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VINYL ANION SYNTHESIS IN THE GAS PHASE

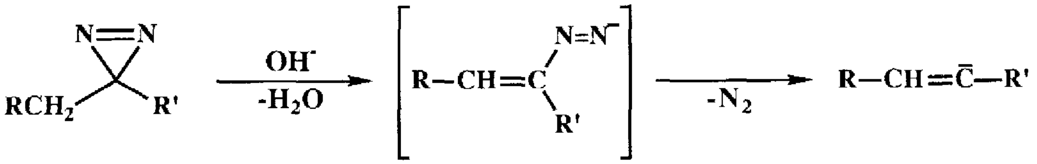
Kraig K. Anderson and Steven R. Kass*
Department of Chemistry, University of
Minnesota, Minneapolis, Minnesota 55455

Abstract: A general and convenient method for the preparation of vinyl anions in a flowing afterglow apparatus is reported. The reactivity of these ions with nitrous oxide has been examined.

Strong bases such as alkyllithiums and lithium dialkylamides are common reagents for generating carbanions in solution.[1] In the gas phase, amide ion is the strongest base which can readily be prepared (PA = 403.6 kcal mol^{-1})[2], and it is frequently used to produce other ions by proton abstraction. Compounds which are less acidic than ammonia, however, can not be readily deprotonated by NH_2^- and the formation of their conjugate bases presents a considerable synthetic challenge. Several ions of this type such as CH_3^-, c-$C_3H_5^-$, and $C_2H_3^-$ have been prepared but only one general method, decarboxylation by collision-induced dissociation (CID) has been reported to date.[3]

$$\mathrm{R\text{-}CO_2^-} \xrightarrow{\mathrm{CID}} \mathrm{R^-} + \mathrm{CO_2}$$

We now report a convenient chemical ionization procedure for the preparation of highly reactive vinyl anions. Using a flowing afterglow apparatus,[4] we have found that the major reaction product of mono and disubstituted diazirines (**1**,**3**,**5**)[5] with hydroxide ion is a vinyl anion (**2**,**4**,**6**).

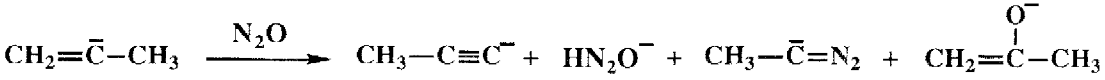


1 R = H, R' = CH_3 **1a** **2**
3 R = Et, R' = H **3a** **4**
5 R = R' = $(CH_2)_4$ **5a** **6**

These ions are very basic and extremely reactive, but do not rearrange to the more stable allylic isomers. Structural assignments are based on: 1) The mass to charge ratios are as anticipated for **2**, **4**, and **6**; 2) The observed $^{13}C/^{12}C$ ratios agree with the expected values; 3) Ethylene, NH_3, and H_2O are all sufficiently acidic to protonate **2**, **4**, and **6**;[6] and 4) Hydrogen/deuterium exchange does not take place upon reaction with D_2O. Of these criteria, the latter two are sufficient to distinguish between the vinyl and allyl isomers. Allylic anions are known to undergo isotopic exchange with D_2O,[7] and are not basic enough to deprotonate ethylene ($\Delta H_{acid} = 408$ kcal mol^{-1}) or NH_3.[2] Therefore, the major product in each reaction is a vinyl anion.[8]

The mechanism for the formation of **2**, **4**, and **6** presumably involves an elimination reaction where the diazirine ring is cleaved to form an intermediate diazenyl anion (**1a**-**3a**). Loss of nitrogen to afford the observed products is expected because these species are known to readily decompose[9] and are produced in an energetically excited state as a result of strain energy relief. This is analogous to a previously suggested pathway for the formation of the methanimine ion from trimethylsilylazide,[10] and indicates that small modifications of these methods may lead to the preparation of a variety of highly reactive ions.

The key to the success of this reaction lies in the choice of the base and in its formation. Reagents such as F^- and CH_3O^- (PA's = 371.4 and 380.6 kcal mol^{-1} respectively)[2] are not reactive enough to afford the vinyl anions; NH_2^- and $(CH_3)_2N^-$ are not suitable for our flowing afterglow experiments because they are produced in the presence of a large excess of their conjugate acids which are acidic enough to rapidly protonate **2**, **4** or **6**. Hydroxide ion (PA = 390.8 kcal mol^{-1}),[2] on the other hand, can be formed under anhydrous conditions by electron impact on a mixture of CH_4 and N_2O and is basic enough to produce the vinyl anions. It is essential to use only a trace of N_2O, however, because it rapidly reacts with vinyl anions to give a variety of products.[11]

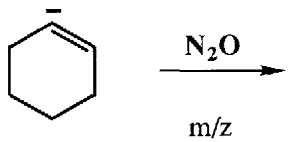


$$CH_2{=}\bar{C}{-}CH_3 \xrightarrow{N_2O} CH_3{-}C{\equiv}C^- + HN_2O^- + CH_3{-}\bar{C}{=}N_2 + CH_2{=}\overset{O^-}{\overset{|}{C}}{-}CH_3$$

2	m/z	39		45		55		57
		~1	:	2	:	1	:	1.5

$$\mathrm{CH_3CH_2CH{=}\bar{C}H} \xrightarrow{N_2O} \bar{\mathrm{C}}\mathrm{HN_2} + \mathrm{Et{-}C{\equiv}C^{-}} + \mathrm{CH_3CH{=}CH\bar{C}{=}N_2}$$

$$\begin{array}{ccccc} \underline{4} & m/z & 41 & 53 & 81 \\ & & \sim 1 : & 3 : & 1 \end{array}$$



Adduct

m/z 125

6

In the case of the 2-propenyl ion (**2**) we observe two additional products at m/z 39 and 45 which were not noted in a previous report.[3a] This difference can readily be accounted for by the different pressure regimes (0.4 Torr (FA) vs ~10^{-6} Torr (FT-MS)) of the two experiments or if **2** was not completely thermalized before it reacted with the N_2O in the FT-MS experiment. In any case, all of the products that we observe can be accounted for by mechanistic pathways previously put forth by Squires et al.[3a]

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References and Footnotes

1. For example see: Brandsma, L.; Verkruijsse, H. "Preparative Polar Organometallic Chemistry 1", Springer-Verlag: New York, 1987.
2. Lias, S. G.; Bartmess, J.E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; and Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, 17, Supplement 1.
3. a) Froelicher, S. W.; Freiser, B. S.; and Squires, R. R. *J. Am. Chem. Soc.* **1986**, 108, 2853. b) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, 110, 607. c) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, 111, 892 and references therein.

4. All experiments were carried out with He buffer gas at room temperature and at pressures of 0.30-0.40 Torr. For descriptions of the technique see: a) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopt, A. *Adv. At. Mol. Phys.* **1969**, 5, 1. b) Graul, S. T.; Squires, R. R. *Mass Spect. Rev.* **1988**, 7, 263 and references therein.
5. The diazirines were readily prepared in two steps following procedures given by a) Schmitz, E.; Ohme, R. *Chem. Ber.* **1961**, 94, 2166. b) Schmitz, E.; Ohme, R. *Tett. Letts.* **1961**, 612. c) Schmitz, E. *Chem. Ber.* **1962**, 95, 688. d) Schmitz, E.; Ohme, R. *Org. Synthesis* **1965**, 45, 83.
6. The reactions with ethylene were all extremely inefficient. This sluggishness maybe due to a kinetic or a thermodynamic barrier.
7. a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; and Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, 99, 7650. b) Grabowski, J. J.; Bierbaum, V. M.; and DePuy, C. H. *J. Am. Chem. Soc.* **1983**, 105, 2565. c) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; and DePuy, C. H. *J. Am. Chem. Soc.* **1983**, 105, 5185. d) Nibbering, N. M. M. *Recl. Trav. Chim. Pays-Bas* **1981**, 100, 297.
8. A minor product (~10%) corresponding to a P-1 ion is observed in the case of the monosubstituted diazirine **3**. The structure of this ion is uncertain but is currently being investigated. Allylic ions are also formed to a small extent (~20%). This was ascertained by observing their characteristic products upon reaction with high concentrations of N_2O. For further information on the reactions of N_2O see: Kass, S. R.; Filley, J.; Van Doren, J. M.; and DePuy, C. H. *J. Am. Chem. Soc.* **1986**, 108, 2849.
9. Kosower, E. M. *Accts. Chem. Res.* **1971**, 4, 193.
10. Kass, S. R.; DePuy, C. H. *J. Org. Chem.* **1985**, 50, 2874.
11. The dehydrogenation products observed in the reactions of **2** and **4** are shown as acetylenic ions but propargylic structures or a mixture of the two are equally plausible. In all three cases, the products were determined at low conversions thereby avoiding contaminants derived from the allylic ions. The product ratios are only approximate because of the possibility of mass discrimination.

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