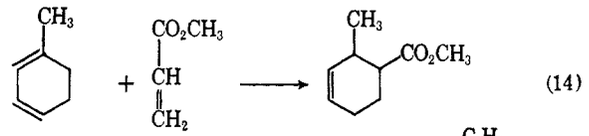
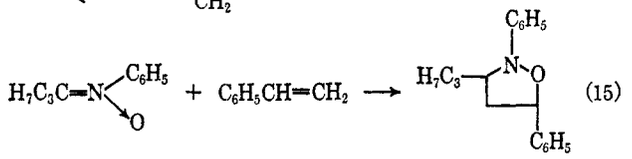
required on occasion as for the phenyl-propyl nonvicinally regiospecific dipolar addition shown in eq 15[18] below.

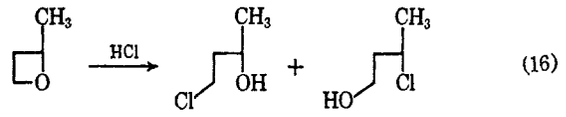


(14)



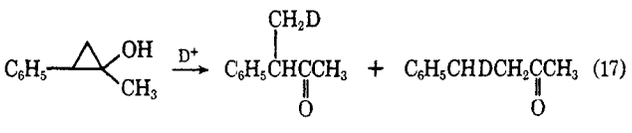
(15)

Ring-opening reactions of heterocycles such as aziridines, epoxides, larger ring ethers, lactams, and lactones as well as of other ring compounds can occur in a regiospecific or selective manner, *i.e.*, the Cl–H over Cl–CH_3 regioselective opening of oxetanes (eq 16)[19] and the D–H over D–phenyl regioselectivity in the opening of cyclopropanols[20] (eq 17).



(16)

80% 20%



(17)

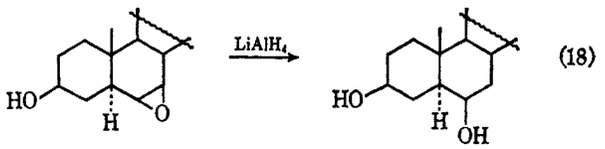
60% 40%

(18) R. Grashey, R. Huisgen, and H. Leitermann, *Tetrahedron Lett.*, 9 (1960).

(19) S. Searles, K. A. Pollart, and F. Blaock, *J. Amer. Chem. Soc.*, **79**, 952 (1957).

(20) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *ibid.*, **88**, 3347 (1966).

Hydride opening of 6β,7β-epoxycholestane is H–(C-7) regiospecific, consistent with diaxial opening of epoxides[21] (eq 18).



(18)

Electrophilic, nucleophilic, or free-radical aromatic substitutions may be *ortho*, *meta*, or *para* regioselective.

In inorganic chemistry examples of regioselective reactions can be found among others in alkylations[22] or deuterium exchange[23] involving decaboranes and halogenation of B_5H_9.[24]

Finally the concept can be applied to positional isomerism, so that **3** and **4** can be termed regioisomers (synonymous with position isomers).[25]

3 4

Acknowledgment.—The author is indebted to Professors P. D. Bartlett, C. H. DePuy, A. Dreiding, E. L. Eliel, J. S. Meek, V. Prelog, J. D. Roberts, J. Sicher, and P. S. Skell for discussions and to Mr. F. Boerwinkle, F. W. Fowler, R. J. Isbister, and G. J. Matthews for valuable suggestions and discussions. This work was supported by U. S. Public Health Service Grant CA-04474 from the National Cancer Institute.

(21) E. J. Corey, *ibid.*, **76**, 175 (1954).

(22) I. Dunston, R. C. Williams, and N. J. Blay, *J. Chem. Soc.*, 5012 (1960).

(23) J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **84**, 1804 (1962).

(24) R. Schaeffer, J. N. Shoolery, and R. Jones, *ibid.*, **80**, 2670 (1958).

(25) M. Svoboda, J. Zavada, and J. Sicher, *Collect. Cvech. Chem. Commun.*, **32**, 2104 (1967).

A General Synthesis of Vinyl Azides from Olefins. Stereochemistry of Elimination from β-Iodo Azides[1a]

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Treatment with base of β-iodo azides, prepared by the addition of iodine azide to olefins, resulted generally in vinyl azides, suggesting a directive effect of the azido function. Terminal olefins, vicinally disubstituted olefins, and unsaturated carbonyl compounds all led regiospecifically to the vinyl azides. Indene, 1,2-dihydronaphthalane, cyclooctene, and 1,3-cyclooctadiene also gave the vinyl azides. However, the iodine azide adducts of cyclopentene and cyclohexene produced the allyl azides. Apparently, the stereoelectronic preference for *trans* elimination is greater than the directive effect of the azido function. An assignment of *cis* configuration to the double bond in the eight-membered-ring vinyl azides, made on the basis of nmr data, suggests *syn* elimination of hydrogen iodide in these systems. Regioselectivity in IN_3 additions to olefins is discussed.

The simplest vinyl azide, azidoethylene, was prepared by Forster and Newman[2] as early as 1910. However, since then very few vinyl azides have been reported[3] and, although some have been found to be valuable intermediates for the synthesis of 1-azirines,[4] their chemistry has not been explored very extensively. Consequently a general synthesis of vinyl azides (Table I) would be desirable for it should allow for the investigation of this relatively unknown class of com-

(1) (a) Stereochemistry. XXXV. For paper XXXIV, see A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968). (b) NASA Predoctoral Fellow, 1965–1967.

(2) M. O. Forster and S. H. Newman, *J. Chem. Soc.*, **97**, 2570 (1910).

(3) (a) J. H. Boyer and F. C. Cantes, *Chem. Rev.*, **54**, 1 (1954); (b) E. Lieber, J. S. Curtice, and C. N. R. Rao, *Chem. Ind.* (London), 586 (1966).

(4) (a) G. Smolinsky, *J. Amer. Chem. Soc.*, **83**, 4483 (1961); (b) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); (c) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2875 (1968).

TABLE I
SYNTHESIS OF ACYCLIC IODO AZIDES AND VINYL AZIDES[a]

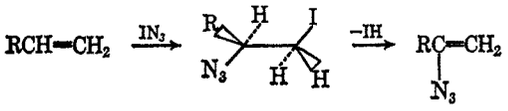
	Olefin, series a	β-Iodo azide, series b	Unsaturated azide, series c
1.	$PhCH{=}CH_2$	$PhCH(N_3)CH_2I$[b]	$PhC(N_3){=}CH_2$[c]
2.	$t\text{-}BuCH_2CH{=}CH_2$	$t\text{-}BuCH_2CH(N_3)CH_2I$[d]	$t\text{-}BuCH_2C(N_3){=}CH_2$
3.	$t\text{-}BuCH{=}CH_2$	$t\text{-}BuCH(I)CH_2N_3$[b]	$t\text{-}BuCH{=}CHN_3$[b]
4.	$CH_3CH{=}CHCH_3$ (*cis*)	$CH_3CH(N_3)CH(I)CH_3$ (*threo*)[b]	$CH_3C(N_3){=}CHCH_3$ (*trans*)
5.	$(CH_3)_2CHCH{=}CHCH_3$ (*cis*)	$(CH_3)_2CHCH(N_3)CH(I)CH_3$[d] (*threo*)	$(CH_3)_2CHC(N_3){=}CH_3$ (*trans*)
6.	$CH_3CH{=}CHCH_3$ (*trans*)	$CH_3CH(I)CH(N_3)CH_3$ (*erythro*)[b]	$CH_3C(N_3){=}CHCH_3$ (*cis*)
7.	EtCH=CHEt (*trans*)	EtCH(I)CH(N₃)Et[d]	EtC(N₃)=CEt (*cis*)[c]
8.	$PhCH{=}CHCH_3$ (*trans*)	$PhCH(I)CH(N_3)CH_3$[d]	$PhC(N_3){=}CHCH_3$ (*cis*)[c]
9.	$t\text{-}BuCH{=}CHCH_3$ (*trans*)	$t\text{-}BuCH(N_3)CH(I)CH_3$[d]	$t\text{-}BuC(N_3){=}CHCH_3$ (*cis*)
10.	$CH_3CH{=}CHCO_2Et$ (*trans*)	$CH_3CH(N_3)CH(I)CO_2Et$	$CH_3C(N_3){=}CHCO_2Et$ (*cis*)[c]
11.	$PhCH{=}CHCO_2CH_3$ (*trans*)	$PhCH(N_3)CH(I)CO_2CH_3$	$PhC(N_3){=}CHCO_2CH_3$[c]
12.	$CH_2{=}CHCO_2CH_3$	$CH_2CH(N_3)CH(I)CO_2CH_3$ (**12b**) + $CH_2CH(I)CH(N_3)CO_2CH_3$ (**13b**)	$HC(N_3){=}CHCO_2CH_3$[d] (**12c**) + $CH_2{=}C(N_3)CO_2CH_3$ (**13c**)
14.	$(CH_3)_2CHCH{=}CH_2$	mixture	$(CH_3)_2CHCH{=}CHN_3$ (**14c**)[d] $(CH_3)_2CHC(N_3){=}CH_2$ (**15c**)[d]

[a] All compounds gave nmr spectra consistent with their structure and indicative of high purity; the mass spectra of these compounds often show absence of parent peaks but are consistent with their structure. [b] See ref 5. [c] Converted into an azirine by photolysis.[4c] [d] Gave correct elemental analyses.

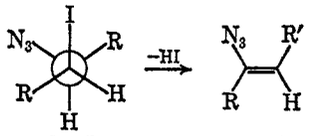
pounds and of possible nitrene intermediates as well as provide a synthesis of 1-azirines.

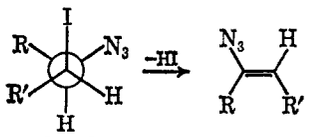
We have previously reported that iodine azide adds to olefins to give high yields of β-iodo azides.[5] If the elimination of hydrogen iodide occurs regiospecifically[6] in the direction of the azido function, β-iodo azides could provide a general synthesis of vinyl azides.

The addition of iodine azide usually occurred in an N_3–R regiospecific[6] manner to terminal olefins (except for **3a**, see later discussion), and elimination of hydrogen iodide with potassium *t*-butoxide in ether from these β-iodo azides presented no problem for the synthesis of 2-azido-1-alkenes (*e.g.*, **1c**, **2c**).



With vicinal iodo azides derived from internal olefins the elimination of hydrogen iodide can occur in two directions to give either the allyl azide, vinyl azide, or a mixture. Brown and coworkers[7] reported that treatment of 2-iodobutane with potassium *t*-butoxide in *t*-butyl alcohol gives 33% of 1-butene and 67% of 2-butene (*cis* and *trans*). If the azido function has little or no directive effect on the elimination of hydrogen iodide then a mixture of allyl and vinyl azide would be expected. Fortunately, the elimination of hydrogen iodide was Saytzeff regiospecific since the iodo azide adducts derived from the 2-butenes gave exclusively the vinyl azides. Moreover, the elimination was stereospecific, the iodo azides derived from *cis*-2-butene (**4a**) and *trans*-2-butene (**6a**) giving *trans*- and *cis*-2-azido-2-butenes **4c** and **6c**, respectively. Iodo azides **6b–11b** derived from *trans* olefins led to vinyl azides **6c–11c** of high purity, even





(5) F. W. Fowler, A. Hassner, L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(6) We have recently introduced the term regiospecific to denote orientationally specific reactions. See paper XXXIV.[1a]

(7) H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **87**, 5517 (1965).

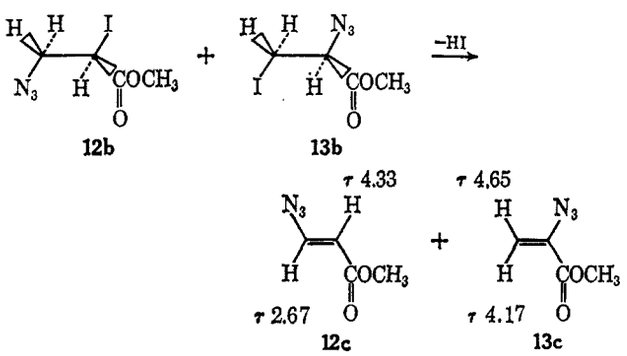
though *trans* elimination of hydrogen iodide required eclipsing of the alkyl groups in the transition state.

Trisubstituted olefins reacted with iodine azide in an electronically regiospecific manner so that the azido function occupied the tertiary position.[5] The unavailability of a hydrogen geminal to the azido function precluded the synthesis of vinyl azides from these adducts.

Iodine azide added to ethyl crotonate to give ethyl 3-azido-2-iodopropionate **10b** in good yield and elimination of hydrogen iodide gave vinyl azide **10c**. This vinyl azide appeared to be identical with that previously prepared by another route by Harvey and Ratts.[8]

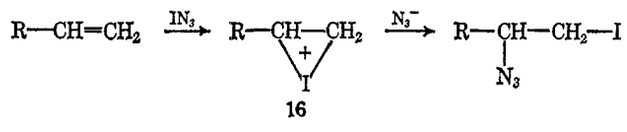
Owing to complications, such as ester cleavage, potassium *t*-butoxide proved to be unsatisfactory for the elimination of hydrogen iodide in these systems. We have observed that the elimination can be carried out very efficiently using 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetone.

The addition of IN_3 to methyl acrylate (**12a**) proceeded in good yield to a mixture of **12b** and **13b** from which elimination of hydrogen iodide gave a mixture of vinyl azides **12c** and **13c**. This conclusion was based on the appearance of two typical absorptions in its nmr spectrum. One, centered at τ 3.56 (J = 14 Hz), accounted for *ca.* 12% of the total product and is attributed to **12c**. The other, centered at τ 4.40 (J = 1.6 Hz), accounted for the remaining 88% and arises from structure **13c**. The possibility that the eliminated product was just a *cis–trans* mixture is unlikely since a coupling constant of only 1.6 Hz would be too small for either the *cis* or the *trans* compound. However,



this coupling constant is consistent with the nonequivalent geminal vinylic protons of vinyl azide **13c**. Vinyl azides **12c** and **13c** were separated by chromatography over alumina.

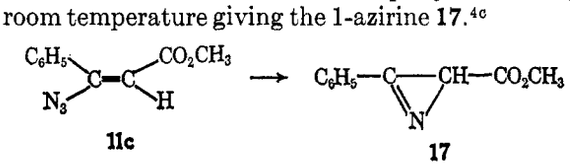
The regiospecific addition of IN_3 to terminal olefins most likely involves the intermediacy of a three-membered ring iodonium ion **16** that is opened at the more substituted carbon for electronic reasons.[5] When R is alkyl or phenyl, inductive effects would be expected to stabilize an incipient positive charge better at the secondary than at the primary carbon in **16**. The



opposite should be true in case of carbonyl substituents which destabilize an adjacent positive center. Accordingly, iodine azide addition to ethyl crotonate gave **10b** exclusively. The regioselective, although not specific, addition of iodine azide to methyl acrylate, appears to constitute an exception. Possibly the preferential formation of **11** can be accounted for in terms of the well-known ease of biomolecular displacement of α halogen in α-halo ketones and esters. This reflects the dual nature of the iodonium ion. That is, while being an ionic species, its ring opening resembles to a certain extent a nucleophilic displacement reaction. On the other hand, ionic addition of hydrogen halides to methyl acrylate give exclusively the β-halo adduct.

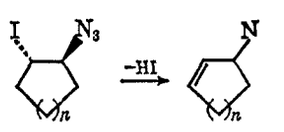
The importance of steric factors in controlling the regioselectivity of IN_3 additions may be seen by comparing the conversion of 3-*t*-butyl-1-propene (**2a**) into **2b** with the conversion of *t*-butylethylene (**3a**) into **3b**. This complete reversal of regiospecificity can be attributed to steric effects in the opening of **16**. Similar steric control on the regiochemistry of addition is seen in the orientation of **5b** and **9b** as opposed to **8b**. The steric effect of the isopropyl group in **14a** is not sufficient to cause I–*i*-Pr regiospecific addition. The nmr spectrum of the dehydroiodination product indicates the presence of 36% of **14c** and 64% of **15c**. The mixture of the two vinyl azides analyzed correctly. If the electronic effects are balanced by symmetrical dialkyl substitution as in olefin **5a** then the steric effect of the isopropyl group becomes dominant and the addition is I–*i*-Pr regiospecific.

Although iodine azide adds well to conjugated carbonyl compounds in general, the vinyl azide can not always be isolated. For example, we have reported[5] that when 2-iodo-3-azido-3-phenylpropiophenone was treated with DABCO only 3,5-diphenylisoxazole was obtained. However, when methyl 2-iodo-3-azido-3-phenylpropionate was treated with DABCO at 5° it does give the vinyl azide **11c**, as evidenced by the ir and nmr spectrum of the crude product. This vinyl azide could not be isolated because it rapidly lost nitrogen at room temperature giving the 1-azirine **17**.[4c]



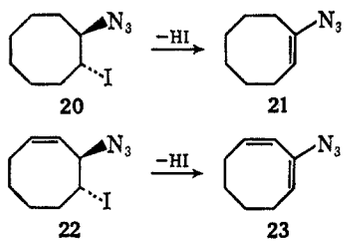
Since the starting methyl cinnamate possessed *trans* stereochemistry, its IN_3 adduct was the *erythro* isomer which on *trans* elimination of hydrogen iodide gave the *cis*-vinyl azide **11c**. The instability of these vinyl azides is probably due to the presence of large or polar *cis* substituents. *cis*-Azidostilbene derived from the iodo azide adduct of *trans*-stilbene[5] is likewise unstable at 0°. If this is the situation, then possibly stable vinyl azides with large substituents could be obtained if the starting olefin has *cis* stereochemistry. This problem is presently under investigation.

Unfortunately, the iodo azides derived from simple cyclic olefins do not yield vinyl azides; instead allyl azides **19** are obtained. Here the stereoelectronic



(8) G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966).

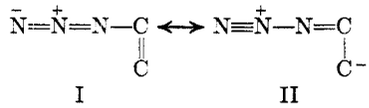
preference for *trans* elimination is greater than the directive effect of the azido function. However, with cyclooctene iodo azides **20** and **22**, where *trans* elimination of hydrogen iodide[9] to a *trans*-vinyl azide is possible, vinyl azides were obtained. The elimination



of hydrogen iodide in these system was very slow and the product from iodo azide **20** was contaminated with 10–15% cyclooctene. The formation of cyclooctene in this reaction is indicative of iodine azide elimination, a phenomenon sometimes observed with β-iodo azides.

Although it is tempting to assign the *trans* configuration to the double bond in 1-azidocyclooctene this does not appear to be justified on the basis of nmr data as well as from the fact that *trans*-cyclooctenes are unstable and react with azides at −100°.[9b]

The nmr absorption of vinylic protons vicinal to the azido substituent occur at relatively high field compared to normal vinylic protons. This is consistent with the nmr spectra of vinyl ethers[10] and can be attributed to contributions from resonance structures such as II which increase the electron density at the vicinal carbon atom. We have previously reported[5] that the proton *cis* to the azido function in azidostilbenes and azido-2-butenes has its nmr absorption shifted upfield from the corresponding proton in the *trans*



isomer. It is now apparent that with simple aliphatic vinyl azides these absorptions for the *cis* and *trans* isomers fall in a very narrow range (see Table II) and are well separated from each other. Evidently, 1-azidocyclooctene possesses the *cis* stereochemistry (**21**) unless some unexpected factor is operative in the cyclic *trans*-vinyl azide causing a downfield shift of the *trans* proton.

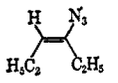
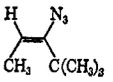
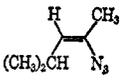
The vinyl azide obtained by hydrogen iodide elimination from **22** can likewise be assigned the *cis,cis* configuration **23**. The vinylic proton vicinal to the azido function occurs as a triplet and is shifted upfield from the other vinylic protons to τ 4.68. Irradiation at 192 cps upfield causes this triplet to collapse into a singlet.

These results could be explained by *cis* addition of IN_3 followed by *anti* elimination of hydrogen iodide. However, there is no precedent for *cis* addition of IN_3 to an olefin. Initial elimination of hydrogen iodide to the allyl azide followed by isomerization to the vinyl

(9) (a) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953); (b) A. C. Cope, C. F. Howell, J. Bower, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

(10) J. M. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. 2, Pergamon Press Inc., New York, N. Y., 1966, p 721.

TABLE II

Nmr absorption for —CH=C(N3)—, τ	
cis isomer	*trans* isomer
 7c, 4.93	 4c, 5.30
 6c, 4.92	
 9c, 4.89	 5c, 5.45
 21, 4.77	

azide is unlikely with the cyclooctene iodo azide since this type of isomerization was not observed with the cyclopentene and cyclohexene iodo azides. In fact, the proton geminal to the azido function in allyl azide **19b** does not exchange after prolonged treatment with potassium deuteroxide in deuterium oxide–acetone-d_6. A better rationalization is that hydrogen iodide was eliminated in a *syn* manner from the *trans*-iodo azide to give the vinyl azide.

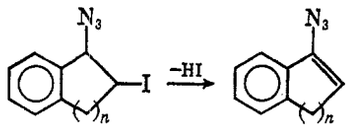
Sicher and coworkers have recently studied the elimination of hydrogen bromide from bromocycloalkanes with potassium *t*-butoxide in *t*-butyl alcohol.[11] In the larger rings it was postulated that the *cis* olefin was produced by ionic *anti* elimination of hydrogen bromide whereas an ion-pair *syn* mechanism was postulated for production of the *trans* olefin. In eight-membered rings *anti* elimination is known to be very slow.[11] Since an ion pair should be more stable with respect to the ions in ether than *t*-butyl alcohol, the *syn* mechanism should play a more important role in ether. This fact, coupled with the known directive effect of an azido substituent, supports the *syn* mechanism for the elimination to the vinyl azides in these systems.

Brown and coworkers[12] have recently reported that E2 elimination from *trans*-2-methylcyclooctyl tosylate with potassium *t*-butoxide gave a 1:1 mixture of the 1- and 3-methylcyclooctene.[12] Although no stereochemical assignment was made to the 1-methylcyclooctene, its isolation is consistent with our results and may indicate a *syn* elimination.

Two other cyclic olefins that we have successfully converted into vinyl azides are indene and 1,2-dihydronapthalene. Possibly a *syn* elimination of hydrogen iodide is also operative with these systems. However, a plausible pathway consistent with the elimination in the cyclopentene and cyclohexene series would involve initial elimination to the allyl azides. Owing to the greater acidity of the allylic hydrogens which in these systems are also benzylic, the allyl azides can rearrange in the presence of base to the vinyl azides **25a** and **b**.

(11) J. Zavada, J. Krupilka, and J. Sicher, *Chem. Commun.*, 67 (1967).

(12) H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **88**, 1430 (1966).



24a, $n = 1$ **25a**, $n = 1$
b, $n = 2$ **b**, $n = 2$

Experimental Section[13]

General.—Both iodo and azido functions are quite labile in the iodo azide adducts and elemental analysis was generally precluded with the higher molecular weight olefins, since extensive decomposition occurred on attempted distillation. However, evidence that addition did take place can be obtained from an examination of the infrared spectrum which shows very strong asymmetric stretching absorption at *ca.* 2100 cm^{-1}. The nmr spectrum in the olefinic region can be used to ascertain whether any unreacted olefin is present and, if it is, generally the amount is quite small. Most iodo azides were converted by reduction into aziridines in good yield.[14] The general procedure for iodine azide addition was followed as described.[5]

A note of caution: We have observed that addition of iodine azide to sulfur-containing olefins results in violent decomposition of the reagent.

The general procedure for the formation of unsaturated azides from iodo azides was as described.[5] The crude unsaturated azides were purified by passage through neutral Woelm aluminum oxide activity I with dry Skellysolve F or A. Removal of the solvent *in vacuo* at room temperature gave the pure unsaturated azide (ir, 2100 ± 20 (vs), 1635 ± 10 cm^{-1} (s)). For possible deviations from these general procedures see the section below for each specific compound. The vinyl azides were likewise unstable and distillation was not advisable. The nmr data for all vinyl azides are consistent with the assigned structures. Most vinyl azides were converted in good yield into azirines or derivatives by photolysis.[4c]

α-Azidostyrene (**1c**) was prepared from α-azido-β-iodoethylbenzene[5] (**1b**) in 67% yield: nmr (CCl_4), τ 2.4–2.9 (m, five aromatic protons), 4.72 (d, 1 (J = 2.4 Hz), C=C**H**), and 5.19 (d, 1 (J = 2.4 Hz), C=C**H**).

1-Iodo-2-azido-4,4-dimethylpentane (**2b**) was prepared from 4,4-dimethyl-1-pentene in 79% yield: nmr ($CDCl_3$), τ 6.2–6.8 (m, 3, C**H**C$N_3$$H_2$) and 9.00 (s, 9, $(CH_3)_3C$).

Anal. Calcd for $C_7H_{14}IN_3$: C, 31.48; H, 5.28. Found: C, 31.51; H, 5.22.

2-Azido-4,4-dimethyl-1-pentene (**2c**) was prepared from 1-iodo-2-azido-4,4-dimethylpentane (**2b**) in 61% yield: nmr ($CDCl_3$), τ 5.25 (s, 1, C=C**H**), 5.38 (s, 1, C=C**H**), 8.08 (s, 2, $-CH_2$), and 9.03 (s, 9, $(CH_3)_3C$).

trans-**2-Azido-2-butene** (**4c**) was prepared from *threo*-2-azido-3-iodobutane (**4b**)[5] in 53% yield: nmr (CCl_4), τ 5.30 (one-proton quartet (J = 7 Hz) of quartets, J = 1.5 Hz, C=C**H**), 8.05 (quintet, 3, J = 1.5 Hz, CN_3CH_3), and 9.12 (three-proton doublet (J = 7 Hz) of quartets (J = 1.5 Hz), $CHCH_3$).

threo-**2-Azido-3-iodo-4-methylpentane** (**5b**) was prepared from *cis*-4-methyl-2-pentene in 95% yield: nmr ($CDCl_3$), τ 6.06 (t, 1 (J = 5.2 Hz), C**H**I), 6.58 (quintet, 1 (J = 6 Hz), CN_3**H**), 7.8–8.8 (m, *ca.* 1, $(CH_3)_2$C**H**), 8.62 (d, 3 (J = 6.6 Hz), CH_3-CHN_3), and 8.97 (d, 6 (J = 6.5 Hz), $(CH_3)_2$CH).

Anal. Calcd for $C_6H_{12}IN_3$: C, 28.47; H, 4.78. Found: C, 28.71; H, 4.75.

trans-**2-Azido-4-methyl-2-pentene** (**5c**) was prepared from *threo*-2-azido-3-iodo-4-methylpentane (**5b**) in 81% yield: nmr ($CDCl_3$), 5.45 (one-proton doublet (J = 9.0 Hz) of quartets (J = 1.0 Hz), C=C**H**), 7.0–7.8 (m, 1, $(CH_3)_2$C**H**), 8.07 (d, 3 (J = 1.0 Hz), CH_3C=C), and 9.08 (d, 6 (J = 6.6 Hz), $(CH_3)_2$CH).

cis-**2-Azido-2-butene** (**6c**) was prepared from *erythro*-2-azido-3-iodobutane (**6b**)[5] in 52% yield: nmr (CCl_4), τ 4.89 (one-proton quartet (J = 6.5 Hz) of quartets (J = 1.0 Hz), C=C**H**), 8.28 (m, 4.5), and 8.42 (q, 1.5 (J = 1.0 Hz)).

erythro-**3-Azido-4-iodohexane** (**7b**) was prepared from 3-hexene in quantitative yield: nmr (CCl_4), τ 5.95 (q, 1 (J = 6.5 Hz), C**H**I), 6.5–7.0 (m, 1, C**H**N_3), and 7.9–9.2 (m, 10).

Anal. Calcd for $C_6H_{12}IN_3$: C, 28.47; H, 4.78. Found: C, 28.54; H, 4.94.

cis-**3-Azido-3-hexene** (**7c**) was prepared from *erythro*-3-azido-4-iodohexane in 77% yield: nmr (CCl_4), τ 4.94 (t, 1 (J = 7.0 Hz), C=C**H**), 7.6–8.2 (m, 4), and 8.7–9.2 (m, 6).

erythro-**1-Azido-2-iodo-1-phenylpropane** (**8b**) was prepared from *trans* 1-phenyl-1-propene in quantitative yield: nmr (CCl_4), τ 5.30 (d, 1 (J = 6.0 Hz), C**H**N_3), 5.75 (quintet, 1 (J = 6.5 Hz), C**H**I), 8.17 (d, 3 (J = 6.5 Hz), CH_3), and 2.6–2.9 (m, five aromatic protons).

Anal. Calcd for $C_9H_{10}IN_3$: C, 37.63; H, 3.48. Found: C, 37.87; H, 3.31.

cis-**1-Azido-1-phenyl-1-propene** (**8c**) was prepared from *erythro* 1-azido-2-iodo-1-phenylpropane (**8b**) in 86% yield: nmr (CCl_4), τ 2.80 (s, five aromatic protons), 4.67 (q, 1 (J = 7.0 Hz), C=C**H**CH_3), and 8.35 (t, 3 (J = 7.0 Hz), $CHCH_3$).

erythro-**2-Azido-3-iodo-4,4-dimethyl-2-pentane** (**9b**) was prepared from *trans*-4,4-dimethyl-2-pentene (**9a**) in 87% yield: nmr ($CDCl_3$), τ 5.74 (d, 1 (J = 3 Hz), C**H**I), 6.75 (one-proton quartet (J = 6.5 Hz) of doublets (J = 3 Hz), C**H**N_3), 8.62 (d, 3 (J = 6.5 Hz), CH_3), and 8.85 (s, 9, $(CH_3)_3C$).

cis-**2-Azido-4,4-dimethyl-2-pentene** (**9c**) was prepared from *erythro*-2-azido-3-iodo-4,4-dimethyl pentane (**9b**) in 72% yield: nmr ($CDCl_3$), τ 4.89 (q, 1 (J = 1.0 Hz), C=CH), 8.15 (d, 3 (J = 1 Hz), CH_3), and 8.89 (s, 9, $(CH_3)_3C$).

Azido-3-methyl-1-butene (**14c and 15c**). The iodine azide adduct to 3-methyl-1-butene (**14a**) was obtained in 92% yield; nmr spectra indicated the presence of primary iodide and azide at τ 6.7, as well as of secondary iodide (τ 5.8) and azide (τ 6.3). Treatment with K-*t*-BuO at 0° gave azido olefin indicated by nmr integration to be a mixture of 36% **14c** and 64% **15c**: nmr ($CDCl_3$) for **14c**, τ 6.17 (d, J = 13.5 Hz), 6.7 (q, J = 13.5 and 6.5 Hz); for **15c**, τ 5.3 (d, J = 1.5 Hz), 5.43 (d, J = 1.5 Hz), and isopropyl group at 7.73 (septet) and 8.9 and 9.1 (two doublets).

Anal. Calcd for $C_5H_9N_3$: C, 54.03; H, 8.16. Found: C, 53.85; H, 8.17.

erythro-**Ethyl 2-iodo-3-azidobutanoate** (**10b**) was prepared from ethyl crotonate in 81% yield: nmr (CCl_4), τ 5.5–6.4 (m, 4) and 8.4–8.9 (m, 6).

cis-**Ethyl β-Azidocrotonate** (**10c**).—To 12.00 g of ethyl α-iodo-β-azidobutanoate (**10b**) was added 6.00 g of 1,4-diazabicyclo[2.2.2]octane in 120 ml of dry benzene. The reaction was allowed to stand at room temperature for 3 days. The reaction was then washed with 5% hydrochloric acid and dried with magnesium sulfate. Removal of the ether at reduced pressure produced 6.64 g of a yellow liquid. This was passed through *ca.* 80 g of aluminum oxide (Merck No. 71707) with petroleum ether (bp 40–60°) which gave, after removal of the solvent, 4.10 g of a pale yellow liquid (50%).

The nmr spectrum was identical with that previously reported.[8] The triphenylphosphine imine derivative was prepared as previously described, mp 135–136° (lit.[8] 135–135.5°).

Addition of IN_3 to Methyl Acrylate.—The adduct was prepared according to the general procedure in 86% yield. The nmr spectrum showed peaks at τ 5.4–6.6 (multiplet with strong singlet at 6.20).

The elimination of HI was carried out on 25.5 g of the adduct in 250 ml of acetone using 1,4-diazabicyclo[2.2.2]octane as a base at 5° for 16.5 hr. The mixture was then added to *ca.* 500 ml of water and 200 ml of a saturated salt solution. This was then extracted with ether. The ether extracts were combined and washed with water, 5% HCl solution, and again with water. The ethereal solution was dried. Removal of the solvent at reduced pressure gave 7.3 g (61%) of an orange liquid. The nmr spectrum showed this to be a 1:4 mixture of methyl β- and α-azido acrylates, respectively. To a dry column of 120 g of silica gel (grade 62, 60–200 mesh, Grace Davidson Chemical, Baltimore, Md.) was added 3.58 g of the above mixture. This was eluted with 10% v/v (150 ml), 20% (200 ml), 40% (200 ml), and 60% (200 ml) of methylene chloride in pentane. The first fractions (300 ml) gave 2.35 g of a pale yellow liquid which proved to be methyl α-azido acrylate (**13c**). This pale yellow liquid rapidly turned orange at room temperature. The nmr spectrum ($CDCl_3$) showed τ 4.17 (d, 1 (J = 1.6 Hz), C=CH),

(13) All melting points were determined on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer IR-21 spectrometer. Nuclear magnetic resonance spectra were recorded with either a Varian A-60 or A-60A spectrometer. Microanalyses were performed by either A. Bernhardt, Mülheim, Germany, or Galbraith Laboratories, Knoxville, Tenn. In nmr descriptions, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

(14) G. J. Matthews and A. Hassner, unpublished results.

4.65 (d, 1 (J = 1.6 Hz), C=CH), and 6.15 (s, 3, OCH_3). The ir spectrum showed strong broad bands at 2150 (N_3), 1745 (C=O), and 1625 cm^{-1} (C=C).

The following fractions (150 ml) of eluent produced 0.56 g of a pale yellow solid that proved to be methyl β-azido acrylate (**12c**). Recrystallization from pentane gave the analytical sample, mp 58–58.5° sublimes. The nmr spectrum ($CDCl_3$) showed peaks at τ 2.67 (d, 1 (J = 14 Hz), C=CH), 4.33 (d, 1 (J = 14 Hz), C=CH), and 6.25 (s, 3, OCH_3). The ir spectrum (KBr) showed absorptions at 2137 (N_3), 1715 (C=O), and 1631 cm^{-1} (C=C).

Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97. Found: C, 37.66; H, 3.87.

cis-**Methyl β-Azidocinnamate** (**11c**).—To 11.0 g of methyl *erythro*-3-azido-2-iodophenylpropionate[5] (**11b**) was added 100 ml of reagent acetone and 7.0 g of DABCO. The reaction mixture was kept at 5° for 38 hr and then 250 ml of H_2O was added. The mixture was extracted with ether. The ethereal extracts were combined and washed with H_2O followed by 5% HCl solution. The ethereal solution was dried with $MgSO_4$. Removal of the ether at reduced pressure gave 7.5 g of an orange liquid which slowly loses nitrogen. The nmr spectrum showed, in addition to absorptions due to methyl α-iodocinnamate,[4c] absorptions at τ 2.69 (s, five aromatic protons), 4.33 (s, 1, C=CH), and 3.47 (s, 3, OCH_3).

Pyrolysis of 7.2 g of the above orange liquid gave 6.7 g of 3-carbomethoxy-2-phenyl-1-azirine (**17**) and methyl α-iodocinnamate. (See ref 4c for a more complete description of this reaction.)

trans-**1-Azido-2-iodocyclopentane** (**18a**) was prepared from cyclopentene in 89% yield: nmr (CCl_4), τ 5.7–6.1 (m, 2, CHN_3—CHI) and 7.5–8.7 (m, 6).

3-Azidocyclopentene (**19a**) was prepared from *trans*-1-azido-2-iodocyclopentane (18a) in 82% yield as a colorless liquid: bp 85° (15 mm), *distillation exploded violently;* nmr (CCl_4), τ 3.8–4.4 (m, 2, CH=CH), 5.5–6.1 (m, 1, CHN_3), and 7.4–8.6 (m, 4).

Anal. Calcd for $C_5H_7N_3$: C, 55.03; H, 6.47. Found: C, 54.84; H, 6.53.

3-Azidocyclohexene (**19b**).—The elimination on **18b**[5] was carried out using potassium hydroxide in methanol and gave a 74% yield of a colorless liquid: nmr (CCl_4), τ 4.17 (four-proton quartet (J = *ca.* 9 Hz) of multiplets, CH=CH), 6.0–6.4 (m, 1, CHN_3), and 7.8–8.6 (m, 6).

Attempted Deuterium Exchange of 19b.—To 0.305 g of **19b** was added 2.888 g of acetone-d_6 and 0.330 g of a 25% NaOD–D_2O solution. The reaction mixture was refluxed for 5 days. The nmr spectrum was unchanged.

trans-**1-Azido-2-iodocyclooctane** (**20**) was prepared from *cis*-cyclooctene in 87% yield: nmr (CCl_4), τ 5.5–6.3 (m, 2, CHN_3—CHI) and 7.6–8.9 (m, 14).

Anal. Calcd for $C_8H_{14}IN_3$: C, 34.42; H, 5.05. Found: C, 35.56; H, 5.19.

1-Azidocyclooctene (**21**) was prepared from 1-azido-2-iodocyclooctane (**20**) in 80% yield: nmr (CCl_4), τ 4.77 (t, 1 (J = 8.5 Hz)) and 7.5–8.7 (m, 12).

3-Azido-4-iodocyclooctene (**22**) was prepared from 1,3-cyclooctadiene in 72% yield: nmr (CCl_4), τ 3.7–4.8 (m, 2, CH=CH), 5.2–6.1 (m, 2, CHN_3—CHI), and 7.4–8.9 (m, 8).

2-Azido-1,3-cyclooctadiene (**23**) was prepared from 3-azido-4-iodocyclooctene (**22**) in 50% yield: nmr (CCl_4), τ 3.8–4.4 (m, 3, vinylic protons), 4.68 (t, 1 (J = 7 Hz), CN_3=CH), and 7.5–8.9 (m, 8).

Anal. Calcd for $C_8H_{11}N_3$: C, 64.40; H, 7.43; Found: C, 65.90; H, 8.01.

1-Azido-2-iodotetralin (**24b**) was prepared from 1,2-dihydronaphthalene in 90% yield: mp 45–46°, from ethanol; nmr (CCl_4), τ 5.27 (d, 1 (J = 4 Hz), CHN_3), 2.82 (s, 4, aromatic protons), 5.54 (q, 1 (J = 4 Hz), CHI), 7.1–7.3 (m, 2), and 7.7–8.1 (m, 2).

Anal. Calcd for $C_{10}H_{10}N_3I$: C, 40.15; H, 3.37; N, 14.05. Found: C, 40.07; H, 3.62; N, 13.77.

1-Azido-3,4-dihydronaphthalene (**25b**) was prepared from 1-azido-2-iodotetralin (**24b**) in 70% yield: nmr (CCl_4), τ 2.2–3.1 (m, 4, aromatic protons), 4.43 (t, 1 (J = 4.5 Hz), C=CH), and 7.1–8.0 (m, 4).

1-Azido-2-iodoindan (**24a**) was prepared from indene in 76% yield: nmr, τ 2.6–2.8 (m, 4, aromatic protons), 4.99 (d, 1 (J = 5 Hz), CHN_3), 5.72 (q, 1 (J = 6 Hz), CHI), and 6.58 (t, 2 (J = 7 Hz)).

Anal. Calcd for $C_9H_8N_3I$: C, 37.92; H, 2.83. Found: C, 37.74; H, 2.92.

1-Azidoindene (**25a**) was prepared from 1-azido-2-iodoindan (**24a**). To 10.00 g of the iodo azide was added 100 ml of benzene and 5.00 g of 1,4-diazabicyclo[2.2.2]octane. The reaction was refluxed for 17.75 hr and then was washed with 5% hydrochloric acid. A polymeric solid formed which was removed by filtration through Celite. The benzene layer was washed again with 10% hydrochloric acid and dried with magnesium sulfate. The benzene was removed at reduced pressure. The residue was dissolved in pentane and decolorized with activated carbon. Removal of the pentane produced 3.48 g of a pale yellow liquid (83%): nmr (CCl_4), τ 2.77 (s, 5, aromatic protons), 4.15 (t, 1 (J = 2.5 Hz), C=CH), and 6.78 (d, 2 (J = 2.5 Hz), CH_2).

Registry No.—**1c,** 16717-64-9; **2b,** 16717-65-0; **2c,** 16717-661-1; **4c,** 16717-67-2; **5b,** 16717-68-3; **5c,** 16717-69-4; **6c,** 16717-70-7; **7b,** 16717-71-8; **7c,** 16717-72-9; **8b,** 16717-73-0; **8c,** 16717-74-1; **9b,** 16717-75-2; **9c,** 16717-76-3; **10b,** 16717-77-4; **12c,** 16717-78-5; **13c,** 16717-79-6; **14c,** 16717-80-9; **15c,** 16717-81-0; **18a,** 16717-82-1; **19a,** 16717-83-2; **19b,** 16717-84-3; **20,** 16717-85-4; **21,** 16719-52-1; **22,** 16719-53-2; **23,** 16719-54-3; **24a,** 16719-55-4; **24b,** 16719-56-5; **25a,** 16719-57-6; **25b,** 16719-58-7.

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