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.

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

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

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

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

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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.

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