analysis and to analysis for tertiary chloride by hydrolysis in 50% ethanol. In the case of isobutane, the excess hydrocarbon was removed, after chlorination was complete, by fractional distillation at a 10:1 reflux ratio in a 40 cm. × 12 mm. vacuum-jacketed column packed with glass helices and fitted with a low temperature head. When reflux no longer occurred, 75 ml. of chlorine-free, neutral dioxane was added to the flask carefully washing the head and column into the flask. The contents of the flask were diluted to 100 ml. with dioxane and aliquots of this solution analyzed as above.

The chlorination products of isobutane were tested for polychloride formation in the following manner. The reaction of 0.068 mole of chlorine with 1.5 mole of isobutane at −15° produced 0.066 mole of alkyl chloride and liberated 0.067 mole of hydrogen chloride. The chlorination product was fractionally distilled until all of the isobutane and most of the *t*-butyl chloride had been removed. The residue containing some of the monochlorides and all of the polychlorides formed in the reaction was analyzed for total chlorine content. The 38.40% chlorine found compares with 38.34% calculated for C_4H_9Cl, indicating the absence of significant amounts of higher chlorinated products.

The results of the chlorination experiments are summarized in Table II.

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[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

p-Methylbenzyl Hydroperoxide

BY E. J. LORAND AND E. I. EDWARDS

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p-Methylbenzyl hydroperoxide was prepared by the free radical-induced oxidation of *p*-xylene with molecular oxygen at 120–130°. Because of a competing reaction consisting in the fusion of two *p*-methylbenzyl radicals to form a crystalline hydrocarbon, the oxidation does not proceed by a chain mechanism. Isolation of the hydroperoxide was based on its solubility in dilute alkali. By-products of oxidation are *p*-methylbenzaldehyde, toluic acid and *p*-methylbenzyl alcohol. The hydroperoxide in a neutral solution is thermally stable up to almost 130°; in alkaline solution only at or below °C. Its acid-catalyzed decomposition yields mainly *p*-cresol (55%) and tolualdehyde (40%). A high melting, but still impure, trihydroperoxide related to the condensed (crystalline) hydrocarbon is also described.

The remarkable susceptibility to attack by oxygen of tertiary carbons adjacent to an aromatic ring, and even of secondary carbons in some cases (*e.g.*, in tetralin), is in sharp contrast to the inertness of the primary carbon under similar conditions. Hock[1] was the first to prepare a primary benzenoid hydroperoxide by the liquid-phase oxidation of *p*-xylene with molecular oxygen. The very low conversions obtained (0.2 to 0.3%), however, were not suitable for the preparation of substantial amounts of *p*-methylbenzyl hydroperoxide. Attempts to prepare this by the acid-catalyzed reaction of hydrogen peroxide and benzyl alcohol were unsuccessful, and a new approach to the oxidation of the methyl group was tried.[2] Free radicals should be able to remove a primary hydrogen, leaving a free *p*-methylbenzyl radical susceptible to the attack of molecular oxygen.

$$CH_3C_6H_4CH_3 + R\cdot \longrightarrow RH + CH_3C_6H_4CH_2\cdot \xrightarrow{O_2} CH_3C_6H_4CH_2OO\cdot$$

It soon became evident that removal of a primary hydrogen from xylene, even by the action of a free radical, required relatively high temperatures and more than catalytic amounts of an initiator to supply the free radicals. In most experiments *t*-butyl peroxide was used, although its relatively low boiling point (109°) limits the temperature of reaction to about 130°, which, in the course of the reaction, is gradually lowered to 120° by increasing amounts of low boiling decomposition products of the peroxide. The hydroperoxide content rises to a maximum of 4–4.5 g./100 cc. (or approximately 4.5–5.0% by weight) in about 2.5–3.0 hours and then drops. About half of the above maximum is reached in less than one hour; the limiting factor, as will be shown, is the autocatalytic decomposition of the hydroperoxide. The following reactions appear to be involved

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \quad (1)$$

$$CH_3C_6H_4CH_3 + (CH_3)_3CO\cdot \text{ (or } CH_3\cdot) \longrightarrow (CH_3)_3COH \text{ (or } CH_4) + CH_3C_6H_4CH_2\cdot \quad (2)$$

$$CH_3C_6H_4CH_2\cdot \xrightarrow{O_2} CH_3C_6H_4CH_2OO\cdot + CH_3C_6H_4CH_3 \longrightarrow CH_3C_6H_4CH_2OOH + CH_3C_6H_4CH_2\cdot \quad (3)$$

$$CH_3C_6H_4CH_2\cdot + \cdot H_2CC_6H_4CH_3 \longrightarrow CH_3C_6H_4CH_2CH_2C_6H_4CH_3 \quad (4)$$

Under the given conditions the *t*-butoxy radical seems to react quite readily with xylene as indicated by the relatively small amount of acetone (reaction 1) found in the reaction mixture and in the Dry Ice trap through which the exit gases passed. It is also to be noted that large amounts of *t*-butyl peroxide are consumed and that much crystalline hydrocarbon is formed according to reaction 4. These facts are inconsistent with the assumption of an oxidation chain of appreciable length which would start by the attack of the peroxy radical (arising from reaction 3) on a xylene molecule.

The free *p*-methylbenzyl radical can react either with oxygen or with another radical to form 4,4'-dimethylbibenzyl. This is apparent from the results of an experiment in which accidental inhibition prevented oxidation. The amount of the crystalline residue per 1000 g. of xylene input was more than 60% higher than in an uninhibited oxidation. The relatively low yield of the pure hydrocarbon "dimer" is accounted for by the further attack of free radicals on the condensed hydrocarbon, thus allowing for "trimer," and perhaps further

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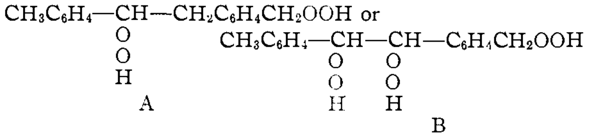
(1) H. Hock and C. Lang, *Ber.*, **76**, 169 (1943).

(2) Since the work reported in this paper was completed, C. Walling and J. A. Buckler (THIS JOURNAL, **75**, 4372 (1953)) have reported the preparation of benzyl hydroperoxide by the oxidation of benzylmagnesium chloride.

polymer homolog formation. That the absence of an oxidation chain (the estimated chain length is less than one) is not due to oxygen starvation was shown by the fact that conversion to the hydroperoxide was not increased when the oxygen pressure was raised to about 80 lb. per sq. in.

As the hydrocarbon "dimer" and "homologs" have secondary carbon atoms and as secondary hydrogens are more labile than primary ones, an oxidative attack on these structures is to be expected. The possibility also exists that both primary and secondary hydroperoxy groups may be present in the same molecule; that is



$$CH_3C_6H_4\text{—}\underset{\substack{O\\O\\H}}{CH}\text{—}CH_2C_6H_4CH_2OOH$$

A

or

$$CH_3C_6H_4\text{—}\underset{\substack{O\\O\\H}}{CH}\text{—}\underset{\substack{O\\O\\H}}{CH}\text{—}C_6H_4CH_2OOH$$

B

A product which may have such a structure was actually isolated from hydroperoxide concentrates stored in a refrigerator. It was a crystalline deposit which, after recrystallization, had a melting range of 132–137°. Its C, H and O content comes very close to that calculated for a mixture of A and B in the ratio of 1:2.

By-products of the oxidation are *p*-toluic acid (recovered from the Na_2CO_3 wash), *p*-tolualdehyde, *p*-methylbenzyl alcohol and the crystalline hydrocarbon. The reaction mixture also contains excess di-*t*-butyl peroxide and its decomposition products *t*-butyl alcohol and acetone. In the recovered product the main impurities are *p*-methylbenzaldehyde and *p*-methylbenzyl alcohol.

A typical concentrate had the following composition

Hydroperoxide, %	87.0 (20.5% O content)
C (by combustion), %	70.46
H (by combustion), %	7.60
O by difference, %	21.94
Aldehyde (polarimetric[3])	6 (0.8% O content)
Alcohol (calcd.)	4.88 (0.64% O by diff.)

The aldehyde is probably formed by the action of NaOH on the hydroperoxide, whereas the alcohol is the product of a Cannizzaro reaction, the equivalent amount of *p*-toluic acid formed remaining in solution after CO_2 neutralization.

The largest amount of by-product formed in the whole course of oxidation is the crystalline hydrocarbon. Although the well-characterized "dimer" (4,4′-dimethylbibenzyl) has been isolated, it is only one of the constituents. This is accounted for by further attack of free radicals on the condensed hydrocarbon, which allows for "trimer" and perhaps further polymer homolog formation by additional fusion.

The hydroperoxide is relatively stable; for example, a 2.65% solution in xylene after 2.5 hours at 130° still contained 2.54% ROOH, although thereafter an increasingly rapid decomposition took place. The reaction appears to be autocatalytic. The catalyst is *p*-toluic acid, a slight amount of which is initially formed during the induction period, and which is produced in increasing amounts after the reaction has been started. In contrast to tertiary hydroperoxides, solutions of *p*-methylbenzyl hydroperoxide in dilute NaOH are stable only at low temperatures. Thus, in 2% aqueous NaOH at 0° the hydroperoxide content was lowered from 4.5 to 4.4% in 17 hours, whereas at 27° there was a drop from 4.4 to 3.8% in less than 7 hours.

The action of alkali on *p*-methylbenzyl hydroperoxide has been described by Hock.[1] In the presence of a mineral acid two competing reactions take place. One of these consists in cleavage of the hydroperoxide into *p*-cresol and formaldehyde, and the other in dehydration to *p*-tolualdehyde.

Experimental

Induced Oxidation of Xylene to Hydroperoxide.—In a typical example 1000 g. of *p*-xylene was oxidized in a 2-liter, 3-necked flask having 2 or 3 vertical indentations and equipped with a motor-driven stirrer, a fritted glass sparge, a thermometer and an Ekert reflux condenser. A 100-g. portion of di-*t*-butyl peroxide (commercial) was first added, followed by 50-g. portions after every hour. The mixture was heated to vigorous boiling by means of a heating mantle. Samples were taken every half hour and analyzed for hydroperoxide by iodine liberation in isopropyl alcohol solution. The following values were typical.

Time, hour	Hydroperoxide in crude oxidate, g./100 cc.
0.5	2.07
1.0	2.70
1.5	3.48
2.25	4.02

The oxidate was cooled rapidly and washed four times with 200-cc. portions of 5% sodium carbonate to eliminate *p*-toluic acid. The hydroperoxide may be isolated by three methods. One consists in precipitation with 25% NaOH at 0° to −3° to obtain a white, relatively hard and filterable crystalline product, which is washed several times with hexane and carefully neutralized to *p*H 8–9 (*e.g.*, with CO_2). The second method, which is favored because of fewer complications, is based on extraction with 1-2% NaOH, at 0 to −3°, in the presence of a small amount of pentane or hexane to avoid crystallization of *p*-xylene. The extracts are washed with hexane, and the caustic is neutralized to a *p*H of about 9 with CO_2. The hydroperoxide separates as an oil and is extracted with a benzene–hexane mixture. After distilling off the solvents at reduced pressure, in the above case, 41.3 g. of product of 84% hydroperoxide content was recovered; in other experiments concentrations up to 90% were obtained. The third method of recovery is based on countercurrent partitioning between pentane and aqueous methanol (1:3 by volume) at 0°. The yield was good, but the concentration of hydroperoxide in the recovered product was only 62%. It is probable that this method can be substantially improved.

Numerous attempts were made to purify the product obtained by the first or second method: (a) by crystallization at very low temperatures, or from solvent mixtures, (b) by low pressure fractional distillation. Both methods gave some improvements, but only at the price of low recoveries.

High Melting Hydroperoxide.—When the hydroperoxide concentrates were stored in a refrigerator (at or below 0°) for a few weeks, a solid crystalline deposit was formed. By filtration and washing several times with cold hexane, the crystals were recovered in amounts of 3.5–7.5% with melting points in the range of 84–91°. Recrystallization in one case from methyl ethyl ketone with hexane raised the m.p. to 132–137°. Combustion of a sample gave the following results.

Calcd. for (A) $C_{16}H_{18}O_4$: C, 70.1; H, 6.57; O, 23.4. Calcd. for (B) $C_{16}H_{18}O_6$: C, 62.8; H, 5.88; O (by diff.), 31.3. Found: C, 64.92; H, 6.33; O (by diff.), 28.75.

A mixture of A and B in 1:2 proportion would give the calculated values: C, 65.24; H, 6.12; O, 28.66.

Recovery of By-products.—The alkali-extracted reaction mixture, from 1360 g. of *p*-xylene, was fractionally distilled first at atmospheric and subsequently at reduced pressure (100 mm.) to remove acetone and *t*-butyl alcohol (formed

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(3) In 0.1 molar ethanolic $(CH_3)_4NCl$ solution; half-wave potential 1.63 v.

from the initiator), unreacted *p*-xylene, and a higher boiling fraction consisting of a nearly 50:50 mixture of *p*-methylbenzaldehyde (calculated from carbonyl determination by Desseigne) and *p*-methylbenzyl alcohol. The distillation residue (81.3 g.) crystallized on cooling. It was recrystallized from methanol, dissolved in hexane and passed through an activated alumina-packed column (200 mesh). The recovered product (16.9 g., m.p. 76–80.5°) was again recrystallized from methanol and dried in a vacuum oven at 40° for 48 hours; obtained 12.8 g., m.p. 78.5–80°.

Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.65; H, 8.58.

In one experiment, *before* the alkaline extractions, the volatile constituents of the reaction mixture were partially distilled off, the distillate was fractionated in a 20-plate column, and the residue analyzed. The oxidation of 404.5 g. of *p*-xylene consumed 0.455 mole of di-*t*-butyl peroxide, or 0.910 mole of the *t*-butoxy group. The amounts of products recovered or estimated were as

Acetone (by fractionation and anal.), mole	0.045
t-Butyl alcohol (by fractionation), mole	.555
p-Methylbenzyl hydroperoxide (by I_2 liberation), mole	.158
p-Toluic acid (by titration and also isolation), mole	.082
p-Methylbenzaldehyde (by polarograph and ultraviolet absorption), mole	.093
p-Methylbenzyl alcohol (by isolation), mole	.090
Crystalline dimer, etc. (by isolation) as $CH_3C_6H_4$-CH_2, mole	.240
	1.263

Acid-Catalyzed Decomposition of *p*-Methylbenzyl Hydroperoxide.—A 4.13-g. sample of the hydroperoxide (82% ROOH) was added dropwise to a 4-cc. methanolic solution of 0.0416 g. of sulfuric acid which had been brought to reflux in a boiling-water-bath. After 90 minutes another 0.0505 g. of sulfuric acid in 2 cc. of methanol was added and the refluxing was continued for 75 minutes. The reaction mixture (8.65 g.) contained 12% *p*-cresol and 12.0% *p*-tolualdehyde, as estimated from ultraviolet absorption (bands at 242 and 298 mμ in alkaline ethanol for *p*-cresol, and absorption maximum at 257 mμ for *p*-methylbenzaldehyde in alcohol).

A 7.7-g. portion of the above mixture was stripped of methanol and methylformal (after neutralizing the catalyst with 2 drops of 50% NaOH). The residue, 3.11 g., was dissolved in a benzene–hexane mixture, and the solution was washed with dilute $NaHCO_3$ and extracted with 6 cc. of 4% NaOH. The NaOH washings were neutralized and extracted with ethyl acetate. The extract was dried and the solvent distilled off, leaving 1.02 g. of strongly colored liquid which, on cooling and seeding with a *p*-cresol crystal, solidified to a crystalline mass. Yield of *p*-cresol about 55% of theory. The NaOH extracted original solution was stripped of solvent, leaving a residue of 1.98 g. from which the $NaHSO_3$ addition product was prepared. The aldehyde was regenerated with 5% Na_2CO_3; 0.5 g., or a yield of 25% based on the hydroperoxide decomposed, was obtained. derivatives prepared were: (a) 2,4-dinitrophenylhydrazone, m.p. 234.5–235.5°; (b) semicarbazone, m.p. 214°.

Anal. Calcd. for 2,4-dinitrophenylhydrazone: N, 18.67. Found: N (Dumas), 18.77. Calcd. for semicarbazone: N, 23.73. Found: N (Dumas), 23.57.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. II. Preparation, Characterization and Polarographic Behavior of Long-chain Aliphatic Peracids[2]

BY WINFRED E. PARKER, CONSTANTINE RICCIUTI, C. L. OGG AND DANIEL SWERN

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A new procedure for the preparation of aliphatic peracids is described. This consists in the reaction of fatty acids with 0.5–2.0 moles of 50–65% hydrogen peroxide in concentrated sulfuric acid solution. The reaction is an excellent example of the nucleophilic character of hydrogen peroxide. Yields of C_6- to C_{18}-peracids range from 61–99%, the reactions are rapid at 10 to 30° and product isolation is readily accomplished. The C_7- to C_{18}-peracids are new compounds and, with the exception of perstearic acid, have been characterized by melting point, ultimate analysis, and chemical and polarographic behavior. Kinetics of decomposition of eight peracids in methanol–benzene have been determined. Pseudo-first order specific reaction rate constants at 25° range from 0.93 to 1.92 $\times 10^{-3}$ min.$^{-1}$ over the molar concentration range of 4–20 $\times 10^{-3}$ mole/l.

Aliphatic peracids were first prepared and their properties examined by D'Ans and co-workers during the first two decades of the twentieth century,[3,4] although dilute aqueous solutions had probably been obtained somewhat earlier.[5-7] D'Ans and co-workers prepared concentrated performic, peracetic, perpropionic and perbutyric acids usually by the reaction of concentrated (up to 98%) hydrogen peroxide with the appropriate acid or anhydride in the presence of catalytic quantities of inorganic acids or acid salts. The products then were purified by distillation and fractional freezing. (It is noteworthy that the original melting and boiling points recently have been confirmed.[8])

With the exception of percaproic acid,[9] m.p. 15°, b.p. 61–62° (13 mm.) and 41–42° (0.5 mm.), the preparation of the remaining *n*-aliphatic peracids has not been described. Occasionally a passing reference can be found to water-insoluble aliphatic peracids,[4] such as perlauric,[10] perpal-

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[1] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented at the Spring Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955. The previous paper in this series is in *Org. Syntheses*, **34**, 90 (1954).

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[7] Parke, Davis and Co., German Patent 156,998 (1902).

[8] A. C. Egerton, W. Emte and G. J. Minkoff, *Disc. Faraday Soc.*, **10**, 278 (1951).

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