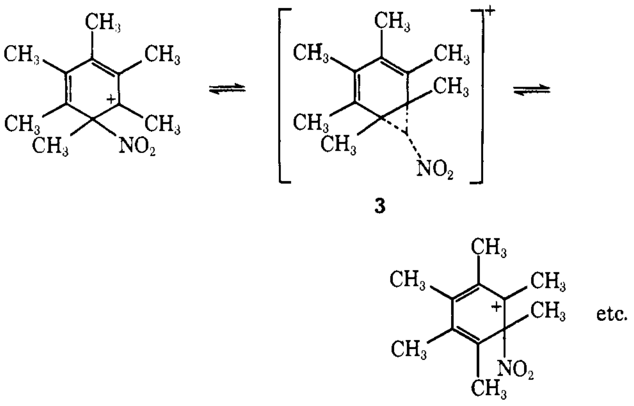
Temperature-dependent pmr spectra of ion **1a** were also observed (Figure 1, left). This behavior indicates that the nitro group (NO_2^+) is not fixed and can undergo a degenerate migration or exchange process. On the right-hand side of Figure 1, we also show the theoretical, computed spectra with various exchange rates.[10] Matching of the line shapes allows the activation energy to be determined as $E_a = 16.8 \pm 1.5$ kcal/mol. The nitrohexamethylbenzenium ion **1a** is slightly decomposing to yet unidentified products at higher temperature (>−8°). It is assumed that excess nitronium ion (NO_2^+) could attack the C–H bond of the methyl groups and give benzylic products. The exchange process was further studied by quenching experiments. When benzene or mesitylene was added to the solution of ion **1a**, nitrobenzene or nitromesitylene was formed.[11] With hexamethylbenzene in slight excess, no formation of nitrobenzene or nitromesitylene was observed, even when the temperature was raised to −20°. If benzene or mesitylene was mixed with hexamethylbenzene in SO_2 before the addition of the nitronium ion solution, formation of nitrobenzene or nitromesitylene was detected. These experimental results strongly support the intramolecular nature of the exchange process. The migration of NO_2^+ is assumed to proceed *via* 1,2-nitro shifts involving three-center-bond benzonium ion transition states **3**.[12]



3

No temperature-dependent nmr spectra of ion **2a** were observed in the temperature range from −70 to −20°. This may be due to the *vic*-fluorine substituent causing a high enough activation energy barrier as to prohibit the nitro group to migrate. The pmr spectra of chlorohexamethylbenzenium ion **1b** and 1-chloro-2,4,6-trifluoromesitylenium ion **2b** were also temperature independent ranging from −70 to −20°. It must be assumed that the leaving ability of "Cl^+" is less than that of NO_2^+, indicating increased barrier for chlorine migration in these chlorinated ions. Such relative migrating ability ($NO_2^+ > Cl^+$) was also observed recently by Perrin.[13] Whereas alkenechloronium ions are well known[14] and even observed as stable species, cycloalkene (polyene) chloronium ions were until now never observed.[15] Higher strain in the latter seems to make them thermodynamically less favorable.

We consider present studies of significance, because they represent the first observation of an intermediate σ complex in electrophilic aromatic substitution reactions (nitration and chlorination) other than protonation and alkylation. Furthermore, they help to understand the strong complexing ability of polyalkylbenzenes with electrophiles.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

(10) The theoretical spectra for various rate constants were calculated by use of a multiple site exchange program originally obtained from Dr. T. Gerig and was adapted to the Univac 1108 computer by Dr. W. E. Heyd. The methyl exchange process of the heptamethylbenzenium ion was previously studied by a more elaborate line-shape method by Professor M. Saunders, as reported in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Ed., Pergamon Press, New York and London, 1967, pp 85–99, who pioneered the study of exchange processes and wrote the original programs.

(11) The resultant solution was quenched with ice and washed with $NaHCO_3$ solution. The nitro products were then extracted with ether and analyzed by gas chromatography.

(12) For the concept of three-center-bond carbonium ions, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(13) C. L. Perrin, *J. Org. Chem.*, 36, 420 (1971).

(14) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 2587 (1968).

(15) G. A. Olah, G. Liang, and Y. K. Mo, *ibid.*, **94**, 3544 (1972).

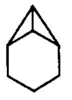
George A. Olah,* Henry C. Lin, Y. K. Mo
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received January 21, 1972

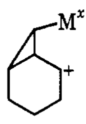
Transition Metal Catalyzed Valence Isomerizations of Tricyclo[4.1.0.0^{2,7}]heptane. Evidence for an Organometallic Intermediate[1]

Sir:

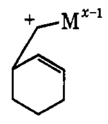
It has recently been suggested that the transition metal catalyzed rearrangement of bicyclobutanes, like **1**, proceeds *via* a stepwise process involving intermediates **2** and **3**[2] with the presence of **2** being established by trapping with methanol. In the course of studies in these laboratories related to these processes,[3] we have found that by using a high catalyst concentration, an organometallic intermediate can be detected by nmr spectroscopy.



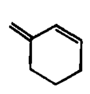
1



2



3



4

With a catalytic amount of $PdCl_2(C_6H_5CN)_2$, **1** rearranges to the diene **4** in deuteriochloroform solutions.[4] Using a 1:1 molar ratio of **1** and the catalyst

---

(1) This work was supported by the National Science Foundation, Grant No. GP-8700.

(2) (a) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971); (b) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); (c) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, 4611 (1971).

(3) (a) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971); (b) W. G. Dauben and A. J. Kielbania, *ibid.*, **93**, 7345 (1971).

(4) Reactions were carried out in base-washed nmr tubes in $CDCl_3$. Molar ratio of **1** to catalyst was approximately 30:1. Products were identified by comparison of spectral properties and vpc retention times with the known compounds. We have found that the following catalysts also bring about a rearrangement of **1** to **4**: $PdCl_2[(C_6H_5)_3P]_2$; $PdCl_2[(C_6H_5)_3As]_2$; $PdCl_2[(C_6H_5)_3Sb]_2$; $PdCl_2[P(OCH_3)_3]_2$; $PdCl_2[P(OC_6H_5)_3]_2$; $PtCl_2[(C_6H_5)_3P]_2$; $PtCl_2[(C_6H_5)_3Sb]_2$; $PtCl_2(pyr)_2$; [Rh(nor)Cl]$_2$; $Rh[(C_6H_5)_3P]_3Cl$, $RhCO[(C_6H_5)_3P]_2X$, X = Cl, Br, I. Pyridine is (pyr) and norbornadiene is (nor).

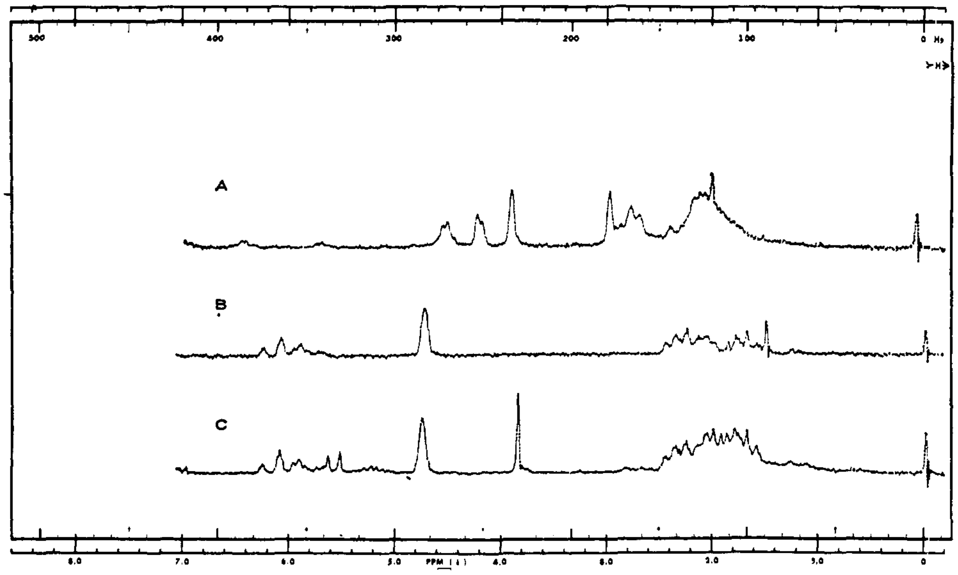
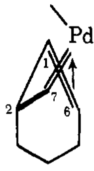
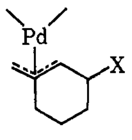


Figure 1. Proton nmr spectra: A, π-allyl complex **6** (X = Cl); B, methylenecyclohexene, **4**; C, mixture of methylenecyclohexene and complex **5** (prepared from a 2:1 ratio of **1** to catalyst, 25°, 2–3 min after mixing).

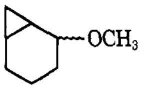
in deuteriochloroform solution, an almost instantaneous reaction occurs, the solution showing nmr absorptions at δ 1.2–2.6 (m, 7), 3.90 (broad s, 1), 5.30 (broad m, 1), and 5.65 (broad d, 1, J = 6 Hz) (see Figure 1). These data are suggestive of an organometallic intermediate like **5** which contains hydrogens of a palladium-complexed disubstituted olefin and a hydrogen on a carbon which is also bonded to palladium.[5] Double resonance studies showed that the C-7 hydrogen (δ 3.90) was not coupled with the vinyl hydrogens on C-1 and C-6; these latter two hydrogens, however, were coupled and the expected spectral changes occurred. 1-Deuteriotricyclo[4.1.0.0^{2,7}]heptane was studied under identical conditions and the expected reductions in the intensities of the absorptions for C-1 (δ 5.65) and for C-7 (δ 3.90) were found. The nmr spectrum of the original sample changed in the course of minutes to an nmr spectrum consistent with π-allyl complex[6] **6** (X = Cl), δ 1.6–2.8 (m, 6), 2.95 (broad s, 1), 3.85 (broad s, 1), 4.15 (m, 1), and 4.55 (m, 1)[7] (see Figure 1), which was isolated as a light orange solid (mp 60–65° dec). Both complexes when allowed to react with excess triphenylphosphine yielded diene **4**.



5



6



7

To evaluate the role of complexes **5** and **6** in the rearrangement process, the following reactions were performed. Using lower catalyst concentrations, *i.e.*, 2:1 and 4:1 molar ratio of **1** to catalyst, rapid reactions occurred to yield only diene **4** and complex **5**.[8] Upon addition of bicyclobutane **1** to the π-allyl complex **6**, measurable quantities of **4** and **5** were formed. Finally, addition of diene **4** to the $PdCl_2(C_6H_5CN)_2$ catalyst, 1:1 molar ratio, gave only complex **6**.[9] The foregoing results suggest that bicyclobutane **1** reacts with the Pd(II) catalyst to give complex **5** which decomposes to diene **4**. Diene **4** in the presence of Pd(II) catalyst then reacts to give complex **6**. However, the rearrangement of **5** directly to **6** cannot be ruled out, although it appears that complex **6** is not necessary in the conversion of bicyclobutane **1** to diene **4**.

This intermediate complex **5** is similar to the earlier postulated structure **3**,[2a] differing only in the involvement of the double bond with the metal. The intermediate **3** was considered to be derived from the metal cyclopropylcarbinyl cation **2**. The evidence for the involvement of cation **2** was the formation in 75% yield of a mixture of 2-norcarane methyl ethers **7** when **1** was treated with $[Rh(CO)_2Cl]_2$ in methanol.[2a] In view of our inability to detect by nmr an intermediate of this type, we have reexamined the experiments performed in methanol.

Using freshly prepared and recrystallized $[Rh(CO)_2Cl]_2$[10] in methanol,[11] bicyclobutane **1** gives better than

---

[5] A molecular model of **5** shows it to be less strained than norbornenylpalladium complexes [*J. Chem. Soc. A*, 3699 (1971)] and also shows that the hydrogen on C-7 is orthogonal to the vicinal hydrogen accounting for the singlet in the nmr spectrum.

[6] (a) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); (b) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964); (c) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc. A*, 1687 (1966); (d) J. Powell and B. L. Shaw, *ibid.*, 1839 (1967); (e) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967); (f) C. W. Alexander, W. R. Jackson, and R. Spratt, *J. Amer. Chem. Soc.*, **92**, 4990 (1970); (g) P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York, N. Y., 1971, pp 175–251, and references cited therein.

[7] Complex **6** showed the proper analysis and when formed from monodeuterio-**1** exhibited the expected reduction in the appropriate nmr band intensities.

[8] Reactions were analyzed by nmr spectroscopy.

[9] The reaction of dienes with Pd(II) is well known to give π-allyl complexes. See ref 6.

[10] J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1966).

[11] Reactions were carried out in base-washed nmr tubes with $NaHCO_3$ present under a dry nitrogen atmosphere. Attempted use of homogeneous bases to scavenge any acid present, such as methoxide or pyridine, resulted in rapid decomposition of $[Rh(CO)_2Cl]_2$ and no reaction was observed. Also, stirring methanol with $NaHCO_3$ (48–72 hr) before $[Rh(CO)_2Cl]_2$ was added resulted in rapid decomposition of catalyst and low conversion of **1** (approximately 10%). See ref 10 and (a) A. C. Yang and C. W. Garland, *J. Phys. Chem.*, **61**, 1504 (1957); (b) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965); (c) J. P. Maher, *Chem. Commun.*, 785 (1966), for reactions of $[Rh(CO)_2Cl]_2$ with nucleophiles and sensitivity to air and moisture.

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.

(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)].

William G. Dauben,* Andrew J. Kielbania, Jr.
Department of Chemistry, University of California
Berkeley, California 94720

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

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

---

(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.