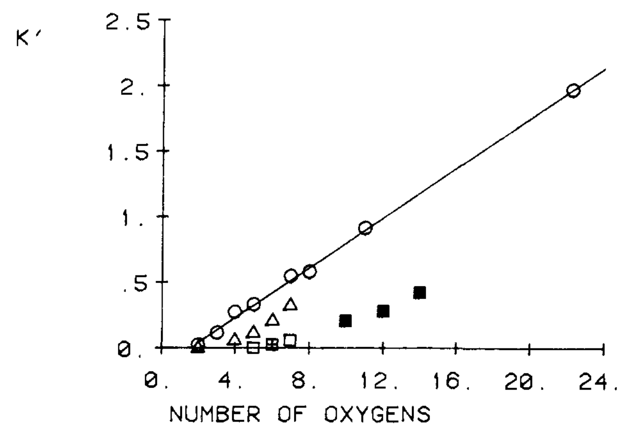
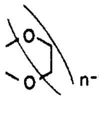
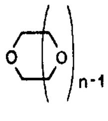


Figure 1. Plot of catalytic rate constant, k', vs. number of oxygens in the polyether catalyst: (○), **1**; (△), **2**; (□), **3**; (■), **4**; (+), dibenzo-18-crown-6.

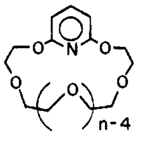
would be expected to decrease in the same order, i.e., **1** > **2** > **3** ≃ **4**.)



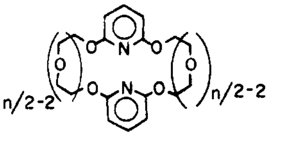
1



2



3



4

In summary, catalysis of the aminolysis of p-NPA in PhCl shows an inverse macrocyclic effect. Catalysis is enhanced by flexible, less constrained polyethers and diminished by polyethers which are conformationally restricted.

Previous studies of catalysis by macrocycles have involved a different approach.[14] In these studies, one of the reactants has an ammonium ion and the other has a reacting group attached to a macrocycle. It is proposed that the binding of the ammonium ion and macrocycle serves to anchor the two reacting groups in close proximity which results in catalysis.

Our approach is to study catalytic effects of polyethers on reactions where ammonium ions are generated in the course of the reaction. The preferential affinity of the polyethers for the cationic intermediates and transition-state structures compared with that of the reactants will result in catalysis. Work is in progress in this laboratory to uncover the exact mechanistic nature of the observed catalysis and to explore other reactions potentially susceptible to polyether catalysis.

Acknowledgment. This research was supported by the Research Corporation. We thank Professor Richard A. Bartsch for generously providing us with a sample of dimethoxy Carbowax 1000. We also express our gratitude to the referees for their suggestions.

References and Notes

(1) Gandour, R. D.; Walker, D. A.; Nayak, A.; Newkome, G. R. *J. Am. Chem. Soc.* **1978**, *100*, 3608–3609.
(2) Izatt, R. M.; Eatough, D. J.; Christensen, J. J. *Struct. Bonding (Berlin)* **1973**, *16*, 161–189.
(3) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hibberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207–4219.
(4) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824–3829.
(5) Menger, F. M.; Vitale, A. C. *J. Am. Chem. Soc.* **1973**, *95*, 4931–4934.
(6) Su, C.-W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854–1857.
(7) Bartsch, R. A.; Juri, P. N. *Tetrahedron Lett.* **1979**, 407–410.
(8) Timko, J. M.; Helgeson, R. C.; Newcomb, M.; Gokel, G. W.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7097–7099.
(9) Izatt, R. M.; Haymore, B. L.; Christensen, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1308–1309.
(10) Weber, G.; Saenger, W.; Vogtle, F.; Sieger, H., *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 226–228.
(11) (a) Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620–7628. (b) Izatt, R. M.; Terry, R. E.; Nelson, D. P.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. *Ibid.* **1976**, *98*, 7626–7630.
(12) (a) Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter, B. E., Jr.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273–6276. (b) The question as to whether or not glymes are better binding agents than crowns toward secondary ammonium ions is currently unanswered. If this turns out to be true, then our data can readily be interpreted on this basis.
(13) The curvature in the crown series may actually be a biphasic plot. The initial phase could represent catalysis resulting from a medium effect, while the latter phase could be catalysis by some type of complexation similar to the glymes. The "lag" in catalytic ability for the crowns and aromatic crowns is likely a direct indication of the ring size needed to achieve the flexibility required for catalysis.
(14) (a) Chao, Y.; Cram, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 1015–1017. (b) Lehn, J.-M.; Sirlin, C. *J. Chem. Soc., Chem. Commun.* **1978**, 949–951. (c) Eyring, E. M.; Farrow, M. M.; Rodriguez, L. J.; Lloyd, L. B.; Rohrbach, R. P.; Allred, E. L. In "Techniques and Applications of Fast Reactions in Solution", Gettins, W. J.; Wyn-Jones, E., Eds.; Reidel Publishing Co.: Dordrecht, Holland, 1979; pp 355–361.

John Charles Hogan, Richard David Gandour*
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received July 25, 1979

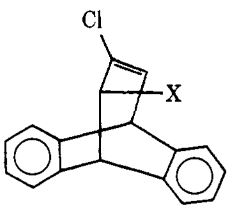
Photochemical Transformations. 27. Acid-Catalyzed Photosolvolytic Reactions and Rearrangements. Evidence for Heterolytic Photochemical Bond Cleavage[1]

Sir:

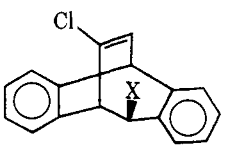
For some time, members of our research group have been interested in photochemically induced solvolyses and photo-Wagner-Meerwein rearrangements, reactions which presumably involve carbocationic intermediates.[2] One interesting question[2a] regarding such reactions is whether the ion pair leading to products is formed directly from the excited-state intermediate or whether it arises by intracomplex electron transfer within a radical pair formed initially. Put another way, is the initial photochemical reaction bond heterolysis or bond homolysis? Kropp and co-workers[3] have proposed that the *seriatim* process obtains, as a result of their studies of saturated alkyl iodides and bromides, where the carbon–halogen bond is the chromophore. Their ideas have been extended to benzyl derivatives,[4] where the aromatic ring is the chromophore, without additional evidence for or against this, as opposed to the idea of competing heterolytic and homolytic processes.[5,6] It is reasonable to assume that different processes are to be found with different substrates and under different conditions, and a conservative view[2a] may suggest that, at low separation distances, the distinction between radical and ion pairs may be blurred or may disappear.[7,8] We now report results that suggest that, for the system being studied at least, the initial photochemical process is not the formation of a classical radical pair.

It has been reported[2a] that direct irradiation with 254-nm light of **1**-Cl in aqueous acetonitrile gives photochemical "Wagner-Meerwein" rearrangement to a mixture of **2**-Cl and **3**-Cl, accompanied by photosolvolysis to give largely **2**-$NHCOCH_3$ and **2**-OH. Similar results were seen with **1**-Br. With the analogous systems *exo*- and *endo*-**4**, photochemical rearrangement gave **5**, and solvolysis produced *exo*-**4**-$NHCOCH_3$, when reaction was carried out in acetonitrile, followed by hydrolysis, or *exo*-**4**-$NHCOCH_3$ and *exo*-**4**-OH in aqueous acetonitrile.[2b] With **4**, photosolvolyses and rearrangements proceeded with X = chlorine, dichloroacetate, and methanesulfonate (good nucleofugal groups) but not with X = hydroxide or acetate. Irradiation of **4**-OH and **4**-OAc resulted instead in di-π-methane rearrangements to **6** species.[2b]

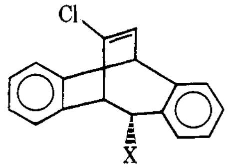
We now report results with **1**-OH, **1**-OAc, and **1**-OCOEt. Like the **4** analogues, when these compounds were irradiated



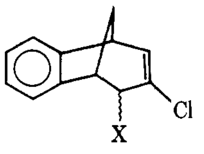
1



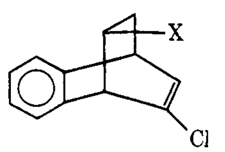
2



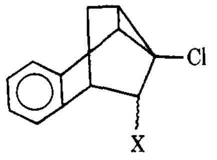
3



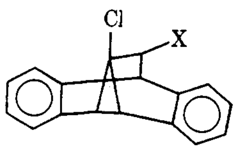
4



5



6



7

in acetonitrile, only the di-π-methane rearrangement isomers **7** were produced (quantum yield of **7**-OAc = 0.10). No products of bond homolysis or bond heterolysis were observed. Irradiation of **1**-OH in acetic acid gave only **7**-OH. On the other hand, when **1**-OAc was irradiated in acetic acid, only 21% was converted into **7**-OAc and the remainder was 43% **1**-OAc, 32% **2**-OAc, and 4% **3**-OAc.[9] The reaction did not continue when the light was removed, and **2** and **3** acetates are known[10] to be less stable than **1**-OAc. Irradiation of **1**-OAc in 70:30 acetonitrile-water, a solvent intended to have a solvating power simulating acetic acid, gave only **7**-OAc, as did irradiation in 9:1 methanol-water, a solvent with a much higher solvating power.[11]

The propionate **1**-OCOEt, irradiated in acetic acid to 53% conversion, yielded 24% **7**-OCOEt, 21% **2**-OAc, 4% **2**-OCOEt, 4% **3**-OCOEt, and a trace of **3**-OAc.[9,12] Irradiation of the propionate **1**-OCOEt in acetonitrile produced only **7**-OCOEt.

With the propionate **1**-OCOEt, the results show that rearrangement (internal return) led to approximately equal amounts of *exo*-**2** and *endo*-**3** propionates, whereas solvolysis gave predominantly **2**-OAc, with only trace amounts of **3**-OAc. The results with **1**-OAc can be similarly rationalized, by assuming that the **3**-OAc arises from rearrangement, along with an equal amount of **2**-OAc, and that the excess **2**-OAc is a solvolysis product. These results are consistent with those previously noted involving internal return and solvolysis, with other nucleofugal groups.[2]

While irradiation of **1**-OH in acetonitrile gave only **7**-OH, irradiation at 0 °C in the presence of 0.5 M 98% sulfuric acid resulted (under conditions where 69% of **1** was converted and where the dark reaction was negligible) in the formation of 17% **7**-OH and 24% **2**-$NHCOCH_3$.[13] In a separate experiment, it was shown that further standing in the dark did not change the composition of the irradiated solution.

We are persuaded by these results that the photoreactions of **1**-OAc, **1**-OCOEt, and **1**-OH are being affected by acid catalysis. Presumably, hydrogen bonding from acetic acid to **1**-OAc and to **1**-OCOEt and proton transfer from sulfuric acid to **1**-OH converts these into compounds with better nucleofugal groups. Dissociation follows light absorption to give photo-Wagner-Meerwein rearrangements and/or photosolvolyses, rather than the otherwise observed di-π-methane rearrangements. We see no rationale for acid catalysis to be involved in the formation of classical radical pairs[14] and we therefore conclude that consideration of their existence as reaction intermediates in these reactions is unwarranted.

Acknowledgment. This work was supported in part by Grant CHE77-20854, awarded by the National Science Foundation.

References and Notes

(1) Paper 26: Cristol, S. J.; Bindel, T. H. *J. Org. Chem.*, in press.
(2) See: (a) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674. (b) Cristol, S. J.; Strom, R. M. *Ibid.* **1979**, *101*, 5707, and preceding papers in series.
(3) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135.
(4) (a) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Chem. Commun.*, **1977**, 108. (b) Hyömäki, J.; Koskikallio, J.; *Acta Chem. Scand.* **1977**, *31*, 321.
(5) Ratcliff, M. A., Jr., Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3112.
(6) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.
(7) Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927.
(8) Fujita, S.; Ozaki, Y; Nozaki, H. *Bull. Soc. Chem. Jpn.* **1972**, *45*, 2571.
(9) Analysis was by ^1H NMR spectrometry using expanded scale integration. Reproducibility was ±2%. Irradiations were conducted in quartz tubes, using nitrogen deaeration and 254-nm lamps.
(10) Cristol, S. J.; Sequiera, R. M.; Mayo, G. O. *J. Am. Chem. Soc.* **1968**, *90*, 5664.
(11) Grunwald, E., Winstein, S. *J. Am. Chem. Soc.*, **1948**, *70*, 846. Fainberg, A. H., Winstein, S. *Ibid.* **1956**, *78*, 2770.
(12) All new compounds were characterized by ^1H NMR, MS, and elemental analysis.
(13) The products were isolated by preparative TLC (silica gel using 35% THF-hexanes.)
(14) It has been shown[15] beyond doubt that acid catalysis converts the thermal decomposition of acyl peroxides from a homolytic into a heterolytic pathway and that the "ionic" products are *not* derived from radical pairs by electron transfer.
(15) (a) Leffler, J. E. *J. Am. Chem Soc.* **1950**, *72*, 67. (b) Bartlett, P. D.; Leffler, J. E. *Ibid.* **1950**, *72*, 3030. (c) Leffler, J. E.; More, A. A. *Ibid.* **1972**, *94*, 2483.

Stanley J. Cristol,* Rory D. Daussin
Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received October 22, 1979