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**Registry No.** 1, 31452-21-8; 2, 40921-46-8; 3, 94500-16-0; 4, 94500-17-1; 5, 16648-23-0; 6, 94500-18-2; 7, 31452-22-9;  $\text{CH}_3\text{SSCH}_3$ , 624-92-0;  $\text{Me}_3\text{Sn}$ , 17272-57-0;  $\text{CH}_3\text{S}$ , 7175-75-9;  $\text{MeCH}_2\text{S}$ , 14836-22-7;  $\text{PrCH}_2\text{S}$ , 16812-18-3;  $\text{BrCH}_2\text{SCH}_2\text{CH}_3$ , 36056-14-1;  $\text{BrCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ , 35420-95-2;  $\text{BrCH}_2\text{CH}_2\text{SBU-}t$ , 5755-60-2;  $\text{BrCH}_2\text{CH}_2\text{SBU-}n$ , 94500-19-3; ethyl disulfide, 110-81-6; ethylene, 74-85-1; cyclopropane, 75-19-4.

## The Decomposition of Cumyl Peracetate on Silica

John T. Barbas and John E. Leffler\*

Department of Chemistry, Florida State University,  
Tallahassee, Florida 32306

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The decomposition of cumyl peracetate follows heterolytic (Criegee), homolytic, or mixed heterolytic-homolytic pathways, depending on the polarity of the solvent and the presence of acid catalysts.<sup>1,2</sup> In acetic acid the rate (moderately fast at room temperature) and products (phenol, acetone, and 2-phenoxypropene) are characteristic of the heterolytic mode.<sup>1</sup> In nonpolar or moderately polar solvents such as toluene, the low rate (conveniently measured at 70 to 90 °C) and the products (mainly carbon dioxide, methane, and acetophenone, with lesser amounts of phenol, acetone, and 2-phenoxypropene) correspond to a mixed homolytic-heterolytic reaction.<sup>2</sup> The yield of 2-phenoxypropene is increased to 83% in the presence of trichloroacetic acid catalyst.<sup>2</sup>

In nonpolar solvents the decomposition rates are often erratic and difficult to reproduce, possibly because of reactions on the wall of the reaction vessel. The rate of the reaction in toluene in a Pyrex container is 40% greater when freshly crushed Pyrex is added.<sup>2</sup> It is also well-known that a number of reactions subject to homogeneous acid catalysis in solution are fast even on neutral silica. These observations impelled us to examine the perester decomposition on silica surfaces, with the object of identifying the heterogeneous part of the reaction.

## Results

The rates of decomposition of the perester in silica slurries were too high to permit the removal of the solvent to confine the reaction to the adsorbed phase. With  $\text{P}_0$  silica<sup>3</sup> the rate constant in a stirred chloroform slurry was  $8.6 \times 10^{-4} \text{ s}^{-1}$  at 26 °C, which is faster than the extrapolated rate in toluene by 6 orders of magnitude and faster than the rate<sup>1</sup> in acetic acid by a factor of 30. The products from the reaction in a chloroform slurry of this silica were phenol (98% and 94%), acetic acid (89% and 92%), and acetone (88%). An IR band at  $1763 \text{ cm}^{-1}$ , probably due to the Criegee rearrangement product, 2-acetoxy-2-phenoxypropane, vanishes when the solution of reaction products is washed with water.

Similar experiments were carried out with slurries of  $\text{P}_1$  silica.<sup>3</sup> Although the properties of  $\text{P}_1$  silica as a medium for reactions confined to the surface, i.e., in the absence of liquid solvent, are often somewhat different from those of  $\text{P}_0$  silica under the same solvent-free conditions,<sup>4</sup> the

results from the two silicas appear to be the same in the present experiments.<sup>8</sup> The rate constant in a stirred chloroform slurry of  $\text{P}_1$  silica at 26 °C was  $9.6 \times 10^{-4} \text{ s}^{-1}$ . The products from the reaction in a pentane<sup>5</sup> slurry of  $\text{P}_1$  silica were phenol (96%), acetic acid (89%), and acetone (91%).

## Experimental Section

The chloroform slurry rates were determined from the carbonyl IR band of the perester in the supernatant liquid of samples of the slurry. The slurry was prepared from 50 mL of  $\text{CHCl}_3$ , 10.0 g of the silica, and 0.010 mol of the perester.

In a typical product determination, a solution of about 1 g of the perester in 25 mL of the solvent was added, with stirring, to a slurry of 25 g of the silica and 50 mL of the solvent. The slurry was filtered, products were removed from the silica by extraction with ether, and the ether combined with the filtrate. Phenol was determined by GLC using 4-methyl-2,6-di-*tert*-butylphenol as the internal standard and confirmed by isolation and weighing of the tribromophenol derivative. Acetic acid was determined by titration with alkali. Acetone was separated from the reaction mixture by distillation after neutralization of the acetic acid. The acetone in the distillate was determined gravimetrically as iodoform.

The perester was made from cumyl hydroperoxide and acetyl chloride as in ref 2. Iodimetric titration of this compound is not quantitative, but the preparation appeared to be pure as judged by its IR (carbonyl at  $1785 \text{ cm}^{-1}$ ) and NMR:  $\delta$  1.65 (s, 6 H), 1.90 (s, 3 H), 7.40 (m, 5 H).

**The Silicas.**<sup>4-7</sup> The silicas were dried in an oven and stored over Drierite before use. Silica  $\text{P}_1$  is the purer of the two and has 0.018% calcium as CaO, 0.005% iron as  $\text{Fe}_2\text{O}_3$ , 0.058% titanium as  $\text{TiO}_2$ , and 0.030% zirconium as  $\text{ZrO}_2$ . The percentages for  $\text{P}_0$  silica are 0.02, 0.03, 0.09, and 0.03.<sup>5</sup> The surface areas ( $\text{N}_2$ ) are  $700 \text{ m}^2/\text{g}$  for  $\text{P}_1$  and  $750 \text{ m}^2/\text{g}$  for  $\text{P}_0$ . Silica  $\text{P}_1$  has a greater H-bond donating ability, in the absence of solvent, as measured by its solvatochromic  $\alpha$  value.<sup>4</sup> Both silicas have solvatochromic  $\pi^*$  values of about 2.0, greatly exceeding those reported for any fluid solvent.<sup>4</sup>

**Registry No.** Cumyl peracetate, 34236-39-0; silica, 7631-86-9.

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(8) The lack of dependence on the silica,  $\text{P}_0$  vs.  $\text{P}_1$ , could be a result characteristic of this perester or it could be due to the presence of solvent. The fact that the products are the same in chloroform as in pentane supports the former interpretation.

## Hydrogen-Deuterium Exchanges in a Friedel-Crafts Reaction

Choi Chuck Lee\* and Hussein F. Zohdi

Department of Chemistry, University of Saskatchewan,  
Saskatoon, Saskatchewan, Canada S7N 0W0

Mohamed M. M. Sallam

Department of Chemistry, Faculty of Science,  
University of Cairo, Cairo, Egypt

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Isotopic scramblings during Friedel-Crafts alkylations have been investigated with  $^{14}\text{C}$ -labeled 2-arylethyl halides.<sup>1</sup> For example, scramblings in the 2-phenylethyl

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(3) See the Experimental Section and ref 4-7.

(1) (a) Lee, C. C.; Forman, A. G.; Rosenthal, A. *Can. J. Chem.* 1957, 35, 220-225. (b) McMahon, M. A.; Bunce, S. C. *J. Org. Chem.* 1964, 29, 1515-1520.