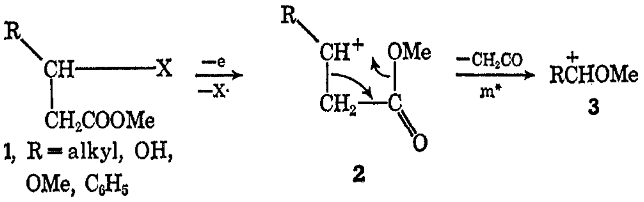
Mass Spectral Decompositions as a Guide to Hitherto Unrealized Reactions in Solution. Ketene Addition to the α-Methoxybenzyl Carbonium Ion

BRUCE DAVIS AND DUDLEY H. WILLIAMS

University Chemical Laboratory, Cambridge, CB2 1EW, England

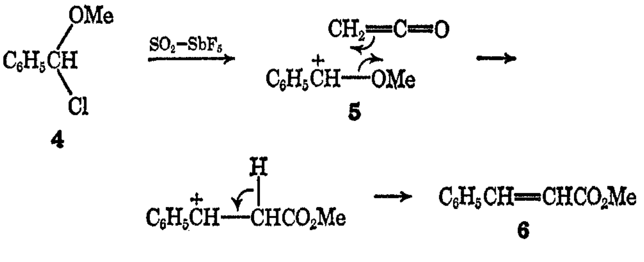
Received December 1, 1969

Carbonium ions of the general formula **2** may be generated upon electron impact from compounds **1** when X is lost as a radical (*e.g.*, X = Br, $COOCH_3$). It has been shown[1,2] that the lowest energy pathway for unimolecular decomposition of the carbonium ions is *via* loss of ketene in a process involving methoxy-group migration (**2** → **3**).



On the basis of the unimolecular gas-phase elimination of ketene from the carbonium ions **2**, we reasoned that the energy of activation of the back-reaction might also be relatively low, *i.e.*, that ketene addition to a α-methoxycarbonium ion, with associated methoxy-group migration, might be realized in a bimolecular reaction in solution.

The α-methoxybenzyl carbonium ion (**5**) was generated by addition of α-methoxybenzyl chloride (**4**)[3] to an SO_2–SbF_5 mixture at $-70°$;[4] formation of **5** was established by nmr spectroscopy. Approximately 1 equiv of ketene was passed through the solution at this temperature and the resulting mixture was quenched with ethanol. Standard isolation techniques gave a 12% yield of methyl cinnamate (**6**) and only 3% ethyl cinnamate.



The gas-phase and solution reactions involving the methoxy migration are represented as concerted only for convenience, and a stepwise process is not excluded.

This example demonstrates that unimolecular decompositions of positive ions in the mass spectrometer may on occasions serve as a guide to the reverse bimolecular reactions of carbonium ions in solution.

Experimental Section

Generation of α-Methoxybenzylcarbonium Ion.—In a typical experiment, 1.0 g of α-methoxybenzyl chloride (6.4 mmol) was added carefully to the surface of a solution of 2.0 g of SbF_5 (9.2 mmol) in 2 ml of SO_2 at $-70°$.[4] When the methoxybenzyl chloride had had sufficient time to cool to $-70°$ (about 5 min), the reaction vessel was shaken to give a clear, deep red, homogeneous solution. The nmr spectrum of this solution, run at $-58°$ on a Varian HA 100-MHz instrument, established the specific formation of the α-methoxybenzylcarbonium ion: τ 5.13 (s, 3), 1.75–2.20 (m, 5), 0.67 (s, 1).

Reaction of the Carbonium Ion with Ketene.—Approximately 1 equiv of ketene, generated by the pyrolysis of acetone, was passed through the carbonium ion solution at $-70°$ over a period of 10 min. The product was quenched by pouring into 5 ml of ethanol at $-70°$; the mixture was then poured into 25 ml of water and continuously extracted with ether. The ether extract was analyzed by gas chromatography using a 4-ft LAC column at 155°, and two peaks having retention times identical with those of methyl and ethyl cinnamates were collected. The nmr and mass spectra (AEI-MS9 instrument with heated inlet) of these two fractions were identical with the corresponding spectra of the authentic esters. The yields, based on α-methoxybenzyl chloride, were 12% methyl and 3% ethyl cinnamate.

Registry No.—**5**, 23790-70-7.

---

[1] I. Howe and D. H. Williams, *J. Chem. Soc., C*, 202 (1968).

[2] R. G. Cooks, J. Ronayne, and D. H. Williams, *ibid.*, 2601 (1967).

[3] F. Straus and H. Heinze, *Ann.*, **493**, 203 (1932).

[4] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 2993 (1967).

The Effect of Solvents with Basic Oxygen in Epoxidation with Organic Peroxy Acids

RAJKO KAVČIČ AND BOŽO PLESNIČAR

Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

Received September 3, 1969

The intramolecularly hydrogen-bonded peroxy acid molecule (or the dipolar form derived from it) has been recognized as the initial reactive species in the epoxidation reaction.[1]

Any reduction in the effective concentration of the cyclically bonded peroxy acid should thus reduce the rate of epoxidation. That epoxidation proceeds at a considerably slower rate in solvents capable of intermolecular association has already been clearly shown by Renolen and Ugelstad.[2]

Schwartz and Blumbergs[3] were the first to measure changes in the carbonyl frequency of *m*-chloroperoxybenzoic acid in methylene chloride containing acetonitrile, suggesting intermolecular association between peroxy acid and acetonitrile, but no further systematic attempts were made, to our knowledge, (1) to confirm or reject this type of association spectroscopically, or (2) to correlate the strength of the intermolecular hydrogen bonding with kinetic and activation parameters of epoxidation in these solvents. The infrared and kinetic studies to clarify this problem have been carried out and are discussed in this paper.

The lowering of the OH stretching frequencies and broadening of the corresponding OH stretching bands of *p*-nitroperoxybenzoic acid in ethyl acetate, diethyl ether, dioxane, tetrahydrofuran, and dimethylformamide, respectively, compared with intramolecularly

---

[1] A. Ažman, B. Borštnik, and B. Plesničar, *J. Org. Chem.*, **34**, 971 (1969), and references cited therein.

[2] P. Renolen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960).

[3] N. N. Schwartz and J. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).