The Mechanism of Interaction of Vinyl Azides with Electrophilic Bromine[1]

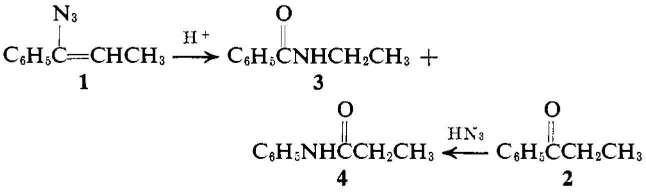
Alfred Hassner* and Alan B. Levy[1b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302.

Received August 25, 1970

Abstract: The pathway of the reaction of vinyl azides with bromine under various conditions has been examined for the first time. In contrast to protonation, bromination of several vinyl azides did not give products resulting from alkyl or phenyl migration to N, but instead involved trapping of electron-deficient nitrogen species (iminodiazonium ions) by nucleophiles. 1-Azido-2-butylethylene (**17**), as an example of a terminal azidoolefin, produced mainly nitrile **18** and dibromoaldehyde **20** on bromination. Bromination of **17** or **22** in methanol proceeded with solvent incorporation giving rise largely to methoxyazides **21** and **23**, respectively. The regiochemistry of the latter products, proven by spectral data and hydrolysis to bromoaldehydes, indicates that the azide function exerts a stronger directive effect in these additions than an alkyl or even a phenyl group. Bromination of nonterminal vinyl azides **25** and **31** led to isolation of imminium salts which were very easily hydrolyzed to α-bromo or α,α-dibromo ketones. Fragmentation to nitriles was also observed. Bromination in methanol led, as for **17** and **22**, to regiospecific solvent incorporated adducts.

A number of recent papers have considered the protonation of vinyl azides[2] and it was found that the reaction proceeded *via* intermediates of type $R_2C{=}NN_2^+$ similar to those found in the Schmidt reaction with the major products being due to alkyl or phenyl migration. Thus, 1-azido-1-phenylpropene (**1**) gives the same ratio of isomeric amides **3** and **4** on exposure to 80% sulfuric acid as does propiophenone (**2**) on treatment with HN_3.

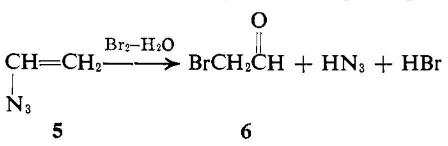


$$\underset{\mathbf{1}}{C_6H_5\overset{N_3}{\overset{|}{C}}{=}CHCH_3} \xrightarrow{H^+} \underset{\mathbf{3}}{C_6H_5\overset{O}{\overset{\|}{C}}NHCH_2CH_3} +$$

$$\underset{\mathbf{4}}{C_6H_5NH\overset{O}{\overset{\|}{C}}CH_2CH_3} \xleftarrow{HN_3} \underset{\mathbf{2}}{C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_3}$$

Whereas reaction mechanisms of electron-deficient carbon have received considerable attention, pathways taken by electron-deficient nitrogen species are not as well understood.

Our discovery of a general synthesis of vinyl azides[3] and the recent findings in the acid hydrolysis of these compounds led us to explore their reactions with halogens. The only report of the interaction of halogens with unsaturated azides appears to be that of Forster and Newman[4] who showed that azidoethylene (**5**) reacted vigorously with bromine–water to give α-bromoacetaldehyde (**6**), presumably according to eq 1.



$$\underset{\mathbf{5}}{\underset{N_3}{\underset{|}{CH}}{=}CH_2} \xrightarrow{Br_2-H_2O} \underset{\mathbf{6}}{BrCH_2\overset{O}{\overset{\|}{C}}H} + HN_3 + HBr \qquad (1)$$

Several pathways (some of which are depicted in Scheme I) can be visualized for the interaction of halogens with azidoolefins, proceeding either by electrophilic attack on N or on C. In the presence of added nucleophile Y^-, attack of halogen on the double bond of $N_3C{=}CR$ offers an opportunity for the formation of regioisomeric products (*cf.* **14** and **15**), depending on whether the azide or the R′ function is better able to stabilize a positively charged intermediate (*cf.* **8** and **13**) or transition state. The formation of bromoaldehyde **6**, as observed by Forster, could have resulted *via* **7** or **8** leading to **9** with loss of N_2 or as suggested by eq 1 with loss of azide ion from intermediate **14**. A pathway involving conversion of **8** to *N*-bromoimine **9** would be novel since iminodiazonium ions usually undergo migration or are trapped at carbon.[4b] Furthermore, rearrangements are possible as in the Schmidt reaction (*cf.* **8** → **10** → **16**). This paper describes the interaction of terminal and nonterminal azidoolefins with bromine in various solvents.

Results

I. Terminal Vinyl Azides. When *trans*-1-azido-2-*tert*-butylethylene (**17**) was treated with an excess of bromine in ether followed by water work-up the only products observed were α-bromo-*tert*-butylacetonitrile (**18**), α-bromo-*tert*-butylacetaldehyde (**19**), and α,α-dibromo-*tert*-butylacetaldehyde (**20**). The relative amounts of products obtained were estimated from the nmr spectrum of the crude reaction mixture by integration of the aldehyde protons of **19** and **20** and the methine protons of **18** relative to the *tert*-butyl signal. The reaction was repeated in a number of solvents using 2 equiv of bromine and the data are summarized in Table I. In none of these cases was solvent incorporation observed. The ratio of nitrile to aldehyde remained essentially constant in the presence of excess calcium carbonate.

Bromination of **17** in methanol gave rise to **18** and 1-azido-1-methoxy-2-bromo-2-*tert*-butylethane (**21**) in a ratio of 25:75. Similarly, 1-azido-2-phenylethylene (**22**) led to 1-azido-1-methoxy-2-phenyl-2-bromoethane (**23**) in about 90% yield. No nitrile was isolated from

---

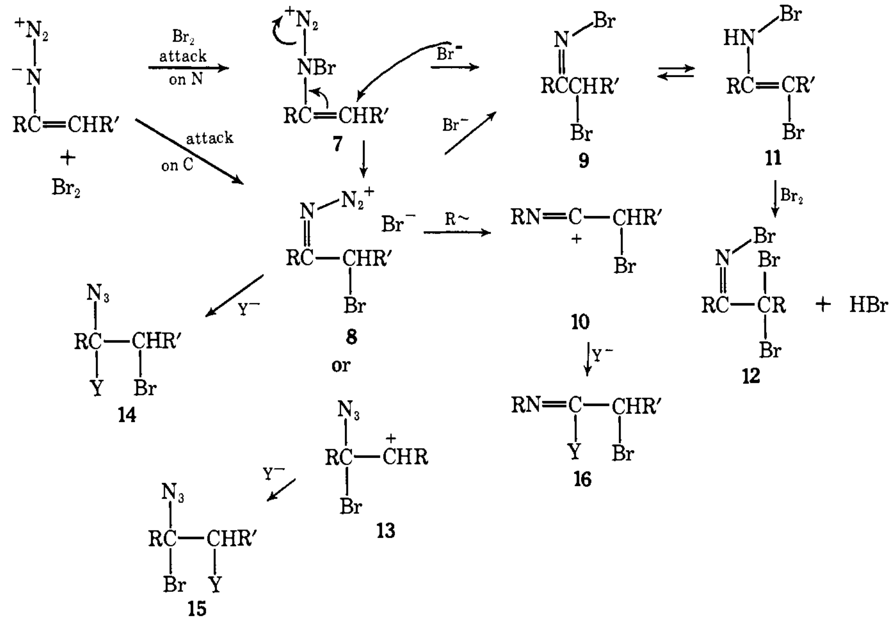
[1] (a) Stereochemistry. LXV. For the previous paper in the series, see G. L'abbe and A. Hassner, *Bull. Soc. Chim. Belg.*, **80**, 209 (1971); (b) NIH Predoctoral Fellow, 1968–1971.

[2] (a) H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970); (b) J. H. Boyer, W. E. Krueger, and R. Modler, *J. Org. Chem.*, **34**, 1986 (1969); (c) A. Hassner, E. S. Ferdinandi, and R. J. Isbister, *J. Amer. Chem. Soc.*, **92**, 1672 (1970).

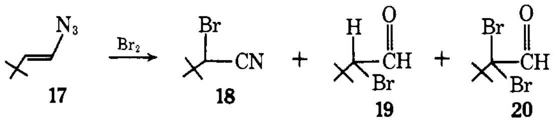
[3] (a) F. W. Fowler, A. Hassner, and L. A. Levy, *ibid.*, **89**, 2077 (1967); (b) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

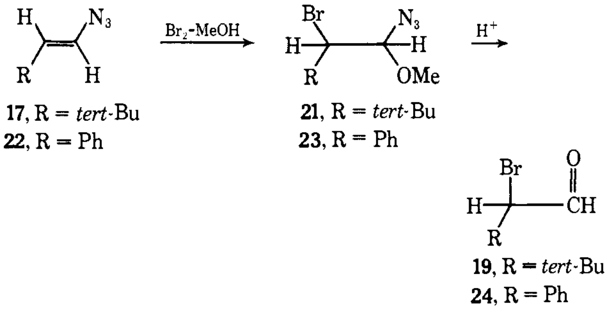
[4] (a) M. O. Forster and S. H. Newman, *J. Chem. Soc.*, **99**, 1277 (1911); (b) P. A. S. Smith "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, p 227.

Scheme I



this reaction. The regiochemistry of the addition was indicated by the mass spectra whose base peak in each case was at m/e (M − RCHBr)$^+$ indicating a terminal methoxy group. No peaks corresponding to m/e (M − RCHOCH$_3$)$^+$ were observed.[5a] Methoxy azides **21** and **23** were hydrolyzed in acid to the corresponding α-bromoaldehydes **19** and **24**.[5b]


17 **18** **19** **20**


17, R = *tert*-Bu
22, R = Ph
21, R = *tert*-Bu
23, R = Ph
19, R = *tert*-Bu
24, R = Ph

Interestingly, the nmr spectra of the adduct **21** formed from the pure *trans*-vinyl azide **17** indicated two methoxy peaks of approximately equal area suggesting the presence of an erythro–threo mixture. Azide **23** also showed two methoxy peaks but in a ratio of ~80:20.

Table I. Product Distribution in the Addition of 2 Equiv of Bromine to *trans*-1-Azido-2-*tert*-butylethylene (**17**)[a]

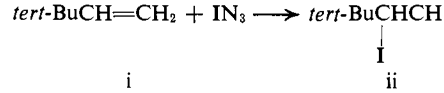
Solvent	% **18**	% **20**	% **19**
Ether	63	37	Trace
Ether–CaCO$_3$	66	33	
Ether[b]	41	12	18
Benzene	73	26	
Acetic acid	52	10	14
DMF	85		

[a] The product distribution was determined by the nmr integration of the crude mixture. [b] Bromine (1 equiv) was used.

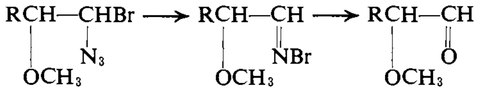
Nonterminal Vinyl Azides. Treatment of 1-azido-*cis*-1-phenylpropene (**25**) with an excess of bromine in ether led to evolution of nitrogen and isolation of a solid to which structure **26** is assigned. **26** was insoluble in most organic solvents except DMSO and could not be further purified. The mass spectrum and analysis of the crude solid were consistent with addition of 2 mol of HBr and loss of nitrogen. The ir spectrum substantiated the absence of azide and showed strong hydrogen bonding and a strong band at 1645 cm^{-1} The nmr spectrum of **26** (two methyl doublets) indicated it to be a mixture of two components with traces of **29** present. Hydrolysis (exposure to water) of **26** led to α-bromopropiophenone (**27**) together with traces (<2%) of α,α-dibromopropiophenone (**30**). Reduction of **26** with LAH in ether led to a 1:1 mixture of *cis*- and *trans*-2-phenyl-3-methylaziridines (**28**) as the sole products, in 43% yield based on vinyl azide **25**.

---

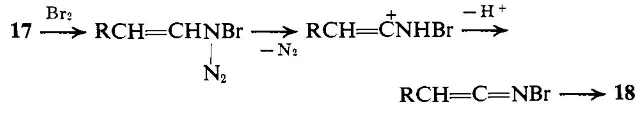
(5) (a) The low yield (53%) of **21** is of some concern. However, since 88% of the product of **22** can be accounted for as adduct **23**, it is unlikely that addition of reverse regiochemistry had occurred in the *tert*-butyl case **17**. It is further known that ionic addition of IN$_3$ to i proceeds regiospecifically to give the terminal azide ii.[3a] (b) The alternate


$$\underset{\text{i}}{tert\text{-BuCH}{=}\text{CH}_2} + \text{IN}_3 \longrightarrow \underset{\text{ii}}{tert\text{-Bu}\underset{\text{I}}{\text{CH}}\text{CH}_2\text{N}_3}$$

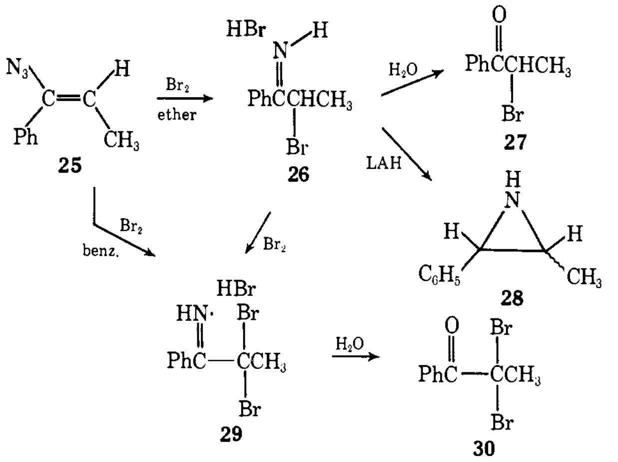
regioisomers of **21** and **23** are expected to lead to α-methoxyaldehydes by the route shown. No methoxyaldehyde products were observedin the


$$\underset{\text{OCH}_3}{\text{RCH}}\text{—}\underset{\text{N}_3}{\text{CHBr}} \longrightarrow \underset{\text{OCH}_3}{\text{RCH}}\text{—CH}{=}\text{NBr} \longrightarrow \underset{\text{OCH}_3}{\text{RCH}}\text{—CH}{=}\text{O}$$

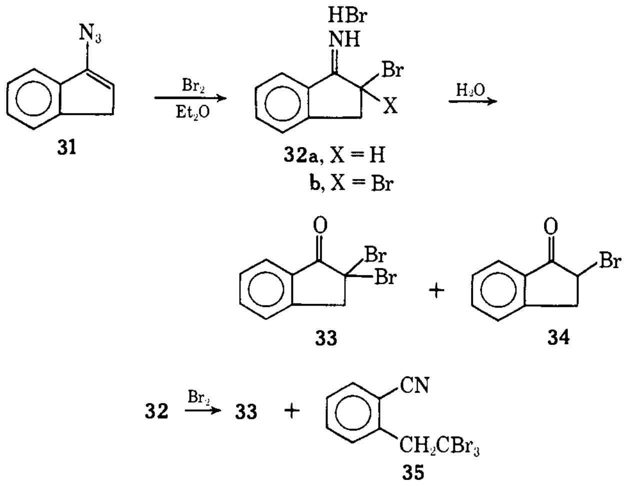
nmr spectrum of the crude product. (c) Although the presence of a regioisomer of **37** cannot be excluded at this time, the formation of a methoxy ketone as expected from the discussion in ref 5b was not observed. (d) The following alternative mechanism has been suggested by a referee.

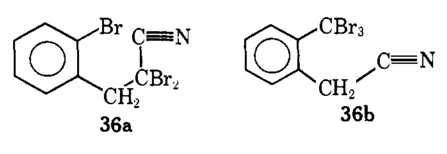

$$\mathbf{17} \xrightarrow{\text{Br}_2} \text{RCH{=}CH}\underset{\text{N}_2}{\text{N}}\text{Br} \xrightarrow[-\text{N}_2]{} \text{RCH}{=}\overset{+}{\text{C}}\text{NHBr} \xrightarrow{-\text{H}^+} \text{RCH{=}C{=}NBr} \longrightarrow \mathbf{18}$$

When the bromine addition was carried out in benzene a different solid precipitated to which structure **29** was assigned. Ir and gc analysis of the supernatant solvent indicated the presence of benzonitrile as well as other compounds in the benzene layer. The nmr spectrum indicated **29** to be free of **26**. Its mass spectrum was also consistent with addition of bromine and loss of nitrogen, yet hydrolysis of **29** led to **30** as the sole product by nmr. Elemental analysis of crude **29** indicated the presence of three bromines, and the ir again showed strong hydrogen bonding. Dibromide **26** can be brominated to **29** as evidenced by its partial conversion to **30** on treatment with Br_2 in benzene followed by hydrolysis. If **25** was treated with 1 equiv of bromine in benzene no solid precipitated but subsequent addition of anhydrous HBr precipitated a salt which by nmr was a 9:1 mixture of **26** and **19**. Hydrolysis of this solid led to **27** and **30** in a ratio of 8:1.



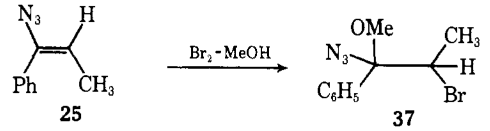
Next we examined the reaction of 1-azidoindene (**31**) in ether or benzene with an excess of bromine. The reactions in both solvents were characterized by evolution of nitrogen and precipitation of a crude solid which is believed to be a mixture of **32a** and **32b** on the basis of nmr and hydrolysis. Treatment of this solid with water led to a mixture of 72% α,α-dibromoindanone (**33**) and 20% α-bromoindanone (**34**). On the other hand, hydrolysis of the crude mixture resulting from bromination of **31** without filtration of **32** led to **33** as the major product together with approximately 30% *o*-(1,1,1-tribromoethyl)benzonitrile (**35**) by nmr.



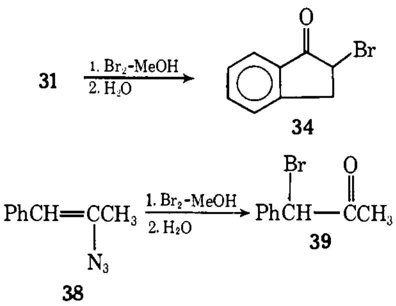


The structure of **35** was evident from its ir, nmr, and mass spectrum. The latter showed characteristic peaks at *m/e* 116 $(M - CBr_3)^+$ and *m/e* 102 $(M - CH_2CBr_3)^+$ eliminating alternative isomeric structures **36a** and **b**. That **35** is a secondary product derived from **32** was shown by treatment of **32** with bromine in benzene for 24 hr, which led to 50% **35**, 34% **33**, and traces of **34**. In a blank run **32** remained unchanged in benzene solution for 24 hr as shown by its hydrolysis to **33** and **34**.

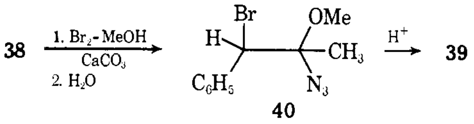
Finally we turned to the reaction of vinyl azides **25** and **31** in methanol. When **25** was treated with bromine in methanol, adduct **37** was isolated in good yield.[5c]



Surprisingly, when **31** or 2-azido-1-phenylpropene (**38**) were subjected to the same reaction conditions only the corresponding α-bromo ketones **34** and **39** were obtained with no visible nitrogen evolution.



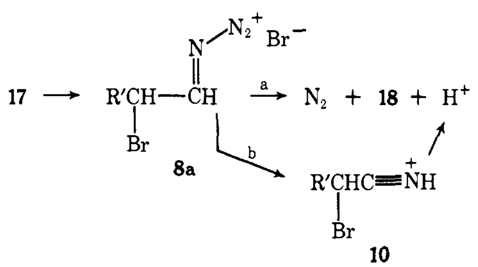
Reaction of **38** in the presence of excess calcium carbonate gave adduct **40** in high yield. Acid hydrolysis of **40** furnished **39**.



Owing to the extreme sensitivity of the BrOMe adduct of **31** to water, we were not able to isolate it in pure form without α-bromoindanone (**34**) present. However, the nmr spectrum of the crude BrOMe adduct of **31** indicated the presence of a compound containing a methoxy group in addition to **34**.

Discussion

The formation of substantial amounts of nitrile from the reaction of the terminal vinyl azide **17** with 1 or 2 equiv of bromine in various solvents suggests the intermediacy of a "long-lived" iminodiazonium ion **8a** which undergoes loss of N_2 and either loss of a proton (path a) or migration of hydrogen leading to **10** followed by loss of a proton (path b). The fact that no products resulting from phenyl or alkyl migration (**8** → **10**) were observed in the bromination of nonterminal vinyl azides (*e.g.*, **25**, **31**, or **38**) is more consistent with path a than path b in the formation of nitrile **18**. Alternatively hydrogen migration could be much faster than



alkyl migration.[5d] The other bromination products of **17**, namely aldehydes **19** and **20**, also do not result from H or alkyl migration but appear to arise from hydrolysis of intermediates similar to **26** and **29**. The lack of alkyl migration in the bromination of terminal vinyl azides is not too surprising since Schmidt rearrangement of aldehydes leads mainly to nitriles.[4b]

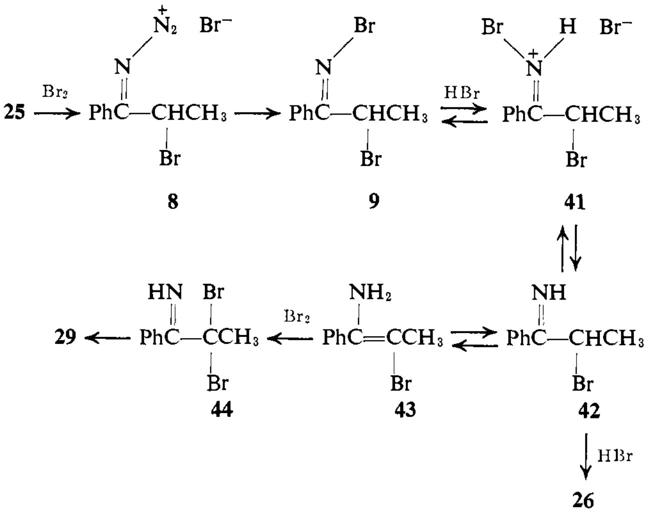
Since the formation of nitrile **18** involves the loss of HBr, it was necessary to determine whether the bromoaldehydes **19** and **20** resulted from reaction of the acid with **17** followed by bromination. That this was not the case was shown by the unchanged bromination products in the absence or presence of $CaCO_3$ (see Table I). The total yield of products in the bromination of **17**, **25**, and **31** ranged from 50 to 90%, leaving open the question whether other products were formed in substantial amounts or whether the lower yields were due to loss during work-up. This was resolved in the case of **17** by changing the work-up from a large amount of water to a small amount of aqueous saturated $NaHSO_3$, in which case the yield of products was improved from *ca.* 70 to 90%. Nmr and tlc indicated the product mixture to consist solely of **18**, **19**, and **20**.

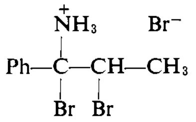
Although no solvent incorporation during Br_2 addition to **17** was observed with DMF or acetic acid,[6] the major product in methanol was the methoxy azide **21**. This product apparently was produced by methanol trapping of intermediate **8**. The regiochemistry of the methoxy group in **21** and **23**, as evidenced by their mass spectra and hydrolysis, indicates that the azide function exerts a strong directing effect, being better able to stabilize a positive charge (*cf.* **8**) than is an alkyl or a phenyl group (*cf.* **13**, R′ = *tert*-Bu or Ph). Such behavior is consistent with the known stabilizing effect of N substituents on a positive charge at the α-carbon as in the bromination of enamines.[7] Since the bromination of enamines gives rise to iminium salts rather than dibromides it is likely that a carbonium ion generated adjacent to an azide exists preferentially as an iminodiazonium–bromide ion pair (*i.e.*, **8**). In a slow step the ion pair may collapse with attack at nitrogen to give the *N*-bromoimine (**8** → **9**). Alternatively, bromide ion may trap ion **8** at carbon reversibly before attack at N.

Further information about the bromination pathway was gained by the isolation of iminium salts **26** and **29** in the bromination of vinyl azide **25**. That these salts are reaction intermediates was obvious from their hydrolysis to mono- and dibromopropiophenone **27** and **30**. It is also clear that **26** and **29** share a common precurser, **9**. The structures of **26** and **29** were assigned on the basis of elemental analysis and spectra. The nmr spectra of both **26** and **29** show a triplet centered near τ 2.0, J = 52 Hz, characteristic of protonated ammonium salts.[8] The ir and mass spectra are also consistent with the assigned structures.

A plausible pathway for the formation of **26** and **29** during the bromination of **25** involves the intermediacy of **8**, **9**, etc., as shown in Scheme II. An analogy for the transformation of **9** to **42** is the conversion of *N*-bromosuccinimide to succinimide and Br_2 by means of HBr.[9] The required HBr for formation of **26** is generated from interaction of bromine with the solvent.[10] The two methyl doublets in the nmr spectrum of **26** suggest that it may exist in solution as a mixture of **42** and **45**. An isomeric enamine structure is excluded since no deuterium is incorporated into **27** upon quenching **26** with D_2O. The reaction of vinyl azide **25** with 1 equiv of Br_2 in benzene apparently produces **9** (no salt precipitates) which can then be precipitated as **26** (plus a small amount of **29**) on addition of hydrogen bromide. Since Br_2 should be formed during the conversion of **9** to **42** with HBr, it is not surprising that a small amount of **29**, from further bromination of **9**, had also arisen. With 2 equiv of Br_2 in benzene, **25** is transformed into **29** (50%) and cleavage products *via* **44**. Conversion of **43** to **44** furnishes the required HBr for salt formation (**44** → **29**).

Scheme II





$$Ph-\overset{\overset{+}{N}H_3}{\underset{Br}{C}}-\underset{Br}{CH}-CH_3 \quad Br^-$$

45

Lithium aluminum hydride reduction of **26** is also consistent with the structure assignments. Thus hydride attack on **42** is expected to give a mixture of diastereomers which on ring closure furnishes the *cis*- and *trans*-2-methyl-3-phenylaziridines (**28**).

In the brominations in methanol, the intermediate of type **8** is trapped by the solvent before it loses N_2. This interpretation is also consistent with the formation of both diastereomers of **21**, **23**, or **40** as evidenced by two CH_3 doublets in the nmr, in the addition of Br_2–MeOH

---

(6) Compare A. Hassner and F. Boerwinkle, *Tetrahedron Lett.*, **36**, 3921 (1968).

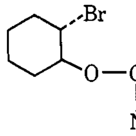
(7) (a) R. L. Petersen, *et al.*, *J. Amer. Chem. Soc.*, **79**, 1115 (1957); (b) A. J. Speziale and J. R. Smith, *J. Org. Chem.*, **28**, 3492 (1963); (c) G. H. Alt, *ibid.*, **33**, 2858 (1968).

(8) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(9) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 3142 (1963).

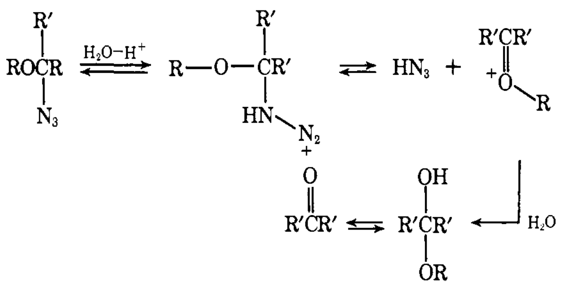
(10) In a blank run, addition of bromine to ether indicated the slow formation of HBr.

to **17**, **22**, and **38**, respectively. Unlike the other α-methoxyalkyl azides in this study, but in analogy with **46**,[6] azide **40** was very sensitive to water and was easily

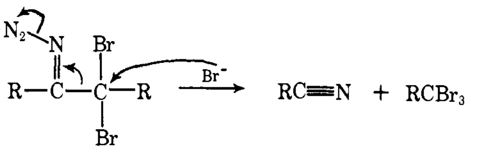


46

converted to ketone **39**. The hydrolysis products of this novel class of α-alkoxy azides suggest the following mechanism.



During the bromination of vinyl azides **25** and **31** an interesting cleavage to nitriles was observed. It appears to proceed *via* α,α-dibromoimines of type **29** but not *via* the monobromo derivatives (*i.e.*, **26**). Thus, bromination of **25** in benzene under conditions of formation of **29** led upon work-up with water to ketone **30** and benzonitrile. No benzonitrile was detected in the bromination of **25** in ether under conditions of formation of **26**. Similarly the amount of nitrile **35** formed from **31** increased as the intermediate **32** was further brominated. These data are consistent with a cleavage mechanism (possibly concerted) analogous to that established for cleavage of α-ketooximes.[11]



This study indicates that the major products from the interaction of vinyl azides with bromine nucleophiles did not result from phenyl or alkyl migration. It appears that electrophilic attack occurs on carbon to produce an intermediate iminodiazonium ion **8** which is trapped by nucleophiles at either carbon or nitrogen. This contrasts the behavior of vinyl azides with sulfuric acid in which the major products arose from migration to nitrogen.[2b] It is clear that electron-defficient nitrogen species can be generated not only by the classical Schmidt reaction but also by electrophilic additions to unsaturated azides. As in the case of carbonium ions, such species show solvent dependent chemical behavior.

Experimental Section

All solvents used were dried reagent grade or dried and distilled. Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra were taken of liquid films unless otherwise noted on a Perkin-Elmer 457 instrument. Nmr spectra were recorded on a Varian A-60 or A-60A spectrometer with TMS as an internal standard using approximately 30% solutions in $CDCl_3$ unless otherwise noted. Glpc data were recorded on a Varian aerograph 90-P3 gas chromatograph with a thermal conductivity detector. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The vinyl azides were prepared from the corresponding olefins by IN_3 addition followed by HI elimination.[3]

General Procedure for the Reaction of Bromine with Vinyl Azides. A 1-g sample of the vinyl azide was dissolved in 25 ml of the anhydrous solvent and 2 equiv of bromine was added. The mixture was stirred overnight or until nitrogen evolution ceased and was then poured into water and extracted with ether. The ether layer was washed with sodium bisulfite solution until colorless and then dried and the solvent removed under vacuum.

Reaction of Bromine with *trans*-1-Azido-2-*tert*-butylethylene (17). A. In Ether. The addition and work-up were carried out as described to give 1.15 g of an oil containing 63% **18** and 37% **20** by nmr. These compounds were separated by preparative thin layer chromatography. Analytical samples were obtained by distillation and sublimation, respectively.

If the reaction was carried out on 0.50 g of **17**, and the reaction worked up by adding saturated sodium bisulfite until the solution becomes colorless, separation and drying the organic layer gave 0.704 g (90%) of an oil containing 64% **18**, 36% **20**, and a trace of **19** by nmr.

α-Bromo-*tert*-butylacetonitrile (18) had bp 85° (0.2 mm) in a Kugelrohr oven; nmr ($CDCl_3$) τ 5.81 (s, 1 H), 8.79 (s, 9 H); ir ν (cm^{-1}) 3000–2860, 2250, 1460, 1370, 1245, 885, 773, 700. *Anal.* Calcd for $C_6H_{10}NBr$: Br, 45.50. Found: Br, 45.34.

α,α-Dibromo-*tert*-butylacetaldehyde (20) had subl pt 90° (0.2 mm); mp 107–108°; nmr τ 0.73 (s, 1 H), 8.63 (s, 9 H); ir (KBr) ν (cm^{-1}) 3000–2860, 1719, 1475, 1460, 1370, 1243, 885, 772, 700. *Anal.* Calcd for $C_6H_{10}OBr_2$: Br, 62.05. Found: Br, 62.25.

B. Reaction of 17 in Ether in the Presence of Calcium Carbonate. The reaction was carried out for 15 min at one-half the scale described. The solution was filtered and worked up in the normal manner to give 0.59 g of a colorless oily solid containing 66% **18** and 33% **20** by nmr.

C. Reaction of 17 in Benzene. The addition was carried out in the normal fashion with stirring for 30 min. The usual work-up gave 1.02 g of oily crystals consisting of 26% **20** and 73% **18** by nmr.

D. Reaction of 17 in Acetic Acid. The reaction was run in the normal manner. After stirring for 10 min 10 ml of water was added, and stirring was continued for an additional 5 min. The reaction was worked up in the normal manner except that the mixture was washed well with 1% sodium carbonate before removing the solvent to give 1.10 g of an oil containing 14% monobromoaldehyde **19**, 10% dibromoaldehyde **20**, and 52% monobromonitrile **18** by nmr.

E. Reaction of 17 in DMF. The reaction was carried out in the normal manner, stirred for 10 min, and worked up as usual to give 1.10 g (65%) of monobromonitrile **18**. The crude material consisted of 85% **18**, and the nmr spectrum indicated the absence of the aldehydes **19** and **20**.

F. Reaction of 17 in Methanol. The reaction was carried out and worked up in the usual manner (with stirring for 45 min) to give 0.91 g of material consisting of 75% 1-azido-1-methoxy-2-bromo-2-*tert*-butylethane (**21**) and 25% monobromonitrile (**18**). Column chromatography on silica with EtOAc–hexane as eluent followed by distillation in a Kugelrohr oven led to 0.55 g of pure **21**: bp 69° (0.5 mm); nmr τ 5.55 (d, 1 H, J = 3.5 Hz), 5.99 (d, 1 H, J = 3.5 Hz), 6.40, 6.45 (two singlets, 3 H), 8.86 (s, 9 H); ir ν (cm^{-1}) 3000–2920, 2120, 1495, 1480, 1250, 1115, 970; mass spectrum m/e (rel abundance) 190 (6.0), 188 (6.0), 151 (2.7), 149 (2.7), 138 (3.4), 136 (3.4), 125 (4.7), 123 (6.1), 86 (100). *Anal.* Calcd for $C_7H_{14}BrON_3$: C, 35.63; H, 5.94. Found: C, 35.79; H, 6.00.

Acid Hydrolysis of 1-Azido-1-methoxy-2-bromo-2-*tert*-butylethane (21). To 0.5 g of the azide **21** in 20 ml of 80% dioxane–water was slowly added 6 ml of concentrated H_2SO_4. The solution was allowed to stand overnight, poured into water, and extracted well with ether, the ether layer washed well with water, and the solvent removed under vacuum to give 0.127 g (32%) of α-bromo-*tert*-butylacetaldehyde (**19**). An analytical sample was prepared by distillation at 60° (0.1 mm) in a Kugelrohr oven: nmr τ 0.66 (d, 1 H, J = 5.5 Hz), 4.10 (d, 1 H, J = 5.5 Hz), 8.86 (s, 9 H); ir ν (cm^{-1}) 3000–2980, 1725, 1480, 1375, 1165. *Anal.* Calcd for $C_6H_{11}BrO$: C, 40.20; H, 6.15. Found: C, 40.01; H, 6.01.

Addition of Bromine to *trans*-1-Phenyl-2-azidoethylene (22) in Methanol. The reaction was run on 0.50 g and worked up as usual to give 0.77 g (88%) of 1-azido-1-methoxy-2-phenyl-2-bromoethane (**23**) as a colorless oil. An analytical sample was obtained by column chromatography and subsequent distillation

---

[11] A. Hassner and I. H. Pomerantz, *J. Org. Chem.*, **27**, 1760 (1962); A. Hassner and W. A. Wentworth, *Chem. Commun.*, **44** (1965).

in a Kugelrohr oven: bp 75° (0.1 mm); nmr τ 2.3–2.9 (m, 5 H), 5.06 (d, 1 H, J = 5.5 Hz), 5.31 (d, 1 H, J = 5.5 Hz), 4.5–4.66 (two singlets, 3 H); ir ν (cm^{-1}) 3100–2900, 2860, 2142, 1505, 1465, 1380, 1345, 1280–1200, 1125, 1040, 990, 850, 790, 720, 680, 620; mass spectrum m/e (rel abundance) 215 (55), 213 (59), 171 (100), 169 (97), 135 (45), 134 (79), 121 (72), 119 (66), 105 (69), 104 (69), 103 (45), 92 (45), 91 (86), 90 (76), 89 (73), 87 (100), 78 (48), 77 (73), 76 (35), 75 (69).

Anal. Calcd for $C_9H_{10}BrN_3O$: C, 42.20; H, 3.91. Found: C, 42.31; H, 4.02.

Acid Hydrolysis of 23. To 1.5 g of the azide in 40 ml of 80% dioxane–water was added 9 ml of concentrated H_2SO_4. The solution was allowed to stand overnight, poured into water, extracted with ether, and dried, and the solvent removed under vacuum. Distillation gave 220 mg (55%) of **24** identical with a known sample prepared by the method of Riehl,[12] bp 85° (1.2 mm) (lit.[12] bp 78–80° (0.8 mm)).

Reaction of Bromine with 1-Azido-1-phenylpropene (25) in Ether. Addition of bromine to **25** in the normal manner caused precipitation of a solid. Filtration gave 1.24 g of **26** which was insoluble in most common solvents except DMSO; hence further purification was not possible: ir (KBr) ν (cm^{-1}) 3200–2500, 1645, 1590, 1445, 1132, 700; nmr (DMSO-d_6) τ 2.5–3.3 (m, 5 H), 3.45 (t, J = 51 Hz), 4.82 (1 H, 2 q, J = 6 Hz), 7.88 and 8.21 (3 H, 2d, J = 6 Hz); after addition of D_2O the nmr indicate a quantitative conversion to **27** with no deuterium incorporation; mass spectrum m/e (rel abundance) 295, 293, 291 (<0.01, ratio 1:3:1, M^+), 213 (38), 211 (3.8), 132 (8.5), 130 (4.3), 106 (4.8), 105 (58), 104 (100), 82 (16.5), 81 (5.3), 80 (15.9), 77 (32.5). *Anal.* Calcd for $C_9H_9NBr_2$: Br, 54.90. Found: Br, 54.93.

When 0.25 g of solid **26** was hydrolyzed in 5 ml of water and the resultant oil extracted with ether, 110 mg (65%) of **27** was obtained, which contains <2% of **29** by nmr. **27** was identified by comparison with Sadtler's nmr and ir spectra.

To 200 mg of **26** in 5 ml of benzene was added 1 drop of bromine and 1 mg of KBr. Upon work-up the resultant oil (77 mg) consisted of 68% **27** and 32% **30**.

When the bromination of **25** was run on one-half the normal scale and the supernatant fluid was separated and subjected to analysis by glc, no benzonitrile was detected.

The reaction was run in the normal manner. The salt **26** was filtered (caution: highly lachrymatory), and immediately added to a solution containing 200 mg of LAH. Basic work-up led to *cis*- and *trans*-2-phenyl-3-methylaziridine (**28**) in 42% yield based on starting vinyl azide (cis:trans ∼50:50 by nmr). The nmr and ir are identical with those reported.[13]

B. In Benzene. The addition and work-up were carried out on a 3-g scale for 2 hr as described. Nmr indicated a 59% yield of α,α-dibromopropiophenone (**30**) which was separated by preparative thin layer chromatography and found to be identical with a known sample prepared by the method of House:[14] nmr (DMSO-d_6) τ 7.28 (s, 3 H), 2.50 (m, 3 H), 1.68 (m, 2 H); ir (KBr) ν (cm^{-1}) 1680, 1250, 1080, 810, 695, 590.

When the reaction was carried out as above on 1 g of **25** except that the solid formed was filtered, 1.18 g (50%) of **29** was isolated: ir (KBr) ν (cm^{-1}) 3400–2600, 1680, 1405, 1260, 1075, 965, 820, 705, 600; nmr (DMSO-d_6) τ 7.28 (s, 3 H), 1.7–3.0 (m, 5 H), 2.79 (t, J = 51 Hz); mass spectrum m/e (rel abundance) 295, 293, 291 (<1%, ratio 1:2:1, m^+), 106 (8.8), 105 (100), 103 (5.7), 77 (32.1), 51 (13.9), 50 (6.1). *Anal.* Calcd for $C_9H_{10}Br_3N$: Br, 64.35. Found: Br, 64.72.

When the reaction was run in the normal manner with 1 equiv of bromine (1 g) no solid precipitated. Bubbling of anhydrous HBr through this solution led to 830 mg of an orange solid consisting of a 9:1 mixture of **26** and **29**. When 250 mg of this solid was hydrolyzed (exposure to water) work-up led to 120 mg of an 8:1 mixture of **27** and **30** by nmr.

Hydrolysis of 0.5 g of solid **29** in 5 ml of water led to 0.171 g of an oil containing 81% **30** by nmr.

When the reaction was run on one-half the normal scale, and the supernatent fluid analyzed by glc, on Carbowax 20M and Se-32 columns, a peak with the same retention time as benzonitrile was detected. The infrared spectrum of the oil after removal of solvent also showed a nitrile band at 2240 cm^{-1}.

C. In Methanol. The reaction was carried out for 1 hr on a 2-g scale and worked up in the normal manner to give 2.68 g (80%) of crude adduct which was 90% pure by nmr integration. Part of this material (1.4 g) was placed on a silica column using EtOAc–hexane as eluent, and after distillation led to 0.50 g of pure **37**: bp 80° (0.1 mm); ir (cm^{-1}) 3040, 3010, 2980, 2940, 2820, 2120, 1490, 1449, 1260, 1090, 1075, 918, 770, 710; nmr ($CDCl_3$) τ 2.57 (s, 5 H), 5.55 (m, 1 H), 6.60, 6.70 (s, s, 3 H), 8.39 and 8.51 (two doublets, 3 H, J = 7 Hz); mass spectrum m/e (rel abundance) 229 (12.0), 228 (17.8), 227 (16.6), 226 (22.2), 162 (50.2), 161 (10.7), 151 (14.7), 148 (19.6), 147 (17.5), 134 (53.2), 132 (19.5), 131 (17.2), 130 (23.1), 119 (100), 117 (49.5), 116 (25.2), 105 (38.8), 104 (26.3), 103 (35.1), 93 (14.2), 91 (21.8), 78 (15.0), 77 (83.9), 76 (18.9).

Anal. Calcd for $C_{10}H_{12}BrON_3$: C, 44.45; H, 4.45. Found: C, 44.62; H, 4.54.

Reaction of Bromine with 1-Azidoindene (31). A. In Ether. The reaction was carried out in the normal manner, and work-up with water led to a brown solid weighing 1.24 g, and consisting of 50% α,α-dibromoindanone (**33**) and 24% *o*-(1,1,1-tribromoethyl)benzonitrile (**35**) by nmr. The separation was carried out as follows. The reaction was repeated as above except that the solid which precipitated out during the addition of bromine was filtered to give 1.5 g of **32**.

Hydrolysis of 0.50 g of **32** in 10 ml of water and 10 ml of ether for 20 min gave 0.241 g of an oil consisting of 72% **33** and 20% **34**.

When the filtrate from **32** was hydrolyzed and worked up in the normal manner it led to 110 mg of pure *o*-(1,1,1-tribromoethyl)benzonitrile (**35**): mp 149–150° (from ethanol); ir 2240 cm^{-1}; nmr ($CDCl_3$) τ 5.43 (s, 2 H), 2.0–3.0 (m, 4 H); mass spectrum m/e (rel intensity) 365 (0.6), 367 (1.8), 369 (1.8), 371 (0.6), 285 (57), 287 (100), 289 (55), 249 (0.3), 251 (0.9), 253 (0.9), 255 (0.3), 206 (62), 208 (64), 128 (81), 116 (71), 102 (17).

Anal. Calcd for $C_9H_6NBr_3$: C, 29.38; H, 1.63; Br, 65.20. Found: C, 29.38; H, 1.63; Br, 65.04.

To 100 mg of **32** in 10 ml of anhydrous benzene was added 200 mg (2 equiv) of Br_2 and the mixture stirred overnight. The benzene layer was washed with water and 2% sodium bisulfite and dried; the solvent was removed under vacuum to give 75 mg of an oil containing 50% **35**, 34% **32**, and only traces of **34** by nmr.

B. In Benzene. The addition was carried out as described, stirred overnight, and worked up in the normal manner to give 1.29 g of red crystals. Nmr indicated 60% **33** and 40% **35**.

C. In Methanol. The reaction was run on twice the usual scale for 20 min and worked up in the usual manner to give 1.71 g (64%) of crude 2-bromoindanone (**34**) identical with a known sample.[14] No nitrogen evolution was observed during the course of the reaction.

Addition of Bromine to 2-Azido-1-phenylpropene (38). A. In Methanol. The reaction was carried out in the usual manner on 0.50 g of the vinyl azide **38**. No nitrogen evolution was observed. The reaction was worked up after stirring for 20 min to give 0.75 g of an oil containing 75% 1-phenyl-1-bromo-2-propanone (**39**). The identity of the latter in the crude oil was indicated by nmr and tlc comparison with a known sample.[15]

B. In Methanol with 1 Equiv of Calcium Carbonate. The reaction was carried out in the usual manner on 0.50 g of the vinyl azide in the presence of 0.31 g of calcium carbonate for 30 min. Work-up in the usual manner led to 0.759 g (89%) of 1-bromo-1-phenyl-2-methoxy-2-azidopropane (**40**). Nmr integration indicates the material to be more than 90% pure. Column chromatography in hexane on silica and distillation in a Kugelrohr oven led to 0.25 g of analytical sample: nmr ($CDCl_3$) τ 8.48 (s, 3 H), 6.56 (two singlets, 3 H), 4.96 (two singlets, 1 H), 2.3–2.8 (m, 5 H); ir (cm^{-1}) 3060–2820, 2100, 1455, 1385, 1250, 1185, 1125, 1095, 1055, 710; mass spectrum m/e (rel abundance) 229 (22), 227 (21), 171 (46), 169 (45), 148 (89), 105 (52), 100 (52), 91 (22), 90 (43), 89 (53), 77 (31), 74 (22), 72 (100). *Anal.* Calcd for $C_{10}H_{12}BrN_3O$: C, 44.45; H, 4.45. Found: C, 44.13; H, 4.38.

General Procedure for the Independent Synthesis of Bromo Ketones and Dibromo Ketones 30, 33, and 34. The procedure used was that of House, *et al.*[14] In general the crude compounds sufficed for identification by ir and nmr: 2-bromoindanone (**34**), mp 36–39° (lit.[14] 38–40°); 2,2-dibromoindanone (**33**), mp 132–133° (lit.[14] 133–134°).

Acknowledgment. Support of this research by Grant GP-19253 from the National Science Foundation and by PRF Grant 5899AC1,4 from the American Chemical Society is gratefully acknowledged.

---

(12) J. J. Riehl, *C. R. Acad. Sci.*, **245**, 1321 (1957).

(13) A. Hassner, G. J. Matthews, and F. W. Fowler, *J. Amer. Chem. Soc.*, **91**, 5046 (1969).

(14) H. O. House, *et al.*, *ibid.*, **82**, 1452 (1960).

(15) A. C. B. Smith and W. Wilson, *J. Chem. Soc.*, 1343 (1955).