kcal/mol for **2**, and by 4.7 kcal/mol for **3**.

Summary

The X-cyclopropenyl cations for all substituents (X = H, CH_3, NH_2, OH, F, CN, and NC) are lower in energy than the isomeric α-X- and γ-X-substituted propargyl cations by at least 17 kcal/mol. This preference for the strained cyclic system results from the stabilization inherent in the Hückel 2π-system. Despite the stability of the 2π-electron system all the substituents continue to function as π-donors as in other carbenium ions, and in two of the X-cyclopropenyl cations (X = NH_2 and OH) this results in a further stabilization.

The overall reaction for conversion of C_3H^+ and HX into CX^+ and C_2H_2 is exothermic for all substituents except X = H and CN, and the X-cyclopropenyl cations, if formed, will have such a large excess of energy that they should easily undergo the orbital symmetry-forbidden dissociation into CX^+ and C_2H_2. On the $C_3H_3^+$ energy hypersurface transition-structure calculations show the barrier to formation of the cyclopropenyl cation from the propargyl cation via intermediate **6** to be ~104 kcal/mol at the 6-31G*//6-31G* level. The transition structure for this rearrangement has almost the same energy as the initial reactants (H_2 and C_3H^+ are 106 kcal/mol above the propargyl ion), and given that C_3H^+ may have some excess kinetic energy it therefore seems likely that the cyclopropenyl cation is formed under experimental conditions.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support, York University Computer Centre for generous allotments of computer time, Professor D. K. Bohme for bringing this problem to our attention, and the referees for constructive comments.

Registry No. c-$C_3H_3^+$, 26810-74-2; c-$MeC_3H_2^+$, 60824-24-0; c-$NH_2C_3H_2^+$, 101671-87-8; c-$OHC_3H_2^+$, 49598-05-2; c-$FC_3H_2^+$, 72247-93-9; c-$CNC_3H_2^+$, 101671-88-9; c-$NCC_3H_2^+$, 101671-89-0; $HC\equiv C-CH_2^+$, 21540-27-2; $HC\equiv CCHCH_3^+$, 72183-36-9; $HC\equiv CCH=NH\cdot H^+$, 101671-80-1; $HC\equiv CCHO\cdot H^+$, 101671-81-2; $HC\equiv CCHF^+$, 72188-22-8; $HC\equiv CCHCN^+$, 101671-82-3; $HC\equiv CCHNC^+$, 101671-83-4; $MeC\equiv CCH_2^+$, 64235-83-2; $H_2C=C=C=NH\cdot H^+$, 101695-35-6; $H_2C=C=C=O\cdot H^+$, 101671-84-5; $FC\equiv CCH_2^+$, 57376-53-1; $CNC\equiv CCH_2^+$, 101671-85-6; $NCC\equiv CCH_2^+$, 101671-86-7; H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; HF, 7664-39-3; HCN, 74-90-8; HNC, 75-13-8.

Supplementary Material Available: Tables V, VI, and VII, giving some structural detailed (bonds and angles involving only heavy atoms) and total energies for isomers on $C_3H_3O^+$ and $C_3H_4N^+$ surfaces (5 pages). Ordering information is given on any current masthead page.

Nitrous Oxide in Gas-Phase Ion–Molecule Chemistry: A Versatile Reagent for the Determination of Carbanion Structure

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Abstract: Nitrous oxide has been found to undergo a wide variety of reactions with anions in the gas phase. The products of these reactions are highly characteristic of the ion's structure and, therefore, this reagent (N_2O) is especially useful in distinguishing between different types of ions. In general, primary carbanions react to produce diazo anions as the major products, secondary carbanions dehydrogenate, and tertiary carbanions afford adducts, oxygen atom transfer, and cleavage products. However, novel reaction channels can be brought about by modifying the reactant ion's structures. For example, deprotonation of methylene cyclopropane produces a strained allylic anion which reacts with N_2O to afford cyanide and the 2-nitrosoallyl anion, while removal of a proton from furan, which has a good α-leaving group, generates the nitrogen atom transfer product, 3-cyanoacrolein radical anion, upon reaction with N_2O. It was observed that proton abstraction from cyclopentene, cyclohexene, and internal olefins without allylic methyl groups does not afford M − 1 ions in the flowing afterglow.

Instrumental methods for studying gas-phase ion chemistry continue to improve, with the most recent additions being the Fourier transform technique for ion cyclotron resonance spectrometry[1] (FT-MS) and the selected ion flow tube[2] (SIFT) and the triple quadrupole[3] versions for the flowing afterglow (FA). These improvements have led to a broader range of reactions which can be studied and a deeper understanding of gas-phase ion chemistry, particularly that of carbanions. Despite these technical advances, methods for the determination of ion structure remain a central problem, especially as experimenters study more complex molecules in which the number of possible isomeric ions increases dramatically. In our work[4-7] we have emphasized chemical methods for ion structure determination; among the useful reagents we have investigated are D_2O, O_2, CS_2, COS, and N_2O. All of these reagents are volatile, readily available, and often highly diagnostic of ion structure.

No neutral reagent in gas-phase anion–molecule chemistry shows the variety of reactions that nitrous oxide, N_2O, does. This simple reagent continues to amaze by the sheer diversity of the

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[1] (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282. (b) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489. (c) Comisarow, M. B.; Marshall, A. G. *Can. J. Chem.* **1974**, *52*, 1997.

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reaction types it displays in its interactions with carbanions. In earlier publications[7] we reported on its reactions with primary carbanions, for example the allyl anion, to form diazo anions (eq 1) and with the phenide ion to form products arising from addition

$$CH_2{=}CHCH_2^- + N{=}N{=}O \rightarrow CH_2{=}CH{-}\bar{C}{=}N{=}N + H_2O \quad (1)$$

and oxygen atom transfer (eq 2). Nitrous oxide reacts in still

$$C_6H_5^- + N_2O \rightarrow C_6H_5O^- + N_2 \qquad \Delta H = -111 \text{ kcal/mol} \quad (2a)$$

$$\rightarrow C_6H_5N_2O^- \quad (2b)$$

another way with the anion from proton abstraction of butadiene, again giving the vinyldiazomethane ion.[7] This product results from the addition of N_2O followed by loss of a formaldehyde molecule (eq 3). In contrast, α-silylcarbanions react by cleavage with loss

$$CH_2{=}CH{-}\bar{C}{=}CH_2 + N_2O \rightarrow CH_2{=}CH{-}\bar{C}{=}N_2 + CH_2O \quad (3)$$

of diazomethane rather than formaldehyde[8] (eq 4). Nitrogen

$$(CH_3)_3SiCH_2^- + N_2O \rightarrow (CH_3)_3SiO^- + CH_2{=}N{=}N \quad (4)$$

atom transfer from N_2O to a radical anion has also been observed[9] (eq 5). In view of this wealth of reaction pathways, we have rather

$$CH_2{=}\bar{C}\cdot + N_2O \rightarrow {}^-CH_2{-}C{\equiv}N + NO \quad (5)$$

routinely allowed any new type of carbanion to react with N_2O. Perhaps surprisingly, in view of the types of reactions already known, we have discovered several new pathways by which N_2O reacts with carbanions, and these are reported in this paper.

Experimental Section

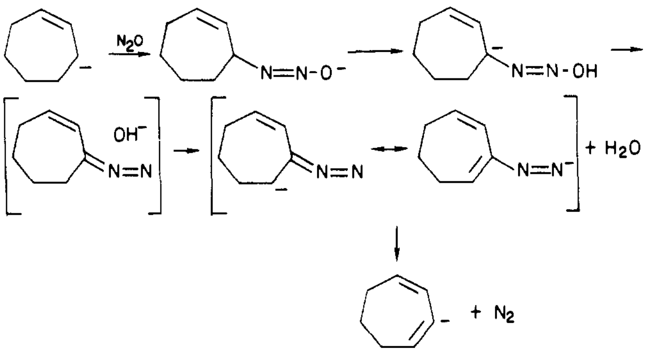
All of our experiments were carried out in a flowing-afterglow apparatus which has previously been described.[10] In brief, the system consists of a 100 × 7.6 cm i.d. cylindrical stainless steel reaction vessel through which helium is passed. A pressure of approximately 0.4 Torr, which corresponds to a helium flow of 200 STP $cm^3\ s^{-1}$, and a velocity of 8000 cm s^{-1} was typically employed. Small amounts of reagent gasses (≤ 1 STP $cm^3\ s^{-1}$) were added upstream such that they pass an electron gun, resulting in ionization and the production of the initial reactant anions. Additional compounds were added through fixed inlets further downstream in order to carry out the reactions of interest. The resulting ions were analyzed by a quadrupole mass filter and detected with an electron multiplier.

All of the reagents used in this study were either commercially available or prepared by known literature procedures, except for methylene cyclopropane, which was generously supplied to us by Professor G. B. Ellison.

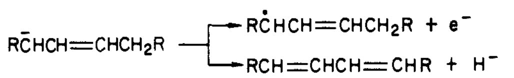
Results and Discussion

Reactions at Secondary Carbon Centers. Since primary carbanions react with N_2O to form diazo anions (eq 1) and carbanions with no α-hydrogens (phenyl, etc.) react by oxygen transfer, addition, or cleavage, we were curious to see how secondary anions (R_2CH^-) might react. This would seem like a straightforward matter to investigate since these ions should result from proton abstractions of an internal olefin, for example, 3-hexene. In fact, none of these precursors gives the corresponding M − 1 ion in the flowing afterglow when allowed to react with either NH_2^- or HO^-, bases which rapidly form large amounts of carbanions from 1-hexene, propylene, and other linear alkenes in which at least one end of the allylic system is a primary anion. When we allow 3-hexene, cyclohexene, cyclopentene, methylenecyclopentane, or methylenecyclohexane to react with amide or hydroxide either in the FA or the SIFT, we observe little or no M − 1 ion. We

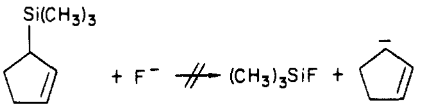
Scheme I



believe that the initially formed anions undergo electron detachment to form a radical or lose a hydride ion to afford a diene (eq 6). Attempts to detect electrons produced in this reaction


$$R\bar{C}HCH{=}CHCH_2R \rightarrow \begin{cases} R\dot{C}HCH{=}CHCH_2R + e^- \\ RCH{=}CHCH{=}CHR + H^- \end{cases} \quad (6)$$

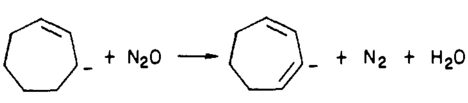
by capture with SF_6 (to form SF_6^-) have been suggestive but not totally conclusive. We also have tried unsuccessfully to form the cyclopentenyl anion from the trimethylsilyl derivative[11] (eq 7). To our knowledge, these difficulties are not inherant to the FA



(7)

since secondary allylic anions have not been reported to be formed in the gas phase by other techniques (e.g., ion cyclotron resonance spectroscopy).[12] The electron affinity of the allyl anion[13] is 8.2 kcal/mol; as alkyl groups are attached to the ends of this system, they should stabilize the radical more than the corresponding anion, and so should lower the electron affinity. In addition, Streitwieser[14] has shown how introducing strain into an alkene lowers its acidity. This should not be a factor in most acyclic olefins, but the above two ideas taken together may account in a general way for the difficulty in generating secondary allylic ions.

We have found that allylic anions can be formed from cycloheptene and cyclooctene by reaction with NH_2^-. The resultant anions are secondary in both resonance structures and have only one α-hydrogen, and thus the formation of a diazo anion upon reaction with N_2O is precluded. As a result, these carbanions react with N_2O in a new way, namely by dehydrogenation to form an $[M - 3]^-$ ion, which we formulate as a vinyl anion (eq 8).



(8)

A reasonable mechanistic pathway for this reaction is shown in Scheme I. The initial steps, addition, proton transfer, and loss of hydroxide ion with the formation of the diazo compound, are identical with those proposed for reactions with a primary carbanion. Since there is no acidic hydrogen left on the diazo carbon, an adjacent β proton is abstracted. These protons are expected to be acidic and loss of nitrogen from the resulting diazenyl ion produces a vinyl anion. This reaction is analogous to the Shapiro reaction[15] in which a tosylhydrazone is allowed to react with 2 equiv of an alkyllithium reagent to form a vinyl anion (eq 9).

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(8) DePuy, C. H.; Damrauer, R. *Organometallics* **1984**, *3*, 362.

(9) Dawson, J. H. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1928.

(10) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.

(11) DePuy, C. H.; Flippen, L., unpublished results.

(12) We have seen small signals of the $[M - H]^-$ ion of cyclohexene in our flowing afterglow and this has also been observed in an FT-ICR (Nibbering, N.M.M., private communication).

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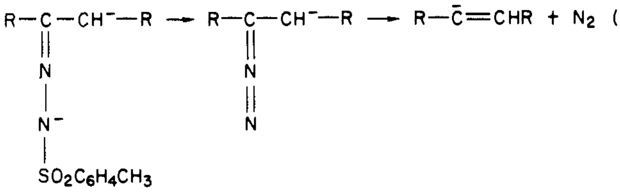
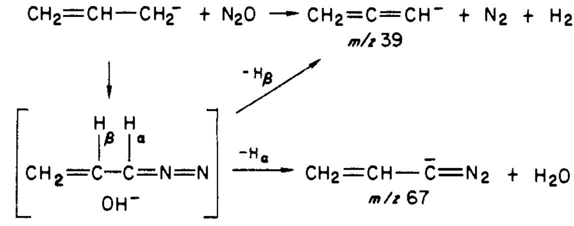
(15) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.



$$R{-}\underset{\underset{\underset{SO_2C_6H_4CH_3}{|}}{N^-}}{\underset{|}{\underset{\|}{C}}}{-}CH^-{-}R \longrightarrow R{-}\underset{\underset{\underset{N}{\|}}{N}}{\underset{\|}{C}}{-}CH^-{-}R \longrightarrow R{-}\bar{C}{=}CHR + N_2 \quad (9)$$

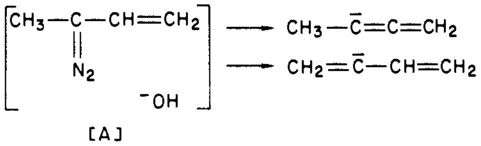
The discovery of this method for the formation of vinyl anions led us to re-examine our earlier work[7] on the reaction of N_2O with the allyl anion since with our present instrument we consistently see small amounts (~15%) of an $[M - 3]^-$ (m/z 39) ion (eq 10). On the basis of its reaction with CS_2 and of H–D exchange studies, the m/z 39 ion was identified as the allenyl anion. Thus, even a primary carbanion can, in part, undergo dehydrogenation upon reaction with N_2O.



$$CH_2{=}CH{-}CH_2^- + N_2O \longrightarrow \underset{m/z\ 39}{CH_2{=}C{=}CH^-} + N_2 + H_2O$$

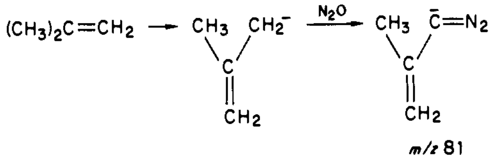
$$\left[\underset{OH^-}{CH_2{=}\overset{H\,\beta}{C}{-}\overset{H\,\alpha}{C}{=}N{=}N}\right] \xrightarrow{-H_\alpha} \underset{m/z\ 67}{CH_2{=}CH{-}\bar{C}{=}N_2} + H_2O \quad (10)$$

Proton abstraction from 1-, *cis*-2,- or *trans*-2-butene produces allylic anions which react with N_2O. The ends of these allylic ions are not equivalent and therefore the initial addition of N_2O can occur at two different positions. Attack at the primary carbon predominates and leads to a diazo anion of m/z 81. Addition to the secondary carbon would form a complex of methylvinyldiazomethane and hydroxide ion [A]. This could, in theory, eliminate nitrogen in either of two ways: by abstraction of a vinyl proton to form an isomeric methylallenyl anion (eq 11a), or by abstraction of a proton from the methyl group to form a butadienyl anion (eq 11b). Since the m/z 53 ion is completely converted to a vinyldiazomethane anion with an excess of N_2O (see eq 3), we believe only the butadienyl anion is actually produced in this reaction.



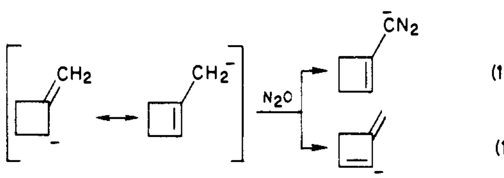
$$\underset{[A]}{\left[\begin{array}{c} CH_3{-}\underset{\underset{N_2}{\|}}{C}{-}CH{=}CH_2 \\ {}^-OH \end{array}\right]} \begin{array}{ll} \longrightarrow CH_3{-}\bar{C}{=}C{=}CH_2 & (11a) \\ \longrightarrow CH_2{=}\bar{C}{-}CH{=}CH_2 & (11b) \end{array}$$

In contrast, the anion from isobutylene reacts exclusively to form a diazo anion (m/z 81) (eq 12). The diazo group can be formed only on a primary carbon, no β-hydrogen is available to induce elimination, thus precluding a dehydrogenation reaction.



$$(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)(CH_2^-)C{=}CH_2 \xrightarrow{N_2O} \underset{m/z\ 81}{(CH_3)(\bar{C}{=}N_2)C{=}CH_2} \quad (12)$$

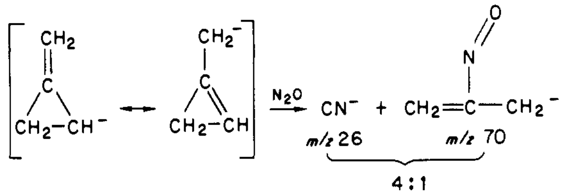
We next extended our investigation to small-ring olefins. Cyclobutene[16] does not form an M – 1 ion with hydroxide ion and produces only a vinyl anion with NH_2^-.[17] However, methylenecyclobutane readily affords an M – 1 ion which reacts with N_2O to form a diazo anion (eq 13a) as the major product and an [M – 3] ion (eq 13b) in substantially smaller amounts.



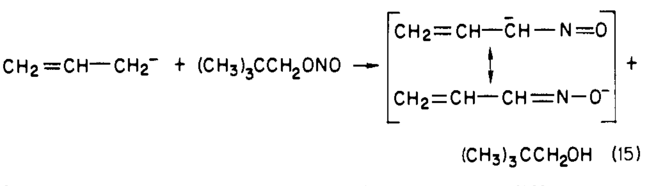
(13a)

(13b)

By analogy, we expected that the allylic M – 1 anion from methylenecyclopropane or 1-methylcyclopropene[18] would also produce a diazo anion and, perhaps, the highly strained anion from methylenecyclopropene. Instead, no diazo anion is formed and an entirely new reaction of N_2O was revealed, resulting in the formation of a mixture of CN^- and an anion of m/z 70 which we formulate as the 2-nitrosoallyl anion (eq 14). These two ions both have even masses and therefore they must each contain a nitrogen atom; together they contain all of the carbon, nitrogen, and oxygen in the two reagents. The m/z 70 ion could, in principle, be the isomeric 1-nitrosoallyl anion; to test for this possibility we prepared this latter ion by the known reaction[19] illustrated in eq 15 and compared its properties with those of the ion produced from methylenecyclopropane. The ions are quite different. In particular, the 1-nitroso ion is much less basic (ΔH_{acid} = 366 ± 3 kcal/mol) than the ion formed by the reaction in eq 14 (ΔH_{acid} = 385 ± 5 kcal/mol), as would be expected from what is in fact an oxime anion.



(14)



$$CH_2{=}CH{-}CH_2^- + (CH_3)_3CCH_2ONO \longrightarrow \left[\begin{array}{c} CH_2{=}CH{-}\bar{C}H{-}N{=}O \\ \updownarrow \\ CH_2{=}CH{-}CH{=}N{-}O^- \end{array}\right] + (CH_3)_3CCH_2OH \quad (15)$$

We propose that the products produced in eq 14 result from the reactions shown in Scheme II. Attack of N_2O occurs exclusively on the ring carbon because attack on the exocyclic methylene leads to a strained endocyclic double bond.[20] Driven by the exothermicity of the addition of N_2O, a vinylcyclopropane rearrangement (either concerted or by way of an intermediate vinyl anion) occurs. Although cleavage of the other ring bond might at first glance appear preferable, because it would give rise to an allylic rather than a vinylic anion, the breaking bond is orthogonal to the double bond and would not be expected to experience much allylic resonance in the transition state. The vinylcyclopropane rearrangement product would be expected to cleave to a cluster of the 2-nitrosoallyl anion and HCN. As is often the case in such clusters, a mixture of ions resulting from incomplete proton transfer between the components is observed. The more stable cyanide ion[21] (ΔH_{acid} = 353 kcal/mol) is formed in the larger amount.

Reactions at Tertiary Carbon Centers. As noted above (eq 2 and 3) carbons with no hydrogens usually react with N_2O either by oxygen atom transfer or by rearrangement, if they react at all. A variable amount of an adduct $[M - 1 + N_2O]^-$ is also occasionally seen. The exact mechanism by which oxygen atom transfer occurs remains undetermined. It is tempting to invoke direct attack on the oxygen with loss of nitrogen, for this is a highly exothermic reaction[21,22] (eq 2a). Nevertheless, we are inclined to discount this direct pathway since other highly basic anions, for example, $(CH_3)_2N^-$, do not react at all with N_2O. It seems more likely that attack occurs first on nitrogen, with rearrangement

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[16] This compound was prepared by slight modification of the method of Cope (*J. Am. Chem. Soc.* **1950**, *72*, 2510) as given by Kass, S., Ph.D. Thesis, Yale University, 1984.

[17] The anion was shown to be vinylic rather than allylic by its reaction with ND_3; only one H/D exchange was observed as expected for the vinyl anion rather than the fives exchanges expected for the allylic ion.

[18] Fisher, F.; Applequist, D. E. *J. Org. Chem.* **1965**, *30*, 2089.

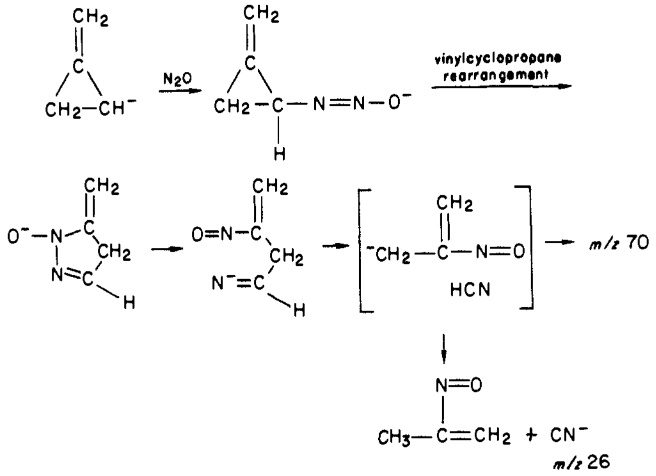
[19] King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133.

[20] Cox, J. D.; Pilcher, G. "Thermochemistry of Ogranic and Organometallic Compounds"; Academic Press: London, 1970.

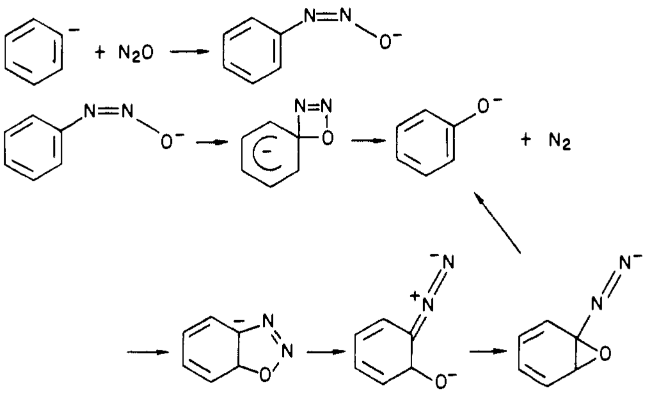
[21] Bartmess, J. E.; McIver, R. T., Jr. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

[22] Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; John Wiley: New York, 1969.

Scheme II

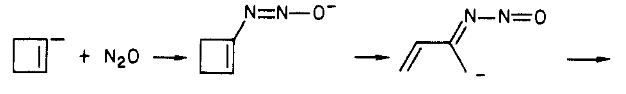


Scheme III



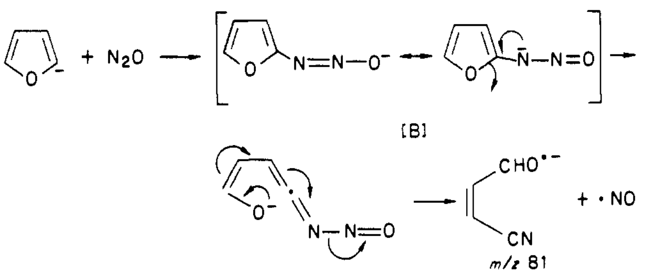
to oxygen following, perhaps through formation of a four- or five-membered ring (Scheme III). The four-membered-ring pathway was suggested for oxygen transfer to silicon anions in reactions of the type shown in eq 16.[8] The oxygen-transfer pathway, whatever its mechanism and despite its great exothermicity, is slow since other reactions take precedence. Thus the reaction of N_2O with the butadiene anion leads to the reported cleavage (eq 3) rather than to oxygen transfer. Analogously, the vinyl anion derived from cyclobutene reacts with N_2O via a cleavage reaction rather than by oxygen atom transfer (eq 17).

$$(CH_3)_3Si^- + N_2O \rightarrow (CH_3)_3SiO^- + N_2 \qquad (16)$$



$$CH_2{=}CH{-}\bar{C}{=}N_2 + CH_2O \qquad (17)$$

Scheme IV



A further example of a vinyl anion reacting at the nitrogen end of N_2O is that of the anion resulting from proton abstraction from furan (Scheme IV). The product, an ion of m/z 81, we formulate as a radical anion. Its proposed mechanism of formation is shown in Scheme IV. Addition of N_2O leads to [B] which can ring open to a highly delocalized anion [C]. Loss of NO from this intermediate would form cyanoacrolein radical anion. Generation of radical products from nonradical precursors is novel in negative ion–molecule reactions.[23]

The structure of the ion produced in Scheme IV is based on the following facts. Proton abstraction from furan affords an anion which exchanges three hydrogens for deuterium upon addition of D_2O to the flow tube. If the exchange is first carried out and then N_2O is added downstream, an m/z 84 ion is formed. Thus the m/z 81 ion must have the formula C_4H_3NO rather than the formula C_3HN_2O which would arise from addition of N_2O and loss of CH_2O. The product is an extremely weak base and does not abstract a proton from H_2S (ΔH_{acid} = 353 kcal/mol).[21] This observation would seem to rule out a nitrene radical anion which would be expected to be quite basic.[24] We thus believe the m/z 81 ion to be the radical anion of 3-cyanoacrolein.

Conclusion

The reactions of N_2O with various anions are highly characteristic of the ion's structure. Therefore this reagent is particularly useful in distinguishing among various isomers. Primary carbanions typically react to generate diazo anions, secondary ions react by dehydrogenation, and tertiary anions afford adducts, oxygen-atom transfer, and cleavage products. However, by making subtle modifications of the ion, such as introducing strain (as in the allylic ion derived from methylene cyclopropane) or by attaching a good leaving group (as in the $[M - 1]^-$ of furan), the usual reaction pathways can be altered. Such a wide diversity of reactions has made N_2O a particularly fascinating reagent to study.

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Registry No. N_2O, 10024-97-2; cycloheptene anion, 100791-90-0; allyl anion, 1724-46-5; 1-butene anion, 59263-54-6; *cis*-2-butene anion, 54078-18-1; *trans*-2-butene anion, 54078-26-1; isobutylene anion, 64480-56-4; methylenecyclobutane anion, 100812-23-5; methylcyclopropane anion, 100812-24-6; cyclobutene anion, 60211-42-9; furan radical anion, 40807-44-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8.

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(23) For two other examples, see: Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 3. Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 6520.

(24) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 5118.