactory microanalysis.[21]



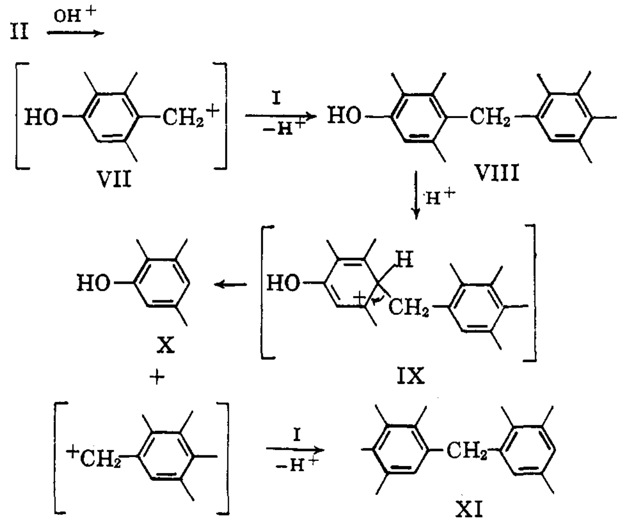
V



VI

Another C_{10} product was obtained in rather substantial amounts from the oxidation without BF_3, but was not produced (or was destroyed) when BF_3 was used. Its structure is not yet certain.[22]

2,3,5- and 2,3,6-trimethylphenols are apparently derived from loss of the 4-methyl group from II and III, respectively. This methyl shows up as the extra carbon atom in the octamethyldiphenylmethane (XI). The trimethylphenols probably do not result from oxidation of demethylated prehnitene, because recovered excess prehnitene was almost free of isomers or lower homologs, and it is unreasonable that trimethylbenzenes should not be recovered if such a process were involved (*i.e.*, there is no reason why trimethylbenzenes should all be oxidized to phenols, when the prehnitene is partially recovered). Furthermore, isomers of X and XII were not detected. A more plausible mechanism for the conversion of II to X and XI is shown in the scheme. Hydride abstraction from an already hydroxylated ring is facilitated by resonance stabilization of the resulting 4-hydroxybenzyl cation. Although postulated intermediate VIII was not isolated in the present reaction, similar products have been obtained with other substrates.[2] The hydroxyl group in VIII facilitates debenzylation, leading ultimately to X and XI. An analogous scheme starting with III accounts for the 2,3,6-trimethylphenol (XII). This mechanism requires that the yield of X plus XII equal the yield of XI. In fact (Table I), this sum exceeds the yield of XI, but the yield of XI is based on isolated, pure crystalline product and may be low (that of X and XII is based on v.p.c. curves). At any rate, they are the same order of magnitude. The ratio of yields of II:III is approximately the same as X:XII, which would be expected if X and XII arise from the demethylation of II and III, respectively, since there should be a negligible difference in the hydride abstraction rates for the two compounds.



The yield of hydride abstraction products (X–XII) is very much lower (and the yield of II and III correspondingly higher) when boron fluoride is omitted (Table I). Either BF_3 is involved (but not necessary) for the hydride transfer, or a "hotter" ozidizing agent is produced with BF_3 present. The yield of dienone IV is also higher without BF_3; this is not surprising, since the Lewis acid might polymerize IV.

Extension of this oxidation to other substrates will be the subject of future reports.

Experimental

Oxidation of Mesitylene.—A methylene chloride solution of peroxytrifluoroacetic acid was prepared by mixing 35 g. (0.167 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride, and 4.0 ml. (0.147 mole) of 90% hydrogen peroxide at 0°, then allowing the solution to warm to room temperature for several minutes. This peracid solution, cooled to 0°, was added dropwise to a solution of 56.1 g. (0.468 mole) of mesitylene in 100 ml. of methylene chloride, during which time boron fluoride was bubbled through the reaction mixture. The reaction was strongly exothermic, and the temperature was kept below 7° by a salt-ice bath. After addition was complete (2.5 hr.), the solution was allowed to warm to room temperature, 100 ml. of water was added, and the aqueous layer was separated and washed with three 25-ml. portions of methylene chloride. Combined organic layers were washed with 10% sodium bisulfite until washings gave a negative potassium iodide reaction, 10% sodium bicarbonate, then dried over anhydrous magnesium sulfate. After solvent removal, the residue was distilled through a 1-ft. helices-packed column, giving 32.0 g. of recovered mesitylene, b.p. 84–86° at 35 mm., and 17.7 g. of mesitol (88.5% based on peracid), b.p. 98° at 10 mm., m.p. and m.m.p. 69–70°. The tarry residue weighed 2 g.

Several modifications gave the following results. When only a slight excess of mesitylene (18.7 g.) was used (all other amounts and conditions constant), 6.0 g. of mesitol (30% based on peracid used), 7.0 g. of recovered mesitylene, and 5.7 g. of tarry residue was obtained.

When boron fluoride was omitted from the experiment described in detail above, but all other conditions were maintained, there was obtained 9.67 g. (45%) of mesitol, 39.0 g. of recovered mesitylene, and 4.25 g. of residue.

A material approximating aluminum trifluoroacetate in composition could be used in place of boron fluoride. To a stirred slurry of 22.3 g. (0.167 mole) of anhydrous aluminum chloride in 50 ml. of methylene chloride was added, dropwise, 57.0 g. (0.50 mole) of trifluoroacetic acid. The vigorously evolved hydrogen chloride was swept by nitrogen into an alkali trap (0.44 mole, 88% of theory for "aluminum trifluoroacetate"). After addition was complete, solvent was removed by warming to 60°, leaving a white-brown precipitate, to which 56.1 g.

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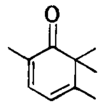
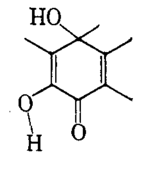
[20] W. Cocker, *Chem. Ind.* (London), 1041 (1955).

[21] The chemical shifts and n.m.r. pattern eliminate this alternative structure for the dienone (see especially ref. 15 for model compounds).



[22] A structure which is reasonably consistent with the data (see Experimental), and which is mechanistically plausible, is shown below, but further work is needed for a positive identification of this product.



(0.468 mole) of mesitylene was added. Peroxytrifluoroacetic acid (from 19.1 g. of trifluoroacetic acid, 50 ml. of methylene chloride, and 4.0 ml. of 90% hydrogen peroxide) was added, the temperature being kept at 25–30° during addition (2.5 hr.) by ice-bath cooling. Work-up gave 37.5 g. of unchanged mesitylene, 13.0 g. (65%) of mesitol, and 2.0 g. of residue.

Oxidation of Isodurene.—The reaction procedure was the same as the first one described for mesitylene. Isodurene (54.0 g., 0.410 mole) in 100 ml. of methylene chloride was treated with peroxytrifluoroacetic acid prepared from 30.9 g. (0.147 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride, and 3.7 ml. of 90% hydrogen peroxide. After hydrolysis and removal of the solvent, the dark brown liquid residue was chromatographed on alumina. Elution with petroleum ether (b.p. 60–90°) gave 33.5 g. of recovered isodurene, b.p. 76–78° at 10 mm. Elution with ether gave 12.9 g. (62.7%) of isodurenol, m.p. 79–81°.[23]

Oxidation of Prehnitene.—The reaction procedure was the same as described in detail for mesitylene, the amounts of reactants being 16.24 g. (0.121 mole) of prehnitene in 100 ml. of methylene chloride, and peroxytrifluoroacetic acid prepared from 9.0 g. (0.0424 mole) of trifluoroacetic anhydride, 30 ml. of methylene chloride, and 1.04 ml. (0.0383 mole) of 90% hydrogen peroxide. After reaction, 100 ml. of water was added, the layers separated, and the aqueous layer was saturated with sodium chloride and extracted with methylene chloride. Combined organic layers were washed with 10 ml. of 10% sodium bisulfite, 10 ml. of 10% sodium bicarbonate, and then extracted with 40 ml. of Claisen's alkali (14 g. of potassium hydroxide dissolved in 10 ml. of water, diluted with methanol to 40 ml.).

The alkaline extract was washed with methylene chloride, acidified with hydrochloric acid, saturated with salt, and extracted with ether. After drying (magnesium sulfate) and removal of the solvent, there remained 1.58 g. of residue which was taken up in carbon tetrachloride and vapor chromatographed[24] at 152°. The five well-resolved peaks were identified in order of retention time as prehnitene (7.6%); 2,3,6-trimethylphenol (15.8%), m.p. 59–61° (lit.[25] m.p. 62°), infrared identical to published spectrum[26]; 2,3,5-trimethylphenol (40%), m.p. 91–93°, λ_{max} (cyclohexane) 282, 278, and 273 mμ, infrared identical to published spectrum[26] (lit.[23] m.p. 95–96°, λ_{max} 282, 278, and 274 mμ); isodurenol (10.2%), m.p. and m.m.p. 81°, infrared and n.m.r. spectra identical with those of an authentic sample; prehnitol (27.4%), m.p. 81–83°, λ_{max} (ethanol) 277.5, 282.5, and 286.5 mμ, infrared identical to published spectrum[26] [lit.[27] m.p. 86–87°, λ_{max}[28] (ethanol) 277.5, 282.5, and 286.5 mμ].

The neutral fraction after Claisen's alkali extraction was washed with water, then dried over magnesium sulfate. After removal of solvent, the residue was distilled through a 7-in. vacuum-jacketed Vigreux column, giving 11.1 g. of prehnitene, b.p. 85–90° at 16 mm., pure by v.p.c., and a second fraction (0.71 g.), b.p. 90–125° at 16 mm. This fraction was analyzed by v.p.c., and contained 79.4% prehnitene, 12.2% **4,5,6,6-tetramethyl-2,4-cyclohexadienone**, 3.65% 2,3,5-trimethylphenol, 2.56% isodurenol, and 2.24% prehnitol, in order of increasing retention time. The ketone had infrared bands at 1663 and 1630 cm.$^{-1}$, a λ_{max} (ethanol) at 327 mμ (log ϵ 3.48), and its n.m.r. spectrum in carbon tetrachloride had singlets at τ 8.85 and 8.15 (six protons each) and doublets at τ 4.19 and 3.26, J = 9.5 c.p.s., one proton each. The ketone was converted to its 2,4-dinitrophenylhydrazone by standing with the reagent in ethanol for 7 days, followed by reflux for 30 min. Water was added to the cooled solution, and the resulting precipitate was extracted with chloroform, dried with magnesium sulfate and Bentonite[29]; the solvent was removed, and the residue was recrystallized from 95% ethanol, giving deep red crystals, m.p. 153°.

Anal.[30] Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.97. Found: C, 58.28; H, 5.53; N, 16.89.

The residue (2.55 g.) from distillation of the neutral fraction was chromatographed on Fluorosil using petroleum ether as eluant. There was obtained 1.10 g. of 2,2′,3,3′,4,4′,5,5′-octamethyldiphenylmethane, m.p. 150–151° (from ethanol). Its ultraviolet spectrum had λ_{max} (cyclohexane) 271 mμ (ϵ 290). The n.m.r. in carbon tetrachloride had bands at τ 7.92, 7.87 and 7.83 (24 protons), at 6.27 (two protons), and at 3.61 (two protons). The mass spectrum[31] had M^+ at 280 (calcd. mol. wt., 280.4).

Anal. Calcd. for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 90.04; H, 9.86.

The material was identical (mixture melting point and infrared and n.m.r. spectra) with an authentic sample prepared from prehnitene, paraformaldehyde, and sulfuric acid.[32]

The remaining neutral product (1.20 g.) was eluted from Fluorosil with ether–methanol. It was tarry, could not be crystallized, and had carbonyl bands in the infrared and n.m.r. bands from τ 7.60 to 8.70, but no bands from 2.0 to 3.8.

The reaction was repeated, except that the peroxide was intentionally omitted. From 8.12 g. of prehnitene there was recovered 7.50 g. (92.5%) of distilled, v.p.c. pure starting material; no other products were isolated.

The oxidation was repeated omitting the boron fluoride but otherwise using the same amounts of materials as described above. The residue from the Claisen's alkali extract weighed 1.05 g. and consisted of 8.1% prehnitene, 6.8% of a mixture of 2,3,6- and 2,3,5-trimethylphenol, an unidentified material (34.5%) not present when BF_3 was used, 20.9% isodurenol, and 29.8% prehnitol. The as yet unidentified[22] product had a molecular weight (mass spectrometry) of 182 (possibly $C_{10}H_{14}O_3$); the base peak was at mass 43. Its infrared spectrum showed hydroxyl (3.0 μ), broad carbonyl (5.8–5.9 μ), and carbon–carbon double bond (6.10 μ). It had a broad λ_{max} (ethanol) at 264 mμ (log ϵ 3.80). Its n.m.r. spectrum had singlets at τ 7.23, 7.87, 7.97, 8.35, and 8.72 with areas roughly 2:6:3:3:3, but the band at 7.87 was probably much too large because of trimethylphenol impurity (peak at mass 136).

The neutral fraction gave 14.28 g. of recovered prehnitene and 1.43 g. of a dark-brown liquid residue. This was separated into volatile (0.63 g.) and nonvolatile (0.80 g.) portions by distillation at 0.07 mm., with a pot temperature of 180°. The volatile fraction consisted of (v.p.c.) 51.2% prehnitene, 26.6% 4,5,6,6-tetramethyl-2,4-cyclohexadienone, 7.5% 2,3,5-trimethylphenol, 12.4% isodurenol, and 2.7% prehnitol. The nonvolatile product contained a trace of the octamethyldiphenylmethane, but was mainly nonaromatic with an infrared spectrum nearly identical with a similar product from the boron fluoride catalyzed oxidation.

Oxidation of Benzene.—A solution of 36.7 g. (0.468 mole) of benzene in 100 ml. of methylene chloride was oxidized, at <7°, with peroxytrifluoroacetic acid prepared from 35.1 g. (0.167 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride, and 4.3 ml. (0.157 mole) of 90% hydrogen peroxide. Boron fluoride was bubbled through the reaction mixture during the oxidation. The reaction mixture turned blue immediately and darkened during the reaction. Hydrolysis precipitated 5.5 g. of a black solid, which burned with difficulty and failed to melt below 250°. Alkaline extraction (20% sodium hydroxide) gave 1.0 g. of phenol; the neutral fraction gave 22.0 g. of recovered benzene.

Repetition, but with a sevenfold excess of benzene (85.7 g., 1.1 mole) gave similar results. Oxidation on this scale, but using "aluminum trifluoracetate" in place of boron fluoride gave only 2.5 g. of phenol. When the original oxidation was repeated without the boron fluoride, the black solid was not produced; much benzene was recovered, plus a small amount of tar.

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[23] D. H. Hey, *J. Chem. Soc.*, 1581 (1931).

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