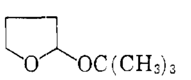
Communications TO THE EDITOR

Reaction of *t*-Butyl Peresters with Ethers

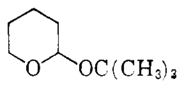
Sir:

In previous communications[1,2] the reactions of *t*-butyl peresters with olefins in the presence of copper salt catalysts were described. In subsequent work[3] the reactions of *t*-butyl peresters were extended to substrates containing activated hydrogen atoms other than olefins. Thus, *t*-butyl perbenzoate with dioxane yielded dioxanyl benzoate, and with phenyl allyl ether yielded 2-benzoyloxy-3-phenoxy-1-propene. In all these reactions the activated hydrogen atom is displaced by an acyloxy group and the *t*-butoxy radical is converted to *t*-butyl alcohol.

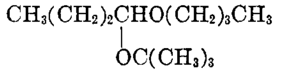
It has now been found that *t*-butyl peresters react with ethers containing only one ether function and two activated adjacent methylene groups, such as tetrahydrofurans, tetrahydropyran, and *n*-butyl ether. In addition to the expected acyloxy compounds, these reactions yield mainly 2-*t*-butoxytetrahydrofuran (I), 2-*t*-butoxytetrahydropyran (II), and 1-*t*-butoxy-1-*n*-butoxybutane (III).



I



II



$CH_3(CH_2)_2\underset{\substack{|\\ OC(CH_3)_3}}{C}HO(CH_2)_3CH_3$

III

Specifically, the reaction of 0.3 mole of *t*-butyl peracetate with 1 mole of tetrahydrofuran in the presence of 0.35 mmole of cuprous bromide for 14 hr. at 67–84° yields 41% of compound I, b.p. 40°/11 mm., n_D^{25} 1.4186. *Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.80; H, 11.02; mol. wt., 144. Found: C, 66.78; H, 11.23; mol. wt., 146.

Similarly, the reaction of 0.3 mole of *t*-butyl perbenzoate and 1 mole of tetrahydrofuran with 0.35 mmole of cuprous bromide for 14 hr. at 67–84° yields 45% of compound I. The reaction of 0.2 mole of *t*-butyl perbenzoate with 0.5 mole of tetrahydropyran for 14 hr. at 86° yields 33% of II, b.p. 56°/13 mm.; n_D^{25} 1.4268. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.30; H, 11.48; mol. wt., 158. Found: C, 68.65; H, 11.61; mol. wt., 154. The compound is identical in all respects with a sample prepared by the method of Paul.[4,5] The reaction of 0.1 mole of *t*-butyl perbenzoate with 0.35 mole of *n*-butyl ether for 48 hr. at 90° gives a 48% yield of III, b.p. 100°/17 mm.; n_D^{25} 1.4148. *Anal.* Calcd. for $C_{12}H_{26}O_2$: C, 71.20; H, 12.96; mol. wt., 202. Found: C, 71.15; H, 12.65; mol. wt., 195. If the reaction is stopped within 6 hr., it is possible to isolate substantial quantities of 2-acyloxy compounds. Due to their instability, these compounds could not be purified sufficiently for elemental analysis.

In the absence of a copper salt catalyst, the reaction of *t*-butyl peresters with ethers proceeds at a much slower rate.

A mechanism which accounts for the formation of the acetals I, II, and III is proposed on the basis of the following results. Dihydropyran reacts with acetic acid at 100° to give 2-acetoxytetrahydropyran.[6] We found that under similar conditions an equimolar mixture of dihydropyran, *t*-butyl alcohol, and either benzoic acid or acetic acid produces mainly the acetal II (40%) and only 13% of the acyloxy compounds. There is no reaction between dihydropyran and *t*-butyl alcohol in the presence of copper salt in the absence of acid. At 130°, 1 hr., 2-benzoyloxyfuran decomposes to 66% 2,3-dihydrofuran plus 69% benzoic acid. An equimolar mixture of 2-benzoyloxytetrahydropyran and *t*-butyl alcohol at 80°, 14 hr., yields compound II plus benzoic acid.

From these results it is reasonable to assume that the *t*-butyl peresters in the presence of copper salt catalysts react with tetrahydrofuran, tetrahydropyran, or *n*-butyl ether to form initially the corresponding acyloxy intermediates, which decompose at the chosen experimental conditions to give free organic acids and an unsaturated ether. This ether, in turn, adds *t*-butyl alcohol in the presence of the corresponding acid to give the observed products, I, II, or III, respectively.

The scope of the reactions of *t*-butyl peresters with ethers is currently being investigated, and the results will be reported at a later date.

The author is indebted to the Quaker Oats Company for free samples of dihydropyran and tetrahydropyran.

Armour Research Foundation George Sosnovsky
Illinois Institute of Technology
10 West 35th Street
Chicago 16, Ill.

Received January 25, 1960

---

[1] M. S. Kharasch and George Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958).

[2] M. S. Kharasch, George Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

[3] George Sosnovsky and N. C. Yang, *J. Org. Chem.*, in press.

[4] R. Paul, *Bull. Soc. Chim.*, (5) **1**, 973 (1934).

[5] G. F. Woods and D. N. Kramer, *J. Am. Chem. Soc.*, **69**, 2246 (1947).

[6] J. G. M. Brenner and D. G. Jones, British Patent 606, 764 (Aug. 19, 1948). *Chem. Abstr.*, **43**, 1442 (1949).