The Decomposition of Cumyl Peracetate in Nonpolar Solvents

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Received October 26, 1971

Cumyl peracetate decomposes in toluene by competing radical and ionic paths. The ionic reaction is catalyzed by added acid with a Brønsted coefficient of 0.56. In carbon tetrachloride the reaction is somewhat erratic but exhibits good first-order kinetics in the presence of added pyridine, which also slows down the reaction. In carbon tetrachloride without added pyridine or with only a small amount, the products are again characteristic of mixed ionic and radical reaction paths. In 0.1 *M* pyridine in CCl_4, the reaction appears to be entirely a radical process. Iodine traps radicals from the reaction in toluene, giving benzyl iodide, but also catalyzes the ionic reaction both in toluene and in carbon tetrachloride.

In nitrobenzene and in acetic acid, cumyl peracetate has been shown to give the ionic Criegee rearrangement exclusively, with very nearly quantitative yields of acetic acid, acetone, and phenol after hydrolysis.[1] In the present paper we wish to report the rather different behavior of cumyl peracetate in the nonpolar solvents toluene and carbon tetrachloride.[2]

The proportion of the reaction going by radical paths can be judged from the yield of carbon dioxide, supported by the yields of acetophenone or cumyl alcohol.

Results

Toluene.—In toluene at 100° the mean rate constant for the decomposition of cumyl peracetate is $(3.43 \pm 0.06) \times 10^{-5}$ sec^{-1} for carefully degassed reaction mixtures, and approximately $(3.13 \pm 0.29) \times 10^{-5}$ sec^{-1} for nondegassed reaction mixtures. Within the analytically convenient range 0.02–0.10 *M* the rate constant is insensitive to changes in the initial concentration of the perester. It is also insensitive to the presence of added pyridine or water or smooth Pyrex beads. Freshly crushed Pyrex, however, increased the rate constant by 40%. The reaction products are given in Table I. Phenyl moieties could be accounted for completely in this solvent.

The decomposition of 0.1 *M* cumyl peracetate in the presence of 0.01 *M* trichloroacetic acid in toluene at 100° gave a greatly increased yield (83%) of the Criegee rearrangement product, 2-phenoxypropene. The reaction is catalyzed by carboxylic acids in general, with a Brønsted α of 0.56 (based on acetic, chloroacetic, dichloroacetic, trichloroacetic, and β-chloropropionic acids). The decomposition of the perester (0.025 *M*) in toluene at 100° in the presence of 0.036 *M* I_2 consumed I_2 at a constant ratio of only 0.48 mol per mole of ester as the ester decomposed. The rate of disappearance of ester was about 5% greater in the presence of the iodine and was observed to decrease somewhat during the run. Benzyl iodide was a product.

The substitution of three deuterium atoms for hydrogen in the acetoxy moiety of the perester decreased the rate constant by only 7% and had little effect on the nature of the products. Substitution of six deuteriums in the methyl groups of the cumyloxy moiety again decreased the rate constant by only 7% and increased the yield of CO_2 from its original value of 75% to 82%.

TABLE I

PRODUCTS FROM THE DECOMPOSITION OF CUMYL PERACETATE[a,b]

	Solvent and concentration of added pyridine, *M*			
Product	Toluene, 0	CCl_4, 0	CCl_4, 5×10^{-4}	CCl_4, 0.1
Methane	80	75[g]	77	22
Carbon dioxide	75	79	*c*	93
Methyl chloride		30[g]	*c*	111
Acetophenone	32[f]	33[g]	33	59
Cumyl alcohol	35[f]	0	0	0
Bibenzyl	34			*h*
2-Phenoxypropene	25[d,e]	16[d]	12[d]	0
α-Methylstyrene	0	9	7	Trace

[a] At 100° and with 0.1 *M* initial perester. [b] Yields in per cent moles per mol of perester. [c] CO_2 plus CH_3Cl was 127%. [d] As phenol, after hydrolysis. [e] In the presence of 0.01 *M* trichloroacetic acid the yield of this product was increased to 83%. [f] A similar experiment with dicumyl peroxide at 100° in toluene gave 114% acetophenone and 81% cumyl alcohol. [g] A similar experiment with dicumyl peroxide in CCl_4 at 100° gave 43% CH_4, 71% CH_3Cl, and 132% acetophenone. [h] 42% hexachloroethane.

Carbon Tetrachloride.—In this solvent at 100° the rate of decomposition of cumyl peracetate is erratic. Individial runs usually show increasing first-order rate constants and the rate constants are appreciably higher for runs of higher initial concentration. For example, the value at 0.05 *M* is $(4.68 \pm 0.20) \times 10^{-5}$ sec^{-1} compared with 4.9×10^{-5} sec^{-1} at 0.10 *M* and 5.5×10^{-5} sec^{-1} at 0.20 *M*. The products from degassed 0.1 *M* solutions at 100° are shown in Table I. Only 58% of the phenyl groups could be accounted for.

An experiment with cumyl peracetate hexadeuterated in the methyl groups of the cumyl moiety, in CCl_4 at 100°, gave substantial quantities of CD_4, CD_3H, CH_4, and CH_3D. An experiment with perester deuterated in all three methyl groups gave both CD_3H and CD_4.

Erratic kinetics for the decomposition of acid-sensitive peresters are not at all uncommon.[3] The usual procedure is to add pyridine, which often slows the reaction and simplifies the kinetics. Small amounts of pyridine added to solutions of cumyl peracetate in CCl_4 considerably reduced the rate constant and simultaneously improved the precision and fit of the first-order plots. As shown in Figure 1, the effect on the rate levels off at about 0.04 *M* pyridine and $k = 2.85 \times 10^{-5}$ sec^{-1}. The products (Table I) are not very much affected by 0.0005 *M* pyridine, although this amount

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(1) V. A. Yablokov, V. A. Shuskunov, and L. V. Kolyaskina, *Zh. Obshch. Khim.*, **32**, 2174 (1962).

(2) F. E. Scrivener, Jr., Dissertation, Florida State University, 1970.

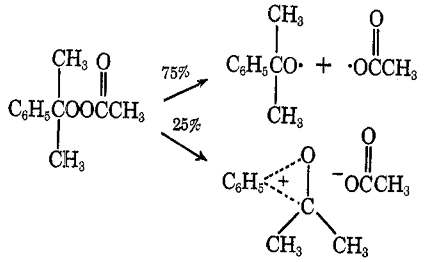
(3) (a) P. D. Bartlett and D. M. Simons, *J. Amer. Chem. Soc.*, **82**, 1753 (1960); (b) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (c) F. D. Greene, W. Adam, and G. A. Knudsen, Jr., *J. Org. Chem.*, **31**, 2087 (1966).

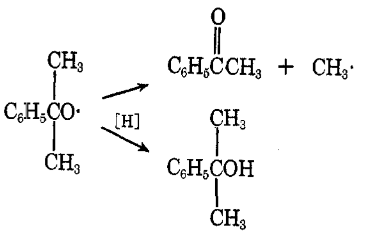
decreases the rate constant by about 15%. In 0.1 *M* pyridine, however, the products are quite different, while the rate constant is lower by about 35–40%.

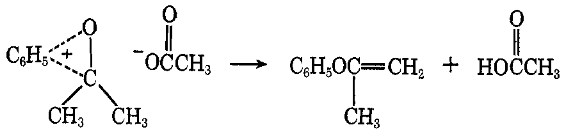
Thiophenol, Koelsch's radical, and iodine were used unsuccessfully in an attempt to separate radical-induced and unimolecular components of the decomposition rate in CCl_4.[2,4]

Discussion

The decomposition of cumyl peracetate in toluene is clearly about 75% radical, judging from the yields of CO_2, acetophenone, cumyl alcohol, and bibenzyl. The remaining 25% is ionic, corresponding to the yield of the Criegee rearrangement–elimination product.







The yield of cumyl alcohol as opposed to acetophenone is greater in the decomposition of the perester than in the decomposition of dicumyl peroxide. This is reasonable in view of the higher concentration of hydrogen-donating radicals such as dimethylcyclohexadienyl in the decomposition of the perester. The major reaction giving cumyl alcohol is probably a disproportionation of the cumyloxy and dimethylcyclohexadienyl radicals, since attack of the latter radical on the perester should be at the less hindered and more electronegative peroxide oxygen of the acetoxy moiety.

The small isotope effects on the rate and on the product yields are consistent with a nonconcerted radical reaction in which the acetoxy radical decarboxylates in a second step. They are also consistent with a concerted ionic reaction in which the aliphatic protons of the cumyloxy moiety have at most only a weak hyperconjugative interaction with the developing positive charge.

The magnitude of the Brønsted α is close to that for the decomposition of several diacyl peroxides which also decompose in part by an ionic route in the absence of catalysts.[5]

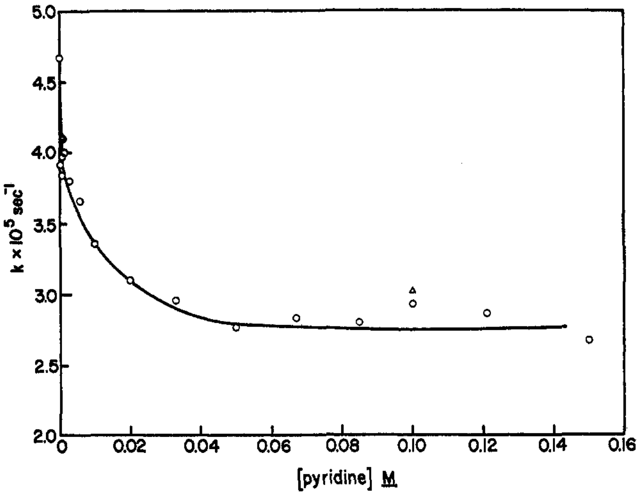


Figure 1.—Effect of added pyridine on the rate in CCl_4 at 100°. The initial perester concentration was 0.05 *M* except for the runs indicated by Δ (0.10 *M*).

The low uptake of iodine in the decomposition in toluene cannot be due entirely to cage recombination in view of the high yield of noncage products. It is probably due in part to the known inefficiency of iodine as a radical trap and in part to the ability of iodine to function as a Lewis acid, which might catalyze the ionic reaction. If catalysis of the ionic reaction did indeed occur, iodine must also have prevented some induced decomposition, since the total rate is not sufficiently enhanced to accommodate a greatly accelerated ionic process without some deceleration of the free-radical process.

The fast, erratic, and partly ionic reaction in CCl_4 is made slower, kinetically simpler, and almost entirely radical by adding 0.1 *M* pyridine. In previous examples,[3] the kinetic effect of pyridine has been attributed to quenching of acid catalysts, either adventitious or products of the decomposition reaction itself. In the present case a possible catalyst might be HCl formed by elimination from some minor product. We prefer this to the alternative explanation in terms of quenching of ionic or ion-pair chain carriers.

The other notable effect of added pyridine is the shift from methane to methyl chloride as the major isolable product of the reaction of methyl radicals. The isotope experiments in CCl_4 without added pyridine showed that the methyl radicals extracted their fourth hydrogen atoms from every conceivable source, both aromatic and aliphatic. In the presence of pyridine the methyl radicals appear to be more selective, reacting preferentially with the weaker C–Cl bonds of the solvent.

Experimental Section[2]

Cumyl Peracetate.—Commercial cumene hydroperoxide, purified *via* its sodium salt, was converted into the peracetate by treatment with acetyl chloride and pyridine in pentane at 0°.[1] The disappearance of perester in the kinetic runs was followed either by means of the carbonyl band at 1786 cm^{-1} or by iodometric titration. The titration procedure was essentially that of

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[4] Cumyl peracetate plus iodine is stable in refluxing CCl_4 solution, but decomposes overnight at room temperature if *solid* I_2 is present. Besides phenol and acetic acid, one of the products of this reaction appears to be 2,4,4-trimethyl-1,4-benzopyran or an isomeric trimethyl-1,4-benzopyran.[2]

[5] (a) J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 67 (1950); (b) J. E. Leffler and A. A. More, *ibid.*, **94**, 2483 (1972).

Silbert and Swern,[6] a ferric chloride catalyzed reaction of the perester with sodium iodide. Since the reaction is not quantitative, a standardized analytical procedure must be carefully adhered to. The concentration of perester is a linear function of the volume of thiosulfate needed to titrate the iodine liberated, but the blank and the slope of the relationship differ somewhat from solvent to solvent.

Reaction Products.—Products were determined by means of standard gas analytical techniques and by gas–liquid chromatography. Chromatographic peaks were identified by retention time and by their infrared spectra using an attenuated total reflectance device.

Registry No.—Cumyl peracetate, 34236-39-0; toluene, 108-88-3; CCl_4, 56-23-5; pyridine, 110-86-1.

Acknowledgment.—The authors wish to acknowledge support of this work by the Army Research Office, Durham, and in part by the Institute of Arthritis and Metabolic Diseases.

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[6] L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

Synthesis of Hydroazulenes by Solvolytic Rearrangement of 9-Methyl-1-decalyl Tosylates[1]

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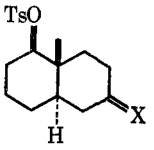
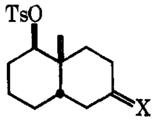
Received August 27, 1971

9-Methyl-1-decalyl *p*-toluenesulfonates **1-4** and **3**-*d* have been synthesized and their solvolyses studied. Trans-fused tosylates **1** and **2** yield predominantly hydroazulenes (**54**, **55**, **33**, and **36**). *cis*-Keto tosylate **3** yields predominantly the unrearranged octalones **13** and **15**. *cis*-Deoxy tosylate **4** yields substantial amounts of both rearranged products (hydroazulenes **33** and **36**) and unrearranged octalins **14** and **18**. No methyl-migrated rearrangement products are obtained in any case. Tosylates **1-4** undergo first-order acetolysis at 100° with relative rates of 1:319:10.8:352. *cis*-Keto tosylate **3** solvolyzes 1.55 times faster than its monodeuterated analog, **3**-*d*. The results are interpreted in terms of a mechanism involving rate-limiting ionization, without participation of the rearranging bond, to an intimate ion pair, which undergoes stereospecific rearrangement to yield hydroazulene or deprotonation to yield hydronaphthalene. With the *cis*-keto tosylate **3**, a conformation is available in which the initial ion pair may decompose with hydride participation to yield a new decalyl cation **58**, the immediate precursor of the unrearranged products

We have recently discussed a stereorational route to guaiazulenic sesquiterpenes which involves (a) construction of an appropriate decalinic intermediate, (b) establishment of the relative stereochemistry of the eventual guaiazulene using established conformational principles, and (c) solvolytic rearrangement of the intermediate to the required hydroazulene.[5] The route has been applied to the total synthesis of the sesquiterpenes bulnesol,[5,6] α-bulnesene,[5] and kessane.[6] As a prelude to that work, we studied, as model substances, the solvolysis of the 9-methyl-1-decalyl-*p*-toluenesulfonates **1–4**. In this paper we report the results of those preliminary studies.



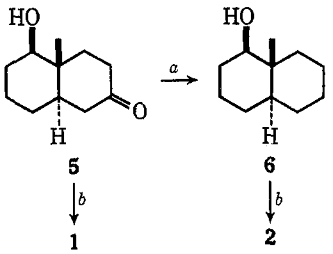
1, X = O
2, X = H_2



3, X = O
4, X = H_2

Synthesis of Tosylates 1–4.—The trans-fused tosylates **1** and **2** were synthesized from keto alcohol **5**[7] as outlined in Scheme I.

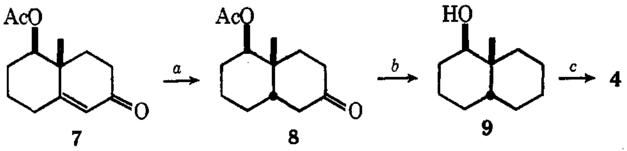
SCHEME I



^{a} Wolff-Kishner reduction. ^{b} *p*-Toluenesulfonyl chloride, pyridine.

The *cis*-keto tosylate **3** was prepared by a route previously reported.[8] *cis*-Deoxy tosylate **4** was prepared from acetate **7**[9] as outlined in Scheme II.

SCHEME II



^{a} H_2-Pd/$SrCO_3$. ^{b} Wolff-Kishner. ^{c} *p*-Toluenesulfonyl chloride, pyridine.

The configuration at the three centers of asymmetry in tosylates **1-4** follows from the methods of synthesis. Corroborative evidence is obtained from pmr spectroscopy. Recent observations of the proton signals adjacent to the *p*-toluenesulfonate group in the four isomeric 1-decalyl tosylates indicate a half-band

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[1] Presented in preliminary form: (a) C. H. Heathcock, R. Ratcliffe, and C. Quinn, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 10, 1969; (b) C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968).

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] National Institutes of Health Predoctoral Fellow, 1967–1970.

[4] Participant in a National Science Foundation Summer Research Program for High School Teachers, 1968.

[5] C. H. Heathcock and R. Ratcliffe, *J. Amer. Chem. Soc.*, **93**, 1746 (1971).

[6] M. Kato, H. Kosugi, and A. Yoshikoshi, *Chem. Commun.*, 185, 934 (1970).

[7] A. J. Birch, E. Pride, and H. Smith, *J. Chem. Soc.*, 4688 (1958).

[8] C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

[9] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).