Free Radical Hydroxylations with Peracetic Acid

Sir:

We wish to report the reaction between peracetic acid and saturated hydrocarbons under conditions conducive to the formation of free radicals. While being irradiated with a 200-watt Hanovia high pressure quartz mercury arc in a Vycor well, excess cyclohexane was treated dropwise with a solution of peracetic acid[1] (23.5 weight %) in ethyl acetate at 22–25°. Vigorous evolution of gas was evident throughout the reaction period (13 hr.); by mass spectral analysis the gas was carbon dioxide, methane, and cyclohexane (52.2, 42.1, and 5.7 mole %, respectively). After neutralizing with aqueous potassium hydroxide and washing, the organic layer was fractionated to give, after recovery of excess cyclohexane, a mixture of cyclohexanol and cyclohexanone, b.p. 150–160°. The mixture contained 6.3% cyclohexanone (hydroxylamine titration) and 90.2% cyclohexanol (phthalic anhydride titration). (2,4-Dinitrophenylhydrazone, m.p. and mixed m.p. with cyclohexanone 2,4-dinitrophenylhydrazone, 156–158°; 3,5-dinitrobenzoate, m.p. and mixed m.p. with cyclohexanol 3,5-dinitrobenzoate, 111–112°.) The infrared spectrum of this mixture was consistent with this analysis. Yield of cyclohexanol was 38%.

cis-Decalin (b.p. 190–193°) treated similarly gave a mixture of isomeric decalols, of which a major portion was *trans*-9-decalol (b.p. 104–106°/20 mm., m.p. 52–54°, infrared peaks at 2.88 and 8.57 μ). *Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76; mol. wt., 154.2. Found: C, 78.05; H, 11.74; mol. wt., 159. The yield of crude tertiary alcohol was 49%; total yield of all oxygenated products was much higher.

Compounds containing carbon-oxygen functions suffered further oxidation at such carbon atoms, as anticipated. γ-Valerolactone gave levulinic acid in 42% yield (b.p. 133–137°/10 mm., n 30°/D = 1.4533, acid equiv. calcd. 116, found, 110, m.p. and mixed m.p. of semicarbazone with authentic semicarbazone of levulinic acid, 190–191.5°). Di-(n-hexyl) ether gave caproic acid (b.p. 98°/10 mm., n 20°/D = 1.4171, m.p. of amide, 95–98°) in 56% yield; the coproduct was n-hexanol (b.p. 156–158°, n 20°/D = 1.4182, m.p. and mixed m.p. of 3,5-dinitrobenzoate with authentic 3,5-dinitrobenzoate of n-hexanol, 57.5–58°) in 67% yield.

Free radical hydroxylation with peracetic acid could also be effected thermally. *endo*-Tetrahydrodicyclopentadiene was heated to 185° and treated dropwise with peracetic acid solution; a high solution temperature was maintained by continuously removing ethyl acetate at the head of a column in the vessel. After washing to remove acid, the products were fractionated; a major product was the tertiary alcohol, *endo*-5,6-trimethylene-5-*exo*-norbornanol[2] [b.p. 125–130°/10 mm., m.p. (ligroin) 131–132°. *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.81; H, 10.66; peak at 3.05 μ].

The previous literature provides little indication of such a reaction. The decomposition of perlauric acid in several solvents or in a melt has been found[3] to proceed predominantly by a non-radical mechanism to give lauric acid and oxygen, with small amounts of an ester that could have arisen by a radical mechanism. Recently, perlauric acid was reported[4] to decompose in a boiling solvent (40–70°) to give mainly products anticipated for a free radical decomposition, *viz.*, n-undecanol and carbon dioxide.

It is probable that a mechanism similar to the one proposed in both earlier publications[3,4] accounts for initiation of the present hydroxylation reaction. Relatively short chains appear to be involved. Chain propagation can be provided as in steps 2, 3, and 4. Several chain-terminating reactions can occur, for most of which there is direct evidence. The reaction is inhibited completely by oxygen; it could be initiated by cobaltic ion, although poorer yields and more complex mixtures of products were obtained. These results will be detailed in forthcoming publications; the new reaction is general and extremely useful.

$$CH_3CO_3H \longrightarrow CH_3CO_2\cdot + \cdot OH \quad (1)$$

$$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2 \quad (2)$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \quad (3)$$

$$R\cdot + CH_3CO_3H \longrightarrow ROH + CH_3CO_2\cdot \quad (4)$$

UNION CARBIDE CHEMICALS COMPANY
RESEARCH DEPARTMENT
SOUTH CHARLESTON, W. VA.

DONALD L. HEYWOOD
BENJAMIN PHILLIPS
HARRY A. STANSBURY, JR.

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(1) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, 79, 5982 (1957).

(2) The proof of structure of this alcohol will be presented in a forthcoming publication by Paul von R. Schleyer.

(3) See W. E. Parker, L. P. Witnauer, and D. Swern, *J. Am. Chem. Soc.*, 80, 323 (1958), and references therein.

(4) D. Lefort, C. Paquot, and J. Sorba, *Bull. Soc. Chim. France*, 1385 (1959).

Reaction of *t*-Butyl Peresters with Thio Ethers

Sir:

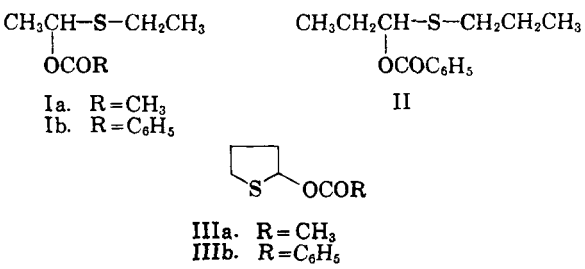
In a previous communication[1] the reaction of *t*-butyl peresters with aliphatic and cyclic ethers in the presence of cuprous bromide was described.

(1) G. Sosnovsky, *J. Org. Chem.*, 25, 874 (1960).

This work has now been extended to include thioethers.[2]

It is well known that sulfides react with various peroxy compounds such as hydrogen peroxide, peracids,[3] and hydroperoxides[4] to give good yields of sulfoxides or sulfones. In contrast, we have found that *t*-butyl peresters react smoothly with aliphatic and cyclic sulfides to give the corresponding acyloxy derivatives and that there is no oxidation of the sulfur atom under the chosen experimental conditions.

Specifically, the reaction of 0.3 mole of *t*-butyl peracetate with 0.35 mole of diethyl sulfide in benzene (50 ml.) in the presence of 0.35 mmole of cuprous bromide for 64 hr. at 80–85° yielded 44% of 1-acetoxy diethyl sulfide (Ia), b.p. 70–72°, 22 mm., n_D^{25} 1.4468, $\gamma_{C=O}$ 1730 cm.$^{-1}$ *Anal.* Calcd. for $C_6H_{12}O_2S$: C, 48.64; H, 8.16, S, 21.60; mol. wt., 148. Found: C, 48.84; H, 8.30; S, 21.97; mol. wt., 146.



Ia. R=CH_3
Ib. R=C_6H_5

II

IIIa. R=CH_3
IIIb. R=C_6H_5

Similarly, the reaction of 0.2 mole of *t*-butyl perbenzoate and 0.5 mole of diethyl sulfide in the presence of 0.35 mmole of cuprous bromide for 26 hr. at 80–90° yielded 31% of Ib, b.p. 75° at 0.1 mm., n_D^{25} 1.5266, $\gamma_{C=O}$ 1715 cm.$^{-1}$ *Anal.* Calcd. for $C_{11}H_{14}O_2S$: C, 62.84; H, 6.71; S, 15.22; mol. wt., 210. Found: C, 63.40; H, 6.98; S, 15.03; mol. wt., 216.

Under similar catalytic conditions, 0.4 mole of *t*-butyl perbenzoate reacted with 0.4 mole of di-*n*-propyl sulfide for 5 hr. at 85–97° to yield 69% of 1-benzoyloxy dipropyl sulfide (II), b.p. 90° at 0.04 mm., n_D^{25} 1.5175, $\gamma_{C=O}$ 1725 cm.$^{-1}$ *Anal.* Calcd. for $C_{13}H_{18}O_2S$: C, 65.53; H, 7.61; S, 13.47; mol. wt., 238. Found: C, 65.59; H, 7.73; S, 13.74; mol. wt., 231. The reaction of 0.3 mole of *t*-butyl peracetate with 0.5 mole of tetrahydrothiophene for 6 hr. at 90° gave 56% of 2-acetoxytetrahydrothiophene (IIIa), b.p. 60–62° at 0.1 mm., n_D^{25} 1.4893, $\gamma_{C=O}$ 1735 cm.$^{-1}$ *Anal.* Calcd. for $C_6H_{10}O_2S$: C, 49.31; H, 6.90; S, 21.90; mol. wt., 146. Found: C, 49.53; H, 7.16; S, 21.86; mol. wt., 141. Also, 0.25 mole of *t*-butyl perbenzoate with 0.5 mole of tetrahydrothiophene for 5 hr. at 90° gave 69% of IIIb, n_D^{25} 1.5650 (after chromatography on alumina), $\gamma_{C=O}$ 1735 cm.$^{-1}$ Because of thermal instability, IIIb could not be purified by distillation. *Anal.* Calcd. for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81; mol. wt., 208. Found: C, 63.13; H, 6.02; mol. wt., 198.

In the absence of the catalyst the acyloxy compounds formed more slowly and in lesser quantity. Similar to the acyloxy derivatives of ethers, the sulfur compounds are sensitive to heat; they pyrolyze slowly at 100° and rapidly at slightly elevated temperatures. Thus, 2-benzoyloxytetrahydrothiophene (IIIb) at 110° for 2 hr. gave benzoic acid plus an 80% yield of 2,3-dihydrothiophene, b.p. 48° at 100 mm., n_D^{25} 1.5268.[5] *Anal.* Calcd. for C_4H_6S: C, 55.76; H, 7.03; mol. wt., 86. Found: C, 55.41; H, 7.21; mol. wt., 87. After several trap-to-trap distillations the product was shown by vapor phase chromatography to contain less than 1% impurities. Our method constitutes a new and improved synthesis of the 2,3-isomer of dihydrothiophene. When a mixture of IIIb and *t*-butyl alcohol was heated at reflux for about 100 hr., benzoic acid was eliminated quantitatively and an oil was isolated (yield 64%), b.p. 90° at 0.5 mm, n_D^{25} 1.6006. The elemental analyses and the molecular weight agree well with the formula for a dimer of dihydrothiophene. *Anal.* Calcd. for $C_8H_{12}S_2$: C, 55.80; H, 7.03; S, 37.17: mol. wt., 172. Found: C, 55.45; H, 6.77; S, 37.15; mol. wt., 179.

Thermal decomposition of the benzoyloxy derivatives of aliphatic sulfides in the presence of *t*-butyl alcohol gave a different result. Thus, Ib and II gave 1-mercaptoethyl diethyl sulfide and 1-mercaptopropyldipropyl sulfide, respectively.

The observations reported here are being investigated further and the details will be published at a later date.

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ARMOUR RESEARCH FOUNDATION GEORGE SOSNOVSKY
OF ILLINOIS INSTITUTE OF TECHNOLOGY
10 WEST 35TH STREET
CHICAGO 16, ILL.

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(2) A brief account of this investigation was presented at the 138th Meeting of the American Chemical Society in New York, N. Y., September 1960.

(3) R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Son, Inc., New York, N.Y., p. 801, 1953.

(4) K. R. Hargrave, *Proc. Roy. Soc., London*, **235A**, 55 (1956).

(5) S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 2556 (1951).

The Free Radical Chemistry of Epoxides: A Radical Rearrangement and Displacement

Sir:

The attack of a free radical or atom on a double bond has long been known,[1] and the corresponding

(1) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957.