90% of diene **4** and less than 10% of the 2-norcarane ethers **7**. Only when $[Rh(CO)_2Cl]_2$ was in contact with air for 1 week prior to its use as a catalyst did **1** give 25% of diene **4** and 75% of ethers **7**. When wet methanol was used as solvent with fresh catalyst, a 50:50 mixture of diene and ethers was formed. Intermediate amounts of **4** and **7** between the two extremes noted above were formed depending upon the care taken to remove acid and water from solvents and the length of time the $[Rh(CO)_2Cl]_2$ methanol solution was allowed to stand before the addition of bicyclobutane **1**.[12] These results show that $[Rh(CO)_2Cl]_2$ in methanol directly catalyzed the rearrangement of bicyclobutane **1** to diene **4** and the formation of the ethers **7** is a side reaction due to impurities.[13,14]

To determine whether complex **5** could rearrange to the 2-norcarane methyl ethers **7**, methanol-d_4 was added to **5**; no change in the nmr spectrum was observed. Using a 2:1 molar ratio of **1** to $PdCl_2(C_6H_5CN)_2$ in methanol, **1** gave only diene **4** and complex **5**. The addition of **1** to a methanolic solution of **5** gave only diene **4**. Upon standing, the methanolic solution of **5** is transformed to the π-allyl complex **6** (X = OCD_3), mp 140–145° dec.[15]

The foregoing results suggest that with transition metal complexes, a metal cyclopropylcarbinyl cation is not involved in the rearrangement of bicyclobutane **1** to diene **4**. The formation of such a cation results from an acid-catalyzed ring opening, and **2** can be an intermediate with a good σ-acceptor metal like Ag(I).[2,3] With a variety of Rh(I), Pd(II), and Pt(II) complexes, the intermediacy of complex **5** in the stepwise rearrangement of a bicyclobutane **1** to diene **4** is indicated.[16]

Acknowledgment. The authors are deeply indebted to Professors Neil Bartlett and Kenneth N. Raymond for their most helpful discussions.

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[12] This dependence of product distribution on the dryness of solvents and length of time before $[Rh(CO)_2Cl]_2$ was used is not surprising in view of the known sensitivity of this catalyst, especially its organic solutions, to air and water. It was reported earlier that $[Rh(CO)_2Cl]_2$ could be recovered from methanol, suggestive that $[Rh(CO)_2Cl]_2$ was catalyzing the rearrangement of **1** to ethers **7** rather than some other catalyst formed from $[Rh(CO)_2Cl]_2$ in methanol. (See ref 2a.) These reported results are not in agreement with our results in which we found more ethers **7** formed with the length of time the $[Rh(CO)_2Cl]_2$ solution was allowed to stand before use. We conducted an infrared study of $[Rh(CO)_2Cl]_2$ in methanol and found that after about 7 hr the carbonyl bands of the catalyst had disappeared, indicating that methanol indeed reacted with $[Rh(CO)_2Cl]_2$ to give a new rhodium species and/or other impurities. Also, in all cases the initially red-orange $[Rh(CO)_2Cl]_2$ solutions turned to a dark brown color.

[13] The following catalysts in the presence of methanol also rearrange **1** to greater than 90% of **4**: $PdCl_2[(C_6H_5)_3P]_2$; $PdCl_2[(C_6H_5)_3As]_2$; $PdCl_2[(C_6H_5)_3Sb]_2$; $Rh(CO)[(C_6H_5)_3P]_2X$, X = Cl, Br, I. No significant change in product distribution was observed on changing from methanol to methanol-d_4 or a 3:1 chloroform–methanol solution.

[14] The sensitivity of **1** to small amounts of acids is well known. See ref 11 and (a) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); (b) K. B. Wilberg and G. Szeimes, *ibid.*, **92**, 571 (1970).

[15] Structure **6**, X = OCD_3, has the following significant nmr absorptions ($CDCl_3$ with methanol-d_4): δ 2.75 (broad s, 1), 3.75 (m, 1), 4.00 (m, 1), 4.75 (m, 1). See ref 6.

[16] Since submission of this communication, Gassman and Williams [*J. Chem. Soc., Chem. Commun.*, 80 (1972)] have reported trapping a cyclopropylcarbinyl cation intermediate from a highly substituted bicyclobutane under acid-free conditions. Reaction pathways have been previously found to be sensitive to the position and stereochemistry of alkyl substituents on bicyclobutanes [M. Sakai, H. Yamaguuchi, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 486 (1971)].

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Received January 19, 1972

Chemical Consequences of Strong Hydrogen Bonding in the Reactions of Organic Ions in the Gas Phase. Interaction of Remote Functional Groups

Sir:

In recent publications we have reported investigations of the chemical consequences of strong hydrogen bonding. The *intermolecular* strong hydrogen bond, formed by the binding of two n-donor bases to a labile proton, plays an important role in a variety of bimolecular reactions, including acid[1–4] and base[5] induced elimination reactions, nucleophilic displacement reactions,[6,7] and a new class of associative fragmentation processes.[8] We wish now to report a modification of the reactivity of bifunctional compounds of the type $X{-}(CH_2)_n{-}Y$ which is introduced by *intramolecular* strong hydrogen bonding (proton bridge) between the remote functional groups X and Y in the protonated parent ions. The results imply the existence of intramolecular strong hydrogen bonding and suggest preferred structural features for bidentate coordination of protons.

We have prepared[9] and examined by ion cyclotron resonance[4] the series of dimethoxyalkanes X = Y = $-OCH_3$, n = 2–6. Ethers can be protonated quite readily in the gas phase by fragments generated from electron impact ionization of the ethers themselves.[10,11] The behavior of the protonated parent ions of the ethers was examined as the pressure of the neutral parent was increased; the only reaction product from the protonated parent ion is the proton-bound dimer. The fractional abundances of proton-bound dimers as a function of pressure are illustrated in Figure 1. While the formation of proton-bound dimer occurs readily for the case $n = 2$ in the range 10^{-5}–10^{-4} Torr, no such process is observed for $n = 5$ and 6 up to 10^{-3} Torr. The cases $n = 3$ and 4 are intermediate in behavior, with formation of proton-bound dimer detected in the range 10^{-4}–10^{-3} Torr. By contrast, the protonated parent of the monofunctional ether 1-methoxyoctane, also shown in Figure 1, is observed to aggregate with the parent neutral at 10^{-5} Torr.

Our observations regarding inhibition of proton-bound dimer formation with increasing chain length in the dimethoxyalkanes can be rationalized in terms of the existence of a proton bridge between the functional groups and the resulting alteration of the thermodynamic changes attending proton-bound dimer formation. The thermochemistry of the latter process may be exemplified by the aggregation of a hydronium ion with a water molecule to form proton-bound dimer, reaction 1. Proton solvation in the gas phase has

$$H_3O^+ + H_2O \rightleftharpoons H_2O\cdots\overset{+}{H}\cdots OH_2 \qquad (1)$$

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[1] J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

[2] J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970).

[3] M. Caserio and J. L. Beauchamp, *ibid.*, **94**, 2638 (1972).

[4] J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

[5] D. P. Ridge and J. L. Beauchamp, unpublished results, described briefly in ref 4.

[6] D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

[7] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *ibid.*, **94**, 2798 (1972).

[8] D. P. Ridge and J. L. Beauchamp, *ibid.*, **93**, 5925 (1971).

[9] H. F. Grützmacher and J. Winkler, *Org. Mass Spectrom.*, **1**, 295 (1968).

[10] M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965).

[11] J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

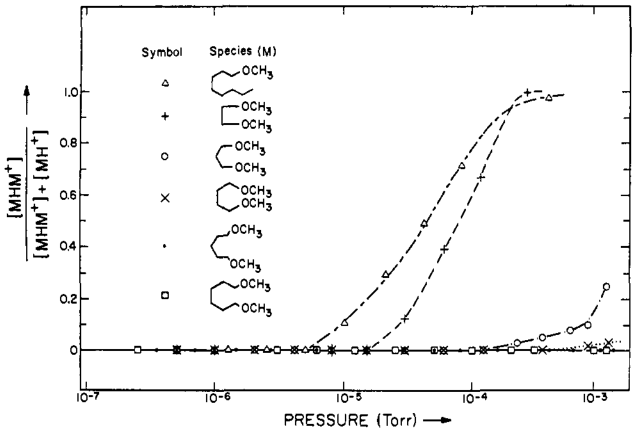
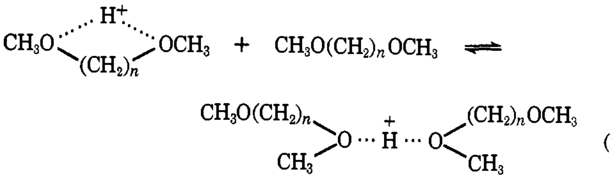


Figure 1. Fractional abundances of proton-bound dimers as a function of pressure.

been studied in detail by Kebarle, *et al.*, who have determined that, for reaction 1, $\Delta H = -36$ kcal/mol and $\Delta S = -33.3$ eu.[12] The negative entropy change represents mainly the loss of translational degrees of freedom of the system when two molecules aggregate,[12,13] and it is the enthalpy term which produces a large negative ΔG for reaction 1.

The aggregation of monofunctional ethers should parallel the example of reaction 1. However, if the proton is already bound to two sites in the protonated parent ion, then the *enthalpy* change for proton-bound dimer formation should be much smaller. The aggregation of bifunctional ethers, reaction 2, demonstrates

 (2)

$$CH_3O\overset{H^+}{\cdots}OCH_3(CH_2)_n + CH_3O(CH_2)_nOCH_3 \rightleftharpoons \begin{matrix}CH_3O(CH_2)_n\\CH_3\end{matrix}\!>\!O\cdots\overset{+}{H}\cdots O\!<\!\begin{matrix}(CH_2)_nOCH_3\\CH_3\end{matrix} \quad (2)$$

this phenomenon. From our results, it appears that the intramolecular proton bridge prefers an 8 member ($n = 5$) or larger ring structure.[14] Our inference is that the intramolecular strong hydrogen bond maintains a strong preference for linear geometry.[15]

Availability of other protonic binding sites in a proton-bridged bifunctional molecule permits proton-bound dimer formation to occur without rupture of the intramolecular strong hydrogen bond.[16,17] For instance, among the series of methoxyalkanols, X = $-OCH_3$, Y = -OH, n = 2-4, proton-bound dimer is observed in the pressure range 10^{-5}–10^{-4} Torr.

We consider that the applicability of these observations is very general and that such investigations of bifunctional compounds may serve as a general basis for detection of intramolecular strong hydrogen bonds. In addition, our examination of the mass spectra and ion–molecule reactions of bifunctional compounds has revealed a large number of processes in which remote functional groups may interact with one another in the same molecule.

Acknowledgment. This work was supported in part by the U. S. Atomic Energy Commission under Grant No. AT(04-3)767-8.

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[12] P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

[13] S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2619 (1969).

[14] For a discussion of the structural preferences for weak hydrogen bonds, see S. N. Vinogradov and R. H. Linell, "Hydrogen Bonding," Van Nostrand, Princeton, N. J., 1971, pp 134–146, and references cited therein.

[15] For calculations describing the geometry of the proton-bound dimer of water, see P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).

[16] Related systems have been examined by I. Dzidic and J. A. McCloskey, *ibid.*, **93**, 4955 (1971).

[17] The case $n = 4$ has been examined in solution by F. Klages, J. E. Gordon, and H. A. Jung, *Chem. Ber.*, **98**, 3748 (1965).

[18] NIH Predoctoral Fellow, 1969–present.

[19] Camille and Henry Dreyfus Teacher-Scholar.

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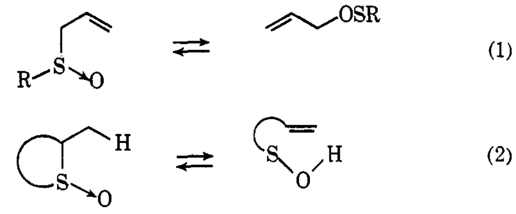
Received February 24, 1972

Nucleophilic Cleavage of Allylic Sulfenate Esters. Mechanistic Observations

Sir:

The role of both sulfenate esters and acids in sulfoxide chemistry has become increasingly apparent. Examples involving sulfur–oxygen scission from these reactive species generated as a consequence of the rearrangement of allylic sulfoxides[1] (eq 1) and the thermal fragmentation of certain cyclic sulfoxides[2,3] (eq 2) have been reported. In addition, the mechanistically interesting ether synthesis involving the desulfurization of sulfenate esters (eq 3) has been demonstrated by Barton and coworkers.[4]



(1)

(2)

$$R{-}S{-}O{-}R' \longrightarrow R{-}O{-}R' \quad (3)$$

As has been shown in each of these cases, trivalent phosphorus derivatives appear to be effective cleavage reagents. The purpose of this communication is to report our observations on the fate of allylic sulfenate esters produced by [2,3]-sigmatropic rearrangement (eq 1) in the presence of trimethyl phosphite and to suggest that the products derived from this reaction are consistent with a general Michaelis–Arbuzov[5] cleavage process.

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[1] (a) D. A. Evans, G. C. Andrews, and C. L. Sims, *J. Amer. Chem. Soc.*, **93**, 4956 (1971); (b) D. A. Evans, C. A. Bryan, and C. L. Sims, *ibid.*, in press; (c) D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C*, 818 (1969).

[2] (a) R. D. G. Cooper and F. L. José, *J. Amer. Chem. Soc.*, **92**, 2575 (1970); (b) D. H. R. Barton, D. G. T. Grieg, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *J. Chem. Soc. D*, 1683 (1970).

[3] J. E. Baldwin, G. Höfle, and Se Chun Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971).

[4] D. H. R. Barton, G. Page, and D. A. Widdowson, *J. Chem. Soc. D*, 1466 (1970).

[5] R. G. Harvey and E. R. DeSombre, *Top. Phosphorus Chem.*, **1**, 57 (1964).