Structures of Isomeric Anions in the Gas Phase: Arylallyl and Arylcyclopropyl Anions

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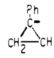
Abstract: The isomeric 1-phenylcyclopropyl and 2-phenylallyl anions have been prepared in the gas phase by proton-abstraction reactions. They have been shown to be distinct, noninterconverting species by their differing reactions with D_2O, O_2, and N_2O. The 2-methyl-1-phenylcyclopropyl and 1-methyl-2-phenylallyl anions are also shown to react differently with these reagents. However, in the presence of H_2O the 1-methyl-2-phenylally anion is converted to the 1-methyl-1-phenylallyl anion by proton addition and reabstraction. The utility of these and other reagents for determining ion structure in the gas phase is discussed.

The determination of ion structure is a central problem in all of mass spectrometry because only the mass-to-charge ratio (m/z) is determined in the usual mass spectrometric experiment. The study of gas-phase organic ion–molecule chemistry, therefore, is complicated by the fact that isomeric ions ordinarily are indistinguishable.[1] For positive ions a number of structure-elucidation techniques have been developed and usefully employed;[1,2] for negative ions only a relatively small number of structural studies have been carried out. Some interesting applications of multiphoton electron detachment as an indirect spectroscopic probe of gas-phase carbanion structures have been described recently.[3] Most structural studies of gaseous anions have relied upon the specific reactivity differences which isomeric ions may exhibit toward selected neutral reagents. For example, the propargylic and acetylenic forms of the $C_3H_3^-$ ion derived from propyne can be distinguished readily by the distinct products of their reactions with either nitrite or formate esters.[4] Furthermore, regioisomeric ketone enolate anions are cleaved in the gas phase in a characteristic manner by nitrite esters.[5] Gas-phase hydrogen–deuterium exchange in carbanions has been a particularly useful tool for structural determinations.[6] The number of hydrogens which exchange, the relative rates of exchange, and the acidity of the reagent required to effect the exchange can all contribute to the solution of a carbanion structure problem.

We have been engaged in the study of gas-phase carbanion reactivity.[7] One important aim of this research has been to develop gas-phase chemical reactions which serve to identify distinct ion structures. It seemed appropriate, therefore, to apply our structure-elucidation methods to a system of potentially rearranging isomeric anions. It is in this context that we wish to report the results of our investigations of the structures and reactivities of carbanions derived from some substituted cyclopropanes and their allylic isomers, **1–6**. Ring-opening rearrangements of substituted cyclopropyl anions have been extensively investigated in solution.[8] The general conclusions from these studies, as well as from molecular orbital calculations,[9] are that interconversions of cyclopropyl and allylic carbanions are impeded by relatively high activation barriers. Limited results from gas-phase experiments are in accord with these conclusions. Dawson and Nibbering demonstrated[10] that the cyanocyclopropyl anion does not rearrange to the 2-cyanoallyl anion under low-pressure conditions at room temperature in an ion cyclotron resonance (ICR) spectrometer.



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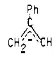

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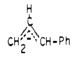

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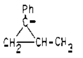

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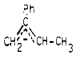

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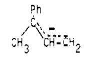

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Experimental Section

Our experiments were conducted at 300 K in a flowing afterglow (FA) apparatus which has been described in detail previously.[11] Briefly, the system consists of a 100 cm × 7 cm i.d. flow reactor affixed to a quadrupole mass spectrometer. A fast flow (80 m s^{-1}) and relatively high pressure (0.3 torr) of helium buffer gas is maintained in the flow tube by a Roots blower. Primary ionic reagents are generated by electron impact in an upstream ion source and are subsequently allowed to react with neutral substrates added at various positions along the flow tube. At the downstream end ions are sampled at an orifice and focused into the quadrupole mass filter where they are separated and then detected by a particle multiplier. The carbanions described in this study were formed from the corresponding hydrocarbons by proton transfer to amide ion which, in turn, was produced by dissociative electron attachment to ammonia.

Reagent Gases and Chemicals. All reagent gases were obtained from commercial suppliers and had the following purities: He (99.995%), NH_3 (99.999%), N_2O (99.99%), and O_2 (99.0%). Deuterium oxide (99.8 atom % D) was obtained from Stohler Isotope Chemicals, Waltham, MA. Methanol-*O-d* (98 atom % D) was prepared by D_2O exchange. A mixture of 75 mL of D_2O (99.8 atom % D) and 40 mL of CH_3OH was distilled through a 50-cm metal helices column. This procedure was repeated with an additional 40 mL of D_2O and the CH_3OD fractionated to give 45 mL of CH_3OD. 2-Phenylpropene, *trans*-1-phenyl-1-propene, and 3-phenyl-1-propene were obtained from the Aldrich Chemical Co., Milwaukee, WI, and were distilled from lithium aluminum hydride directly into the FA system. Phenylcyclopropane was also obtained from

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(1) (a) Ausloos, P. A.; Lias, S. G. In "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972; Vol. 2. (b) Holmes, J. L.; Burgers, P. C.; Mollah, M. Y. A.; Wolkoff, P. *J. Am. Chem. Soc.* **1982**, *104*, 2879–2884. (c) Wagner-Redeker, W.; Illies, A. J.; Kemper, P.; Bowers, M. T. *Ibid.* **1983**, *105*, 5719–5724, and references cited therein.

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(3) (a) Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499–6501; *Ibid.* in press. (b) Meyer, F. K.; Jasinski, J. M.; Rosenfeld, R. N.; Brauman, J. I. *Ibid.* **1982**, *104*, 663–667.

(4) (a) King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133–7140. (b) Dawson, J. H. J.; Kaandorp, T. A. M.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1977**, *12*, 330–333. (c) Mackay, G. I.; Bohme, D. K. *Ibid.* **1980**, *15*, 593–595.

(5) Squires, R. R.; DePuy, C. H. *Org. Mass Spectrom.* **1982**, *4*, 187–191.

(6) (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653. (b) DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *Ibid.* **1978**, *100*, 2921–2922. (c) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *Ibid.* **1981**, *103*, 4256–4258. (d) Hunt, D. F.; Sethi, S. K. *Ibid.* **1980**, *102*, 6953–6963.

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(9) (a) Merlet, P.; Peyerimhoff, D. S.; Buenker, R. J.; Shih, S. *J. Am. Chem. Soc.* **1974**, *96*, 959–969. (b) Clark, D. T.; Armstrong, D. R. *Theor. Chim. Acta* **1969**, *14*, 370–382. (c) Sauer, J. *Tetrahedron* **1979**, *35*, 2109–2112. (d) Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, *47*, 2614–2618.

(10) Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *334*, 3–19.

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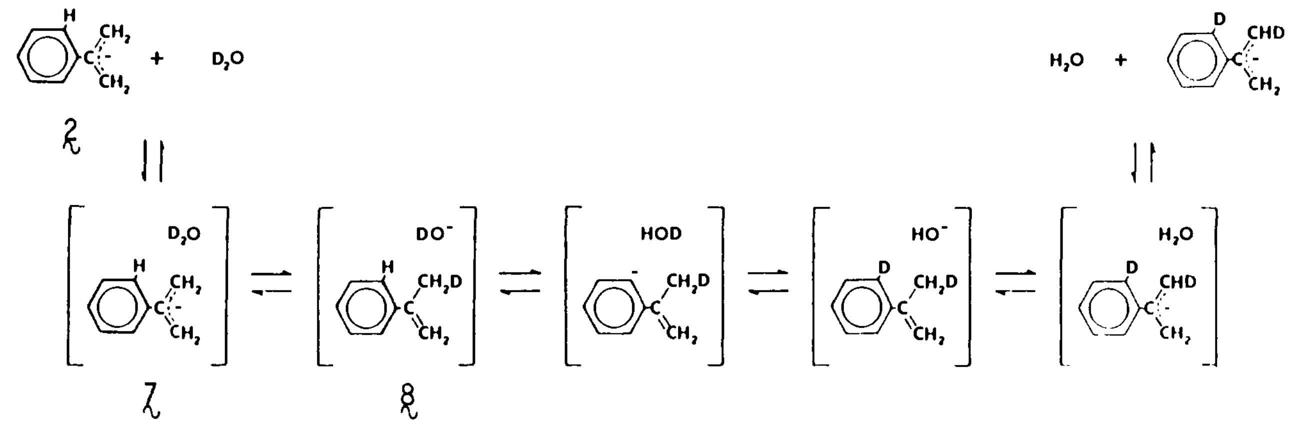
Scheme I



Aldrich but required further purification for these studies:[12] a pentane solution of phenylcyclopropane was treated with bromine at -60 °C in a dry ice-acetone bath. After the solution was washed with 0.2 M NaOH, dried (K_2CO_3), filtered, and distilled under vacuum (bp 26-30 °C (1 torr)), it was judged to be >99% pure by both NMR and mass spectral analysis.

2,2-Dideuteriophenylcyclopropane. The deuterated phenylcyclopropane was prepared by reduction of 2,2-dibromophenylcyclopropane using the procedure of Leermakers and Ross[12] where CH_3OD and D_2O were used in place of the undeuterated reagents specified in the original procedure. The product was isolated by vacuum distillation (bp 30-32 °C (1 torr)). NMR and mass spectral analysis showed the product to be 98% d_2 and 2% d_1.

1-Methylphenylcyclopropane and *trans*-2-Methylphenylcyclopropane. The methylphenylcyclopropanes were prepared by the modified Simmons-Smith reaction described by Rawson and Harrison.[13] Alkene starting materials and side products were removed by the low-temperature bromine treatment described above for phenylcyclopropane. Each product was isolated by vacuum distillation (bp 28-35 °C (1 torr)).

2-Phenyl-1-butene. α-Ethylstyrene was prepared by elimination from the tosylate of 2-phenyl-1-butanol (Aldrich Chemical Co.) using neat 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) at 95-105 °C for 12 h.[14] The product was isolated by vacuum distillation (bp 34-45 °C (1 torr)) and identified by NMR analysis ($CDCl_3$): τ 1.2 (methyl, t, 3 H), 2.6 (methylene, q, 2 H), 5.15 (vinyl, m, 1 H), 5.35 (vinyl, broad s, 1 H), and 7.35 (aromatic, m, 5 H).

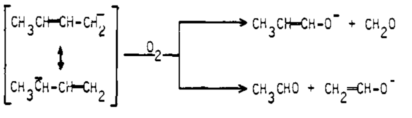
Results and Discussion

Reactive Probes of Carbanion Structures. Of the gas-phase reactions of carbanions we have studied, three have been found to be especially useful for investigations of ion structure.[7] The first of these, and by far the most useful, is hydrogen-deuterium exchange.[6] The way a carbanion reacts with D_2O in the gas phase can be extremely informative in assigning a structure. If the carbanion is strongly basic, it may simply be neutralized, forming OD^-. This observation indicates that its conjugate acid is weaker than D_2O. This situation is rare. Among the accessible gas-phase anions only a few vinyl and aryl carbanions fall into this category. More commonly an anion will exchange some or all of its protons for deuterons. The number of exchanges, as well as the rates at which the exchanges proceed, can provide information about ion structure. If the carbanion is a much weaker base than DO^-, no exchange occurs with D_2O. In this case isotopic exchange can usually be induced through the use of a stronger gas-phase acid, e.g., CH_3OD, CF_3CH_2OD, etc. A second method which is useful for relatively basic carbanions (such as those which undergo isotopic exchange with D_2O) makes use of reaction with nitrous oxide (N_2O).[15] For example, the allyl anion reacts with N_2O with loss of H_2O to form the vinylidiazomethane anion (eq 1).[15]

$$CH_2CHCH_2^- + N_2O \longrightarrow CH_2CHCN_2^- + H_2O \qquad (1)$$

The basicity of the anion and its rate of reaction with N_2O have been found to be related. Thus, allyl and some benzyl anions react with N_2O while dienyl and trienyl anions do not.[15] It should be noted that in order to produce a diazo anion by reaction with N_2O, a carbanion must be primary. Anions other than primary ones generally add to N_2O without loss of H_2O, if reaction occurs at all.

The third method we have employed for ion structure determination is reaction with oxygen. Many carbanions react with oxygen by cleavage to form enolate anions.[16] Generally, cleavage occurs at each carbon which bears a negative charge, so that in a delocalized ion the cleavage fragments aid in determining the structure of the ion (eq 2). Electron transfer from the carbanion



(2)

to oxygen, forming superoxide (O_2^-), is also seen when the reaction is exothermic. If no reaction occurs with ground-state oxygen, it can often be induced using singlet oxygen ($^1\Delta O_2$). We believe these oxygen reactions occur by electron transfer to oxygen followed by formation of a hydroperoxy anion (eq 3). Allylic

$$RCH_2^- + O_2 \longrightarrow [R\dot{C}H_2 + \dot{O}_2^-] \longrightarrow RCH_2\text{-}O\text{-}O^- \qquad (3)$$

hydroperoxy anions decompose to enolate anions, often in high yield, while benzylic hydroperoxy anions form phenoxide anion and other products.

1-Phenylcyclopropyl and 2-Phenylallyl Anions. Proton abstraction by NH_2^- from phenylcyclopropane, 2-phenylpropene, or 3-phenyl-1-propene gives exclusively m/z 117 product ions. These isomeric ions, **1**, **2**, and **3**, are readily distinguishable using the reagents described above. We have previously noted the H-D exchange pattern produced from the interaction of D_2O with ion **2**.[6c] Here, not only do the four allylic hydrogens exchange, but also four out of five of the weakly acidic aryl hydrogens as well. We have postulated a mechanism for this exchange wherein the formation of an incipient aryl anion is driven by the excess internal energy present within the D_2O-carbanion collision complex (Scheme I).

The exchange pattern for the 1-phenylcyclopropyl anion, **1**, is strikingly different from that of **2**. At D_2O flow rates where **2** is almost completely converted to the d_4 anion, **1** still shows appreciable amounts of the parent ion (m/z 117) with declining amounts of d_1-d_5 ions. At the same time, when D_2O is added to **1** (but not when added to **2**), large amounts of DO^-, $DO(D_2O)^-$, and higher D_2O clusters of DO^- appear in the spectrum. Therefore, **1** probably has a higher proton affinity than does **2** and is similar to DO^- in base strength. The observed H-D ex-

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(12) Leermakers, P. A.; Ross, M. E. *J. Org. Chem.* **1966**, *31*, 301-304.

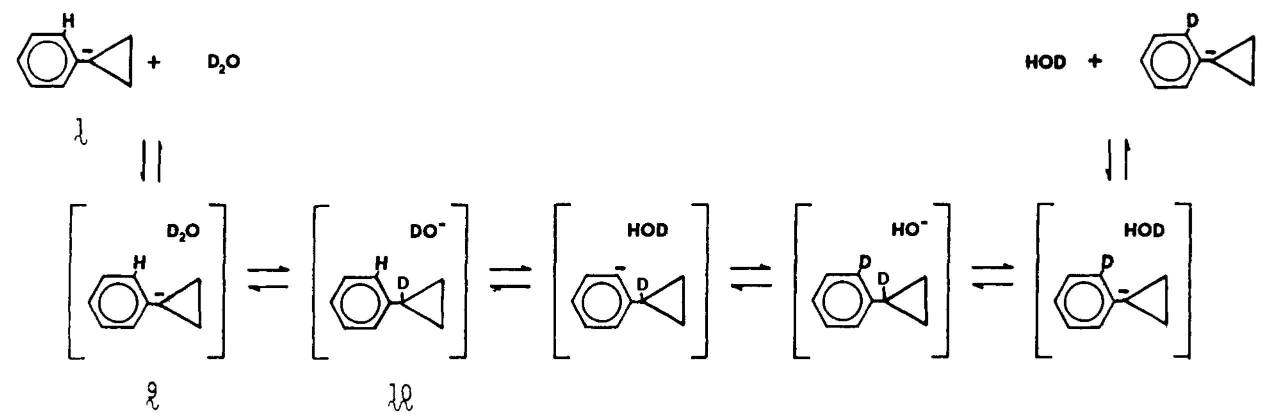
(13) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057-2058.

(14) Oediger, H.; Moller, F.; Eiter, K. *Synthesis* **1972**, 591-598.

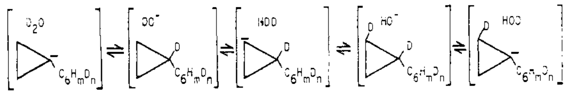
(15) (a) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800-5802. (b) Dawson, J. H. J.; Nibbering, N. M. M.; Noest, A. J. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 205-222.

(16) (a) Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 6443-6444. (b) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. *Environ. Health Perspect.* **1980**, *36*, 119-134.

Scheme II



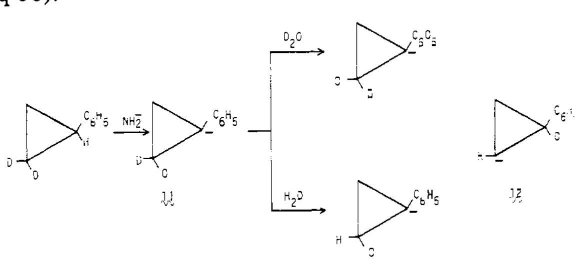
change pattern in **1** is ascribed to exchange of the aryl hydrogens (Scheme II). We expect this exchange to be more facile in **1** than in **2** because of the greater proton affinity of the former ion. This can be illustrated in the following way. A carbanion will be attracted to D_2O by ion-dipole and ion-induced dipole forces which may become appreciable (15–20 kcal/mol) by the time they reach reaction distance and enter into a long-lived collision complex. Presuming a similar magnitude of excess internal energy present within complexes **7** and **9**, we can say that less of this energy is required to fuel the initial endothermic deuteron abstraction step **9** → **10** than for **7** → **8**, since in the former case the carbanion is a stronger base. Hence, more internal energy would remain in intermediate **10** relative to **8** and subsequent ring-exchange steps will proceed faster. At high D_2O flow rates we can clearly distinguish even a sixth exchange in **1** and the beginning of a seventh exchange. This exchange of the hydrogens on the cyclopropane ring could occur as illustrated in eq 4.



(4)

However it seemed surprising that exchange of such weakly acidic hydrogens would take place by this mechanism.

To investigate this further we examined the exchange process in 2,2-dideuteriophenylcyclopropane. Deprotonation by NH_2^- results in exclusive formation of a $(M - H)^-$ product ion. This observation confirms that only the benzylic hydrogens (and/or the aryl hydrogens) are abstracted in the initial proton-transfer reaction with NH_2^-. Exchange with D_2O readily introduces five more deuterons (eq 5a). Exchange with H_2O is extremely slow, but at H_2O flow rates similar to those for which six exchanges were observed in **1**, loss of deuterium in **11** is observed to occur (eq 5b).

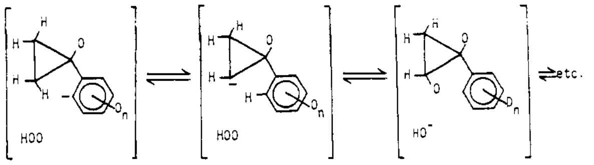


(5a)

(5b)

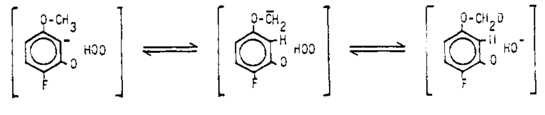
Exchange of the cyclopropyl hydrogens in **1** must involve the formation of a nonbenzylic cyclopropyl anion **12**. We have previously observed the exchange of aryl and vinyl protons, but this represents a novel example of H–D exchange on a saturated hydrocarbon.[17]

The acidity of the hydrogens on the parent cyclopropane ring is unknown; however, we estimate that ethylene is about 3 kcal/mol less acidic than ammonia,[18] which, in turn, is 12 kcal/mol less acidic than water.[19] The hydrogens on cyclopropane should be even less acidic, perhaps 20–25 kcal/mol less acidic than water. The polarizability as well as the inductive effect of the phenyl group in **1** should stabilize anion **12** somewhat, but it is remarkable that water is capable of effecting exchange of these cyclopropyl hydrogens. A possible explanation is that formation of the intermediate cyclopropyl anion **12** occurs via intramolecular proton transfer (eq 6).



(6)

Good evidence for an analogous intramolecular proton-abstraction step during H–D exchange of the methyl protons in *p*-fluoroanisole anion was recently reported by Ingemann and Nibbering[20] (eq 7). The fact that we can observe six or more



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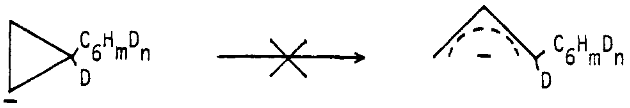
exchanges in **1** and **11** also implies that **12** does not ring open (eq 8). An electrocyclic ring opening of a 2-phenylcyclopropyl anion



12 13

(8)

12 would produce **13** whose unlabeled analogue **3** does not undergo H–D exchange with D_2O. If **12** did open to the 1-phenylallyl anion **13**, the extensive H–D exchange in **1** and the washing out of deuterium from **11** would not be possible. In solution the cyclopropyl anion to allyl anion rearrangement is observed when ring opening produces a benzylic anion.[8d,21] Our exchange experiments suggest that such a rearrangement does not occur in the gas phase, at least on the time scale of the FA experiment.

The fully conjugated anion **3** which is formed by proton abstraction from either 1-phenyl- or 3-phenylpropene, does not

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(17) Other examples of H–D exchange at saturated carbons in gas-phase carbanions have been reported recently: (a) Noest, A. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1980**, *102*, 6427–6429. (b) Bartmess, J. E.; Caldwell, G.; Rozeboom, M. D. *Ibid.* **1983**, *105*, 340–344.

(18) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565–2571.

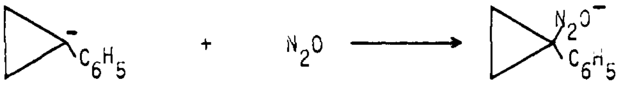
(19) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T. Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(20) Ingemann, S.; Nibbering, N. M. M. *J. Org. Chem.* **1983**, *48*, 183–191.

(21) Newcomb, M.; Ford, W. T. *J. Am. Chem. Soc.* **1974**, *96*, 2968–2974.

exchange any hydrogens with D_2O. This is consistent with our previous findings[6a,b] that conjugated dienyl anins do not undergo exchange under these conditions, presumably because deuteron transfer from D_2O to the anion is too endothermic to occur. A maximum of three exchanges can be observed in **3** when the more acidic deuterium source CH_3OD is used.

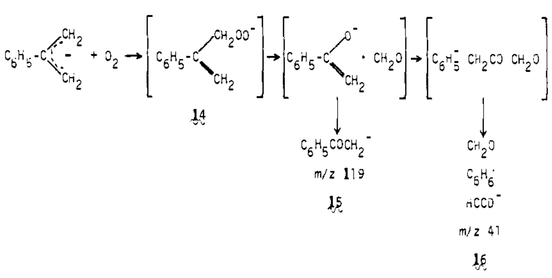
The three ions **1**, **2**, and **3** exhibit differing reactivity toward N_2O. The tertiary ion **1** simply adds N_2O slowly (eq 9). Addition



(9)

reactions are usually slow in the gas phase because the excess energy in the adduct must be removed by subsequent collisions with the buffer gas. At relatively high N_2O flow rates, roughly one-third of the phenylcyclopropyl anion can be converted to the N_2O adduct. In accord with results for related allylic anions,[15] the 2-phenylallyl anion **2** reacts with N_2O to form the diazo anion while the fully conjugated anion **3** does not react at all.

Each of the three anions also behaves differently in reactions with oxygen. The reaction of O_2 with **2** is rapid and only two products at m/z 119 and 41 are formed (eq 10). We propose



(10)

that these ions correspond to the enolate anions of acetophenone **15** and ketene **16**, respectively. Cleavage of the initially formed peroxy anion **14** would generate the ketone enolate **15** in a highly exothermic reaction. Further cleavage of this enolate to ketene and phenide anion followed by proton transfer would lead to **16**.

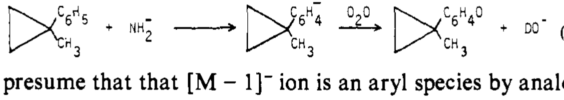
The proposed structures of **15** and **16** can be further substantiated by first introducing deuterium into **2** by exchange with D_2O and then treating it with O_2. If four deuterons are introduced into **2** in such a manner and subsequently O_2 is added, we observe that the m/z 119 ion becomes m/z 121 and m/z 41 becomes m/z 42. This experimental finding confirms that the first four deuterons introduced by exchange go onto the allylic carbons rather than onto the benzene ring. Oxygen cleavage leaves two behind on the acetophenone enolate anion **15**.

Ion **1** reacts more slowly with O_2 than does **2**. At relatively high O_2 flow rates several reaction products are formed (eq 11).

$$\mathbf{1} + O_2 \longrightarrow \begin{array}{l} m/z\ 93\quad C_6H_5O^- \\ m/z\ 17\quad HO^- \\ m/z\ 103 \\ m/z\ 107 \\ \text{trace } m/z\ 41,\ 74,\ 121,\ 43,\ 144 \end{array} \qquad (11)$$

Under these conditions, further reactions of the primary product ions with O_2 are likely and may be responsible for some of the detected product ions shown above. Interestingly, under similar conditions anion **3** is not observed to react with O_2. This is in contrast to our earlier findings that conjugated dienyl anions undergo cleavage reactions with oxygen.[16]

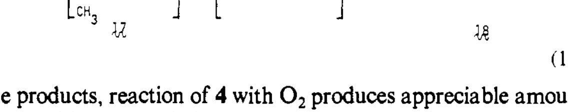
Methylphenylcyclopropyl and Phenylbutenyl Anions. We next turned our attention to the methyl-substituted phenylcyclopropanes and their butenyl isomers. When 1-methyl-1-phenylcyclopropane is allowed to react with NH_2^-, an $[M - 1]^-$ ion (m/z 131) is formed, but this ion is completely neutralized by D_2O (eq 12).



(12)

We presume that that $[M - 1]^-$ ion is an aryl species by analogy with the reaction between NH_2^- and *tert*-butylbenzene which yields the corresponding substituted phenide anion.[22]

The anion formed upon NH_2^- deprotonation of *trans*-2-methyl-1-phenylcyclopropane responded to all of our reactive probes in a manner consistent with cyclic structure **4**. With D_2O it gradually exchanges its five aromatic hydrogens and traces of a sixth exchange are detectable. It reacts slowly with N_2O by addition. If partial H–D exchange is carried out before N_2O treatment, the N_2O adduct has essentially the same deuterium distribution as the parent ion. The products of the reaction of **4** with O_2 are interesting. In contrast with its lower homologue **1**, which forms only a trace of an O_2 adduct, anion **4** yields the oxygen adduct **17** (m/z 163) as a major product. Some OH^- is also produced, which is consistent with the observations that another major product ion is m/z 145. By analogy with eq 10, we formulate these reactions as shown in eq 13. In addition to

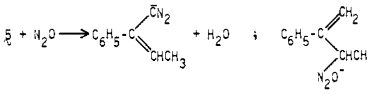


(13)

these products, reaction of **4** with O_2 produces appreciable amounts of phenoxide (m/z 93), benzoate (m/z 121), and an anion at m/z 107. Minor peaks at m/z 41, 43, and 67 also appear.

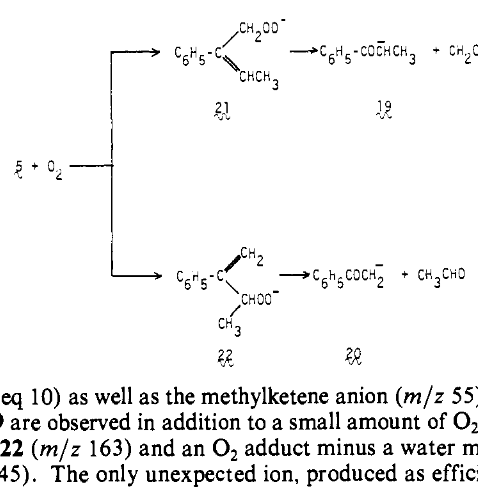
In order to test our hypothesis that H–D exchange occurs in the aromatic ring in this anion, we first carried out partial H–D exchange of **4** with D_2O and then oxidized the resulting partially exchanged anion with O_2. We observed that the phenoxide and benzoate anions were deuterated with the same ratio of d_0:d_1:d_2 ions as was present in the partially exchanged $[M - 1]^-$ ion. In contrast with this result, the m/z 67 ion was not deuterated, which suggests that it has the molecular formula $[C_4H_3O]^-$ and is derived from the nonaryl carbons of the *trans*-2-methyl-1-phenylcyclopropane.

The allylic anion **5** which could be formed by electrocyclic ring opening of **4** can be independently produced by deprotonation of 2-phenyl-1-butene; the ion formed in this way reacts with N_2O to form a 2:1 mixture of N_2O adduct (m/z 175) and diazo anion (m/z 157). This result most likely reflects addition of N_2O to the secondary and primary carbons, respectively, of **5** (eq 14).



(14)

Reaction with O_2 is also illustrative of the structure of **5**. The expected enolate anions **19** (m/z 133) and **20** (m/z 119) are the major products (eq 15). The ketene anion (m/z 41) derived from



(15)

20 (see eq 10) as well as the methylketene anion (m/z 55) derived from **19** are observed in addition to a small amount of O_2 adducts **21** and **22** (m/z 163) and an O_2 adduct minus a water molecular (m/z 145). The only unexpected ion, produced as efficiently as

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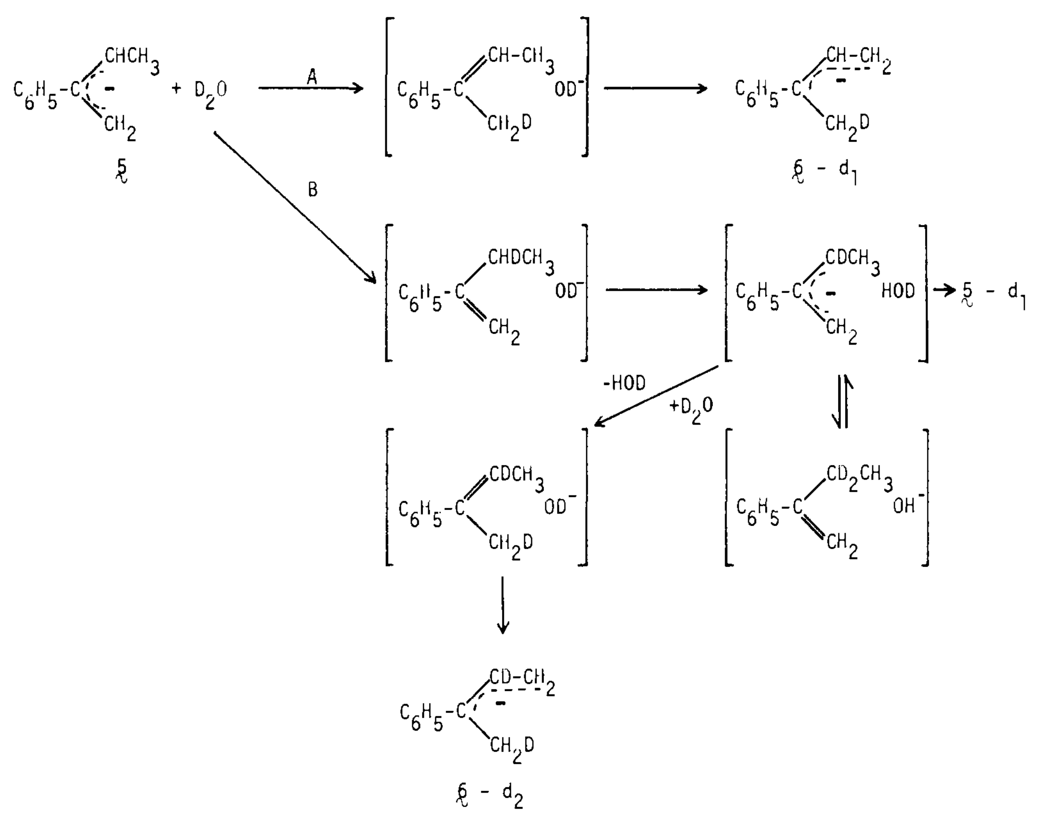
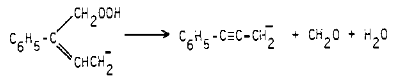
(22) The $[M - 1]^-$ ion produced from *tert*-butylbenzene and NH_2^- slowly exchanges a maximum of four hydrogens for deuterium with ND_3: Squires, R. R.; DePuy, C. H., unpublished results.

Scheme III

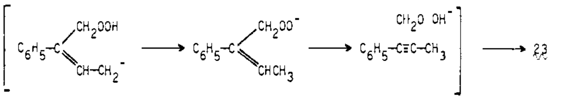


the m/z 133 ion in this reaction, is one at m/z 115 which corresponds to structure **23** or an isomer (eq 16).

 (16)

$$C_6H_5\text{-}C(CH_2OOH)(CHCH_2^-) \longrightarrow C_6H_5\text{-}C{\equiv}C\text{-}CH_2^- + CH_2O + H_2O \quad (16)$$

If this reaction proceeds by intramolecular proton transfer (eq 17), the m/z 115 product **23** could be formed only from the primary peroxy anion **24**. This reaction would provide a pathway for decomposition of the primary peroxy anion **24** which is not available to the isomeric secondary peroxy anion. This mechanistic formulation (eq 17) would account for the observed larger amounts (2:1) of **20** (m/z 119) and its cleavage product (m/z 41) than **19** (m/z 133) and its cleavage product (m/z 55).

 (17)

Finally, by analogy with anion **3**, we may reasonably expect that the completely conjugated homologue **6** will not react with either D_2O, N_2O, or O_2. The foregoing results show that the two anions **4** and **5** (and most likely **6**) as initially produced retain their structural integrity. However, an isomerization of **5** into **6** can be induced by reaction of the former with water. This can be demonstrated in two separate ways. The most convincing evidence comes from the distinct D_2O exchange patterns of ions **5** and **2**. While **2** exchanges four protons rapidly (and an additional four slowly), **5** reacts rapidly with D_2O to yield approximately equal amounts of d_1 and d_2 ions with a smaller amount of d_3 and only a trace of d_4, without exchanging further. We believe this result is to be expected if **5** isomerizes to **6** in the presence of D_2O as shown in Scheme III. Initial deuteron addition can occur at either the primary (path A) or secondary (path B) position of the delocalized ion. When path B is followed, ion **5** (or its deuterated analogue) must be formed upon subsequent deprotonation. When path A is followed, ion **6** can be generated directly through abstraction of the more acidic hydrogen. It is important to note that the d_0 anion will always have structure **5**, the d_1 anion will be a mixture of **5** and **6**, d_2 will be mainly **6**, and eventually all anions will have the completely conjugated, and hence unreactive, struture **6**.

A corollary of this scheme is that treatment of ion **5** (which reacts rapidly with either N_2O or O_2) with water should render it unreactive toward N_2O or O_2 owing to isomerization into ion **6**. Indeed when a sufficiently high flow of water is added to isomerize all of **5** to **6** and then either N_2O or O_2 is added to the flow tube further downstream, neither diazo anion nor enolate anion products are detected. However, these experiments are not totally conclusive because, when the order of addition is reversed (by adding N_2O or O_2 to generate diazo anion or enolate anion from **5** and then adding a high H_2O flow), these product ions also disappear through the formation of hydrate clusters.

A more subtle experiment was employed to demonstrate the validity of Scheme III. To ion **5** was added a very small flow of D_2O. In one experiment we chose a D_2O flow such that m/z 131:132:133 (d_0:d_1:d_2) was 30:46:24. From our previous analysis (vide supra) the m/z 131 ion should be completely structure **5**, m/z 132 a mixture of **5** and **6**, and m/z 133 mainly **6**. This mixture of deuterated ions was then allowed to react with N_2O and the adduct $[M - 1 + N_2O]^-$ was analyzed for deuterium content. As predicted by Scheme III, the m/z 175 (d_0) was twice as intense as the m/z 176 ion (d_1) while only a trace of m/z 177 (d_2) could be detected. At the low D_2O flow rate necessary for this partial H–D exchange, removal of the adducts through hydrate clusters is not a problem and in any event would occur equally well with m/z 175, 176, or 177.

A similar set of experiments was carried out with the O_2 reaction. Just enough D_2O was added to **5** to produce a d_0:d_1:d_2:d_3 ion ratio of 32:42:23:3 and then O_2 was added downstream. The ratio of these four ions rapidly changed to 14:34:46:6, clearly demonstrating depletion of the d_0 and d_1 ions, which are mostly **5**, relative to the d_2 and d_3 ions, which are mostly **6**. At the same time the oxidation products contained relatively little deuterium. For example, the ratio of m/z 119:120 in this last experiment was 80:20 while the m/z 41:42 ratio was 83:17. Thus these experiments demonstrate unequivocally that isomerization occurs during H–D exchange, and that the experimental methods can detect such isomerization.

Conclusion

The results reported in this paper show that anions in the gas phase, like those in solution, are much less susceptible to rearrangement than are cations. Isomerizations can be induced, however, even by reaction with a water molecule. As a result, chemical methods for distinguishing isomeric structures are especially important. We have shown how a combination of reactions of D_2O, N_2O, and O_2 can be used to distinguish among isomeric allyl and cyclopropyl anions, and to follow the isomerization of allyl ions induced by water. These techniques should be of use in many other systems.

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Registry No. 1, 88377-54-2; **2**, 78427-91-5; **3**, 88377-55-3; **4**, 88377-56-4; **5**, 88377-57-5; **6**, 12558-40-6; **14**, 88377-61-1; **15**, 34172-40-2; **16**, 64066-01-9; **17**, 88377-62-2; **19**, 88377-60-0; **21**, 88377-63-3; **22**, 88377-64-4; **24**, 88377-65-5; NH_3, 7664-41-7; NH_2^-, 17655-31-1; N_2O, 10024-97-2; O_2, 7782-44-7; H_2O, 7732-18-5; CH_3OD, 1455-13-6; H_2, 1333-74-0; 1-phenyl-1-propene, 637-50-3; phenylcyclopropane, 873-49-4; 2,2-dideuteriophenylcyclopropane, 88377-58-6; 2,2-dibromophenylcyclopropane, 3234-51-3; 1-methylphenylcyclopropane, 2214-14-4; *trans*-2-methylphenylcyclopropane, 5070-01-9; 2-phenyl-1-butene, 2039-93-2; 2-phenyl-1-butanol tosylate, 88377-59-7; 2-phenylpropane, 98-83-9; 3-phenyl-1-propene, 300-57-2.

Time-Resolved Fluorescence and Absorption Spectra and Two-Step Laser Excitation Fluorescence of the Excited-State Proton Transfer in the Methanol Solution of 7-Hydroxyquinoline[1]

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Abstract: Steady-state and transient fluorescence studies of 7-hydroxyquinoline in hexane–methanol mixed solution reveal that two stoichiometric hydrogen-bonding complexes of 7-HQ and methanol (1:1 and 1:2) exhibit nearly the same wavelength fluorescences at 350–400 nm at room temperature. The 1:2 complex (N*) further exhibits a long-wavelength fluorescence at 530 nm attributable to the tautomer (T*) generated by excited-state proton transfer. The activation energy of the excited-state proton transfer of $N^* \rightarrow T^*$ was determined to be 0.54 kcal mol^{-1} in CH_3OH from the temperature dependence of the fluorescence rise time of T*. The transient absorption spectrum due to the ground-state tautomer (T) was observed with the lifetime of 3.5 μs, which is consistent with the recovery time (3.6 μs) of the ground-state bleaching of the absorption band. The two-step laser excitation (TSLE) fluorescence of T*, which consists of the formation of T by the first laser excitation and the second laser excitation of the T absorption band within the lifetime of T, was observed for the first time. The lifetime of T was also determined by the TSLE fluorescence intensity changes in the variable delay times of the second laser pulse from the first one. The extraordinarily large deuterium isotope effect of the T lifetime was observed in CH_3OD (τ_T = 30 μs) compared with that in CH_3OH (τ_T = 3.5 μs). The activation energy of the ground-state reaction of $T \rightarrow N$ was determined in CH_3OH (E_a = 4.2 kcal mol^{-1}) and in CH_3OD (5.5 kcal mol^{-1}) solutions by the temperature dependence of the T lifetimes determined by the variable delay technique of the TSLE fluorescence. These facts demonstrate the comprehensive mechanism of the proton transfer in the excited state as well as in the ground state and really are evidence for the intervention of the stable ground-state tautomer T in the relaxation process of T* to N.

A large number of inter- and intramolecular hydrogen-bonding systems provide us with interesting photochemical and photophysical properties of the excited-state proton transfer, which have been extensively studied by nano- and picosecond fluorescence spectroscopy. Mason et al.[2] reported that the OH group of 7- and 6-hydroxyquinolines is more acidic and the ring nitrogen atom more basic in the excited state that in the ground state. The two-stage prototropic change in the excited state from the neutral molecule to the zwitterion form was proposed to take place. Recently, Thistlethwaite and Corkill[3] have reported the picosecond fluorescence study of this excited-state proton transfer in a methanol solution of 7-hydroxyquinoline (7-HQ). They observed the excitation wavelength dependence of the fluorescence intensity ratio of the normal and zwitterion form (tautomer, T) of this compound and suggested several possible mechanisms of the excitation energy dependence of the proton transfer, including that via upper vibrational states (S_1). Very recently, Thistlethwaite[4] has reported the reexamination of this phototautomerization suggesting an important participation of the solvent methanol or ethanol molecules. On the other hand, the transient absorption study that may provide us with valuable information on the existence of the ground-state tautomer (T) and on the reverse proton transfer in the ground state reproducing the parent molecule has never been reported except for a few papers.[1,5,6] In the excited-state proton transfer of *o*-hydroxybenzophenone in ethanol, Hou et al.[7] reported a very rapid recovery of the ground state.

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