

Regiochemistry of Halogen Azide Addition to Allenes¹

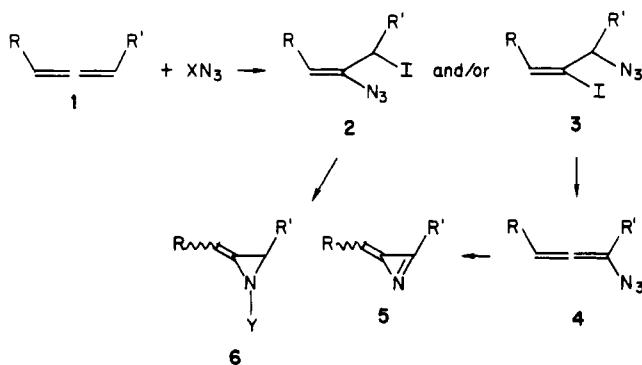
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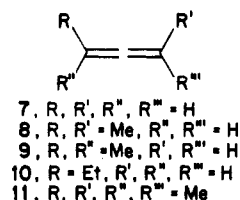
Iodine azide was found to undergo monoaddition to alkyl-substituted allenes 8-11, producing regioselectively allyl azides that can undergo [3,3]-rearrangement. Allene itself is an exception and adds IN_3 at room temperature to form a bisadduct, shown to have a *gem*-diazide structure and to be derived from a vinyl azide monoadduct. BrN_3 tends to behave as an ionic reagent analogous to IN_3 at -65°C , but at room temperature it adds to allenes in a free radical manner, leading to bisadducts which are unstable and can decompose explosively. The chemistry of the adducts was briefly explored.

Previous work in these laboratories has shown that halogen azides usually add regio- and stereoselectively to alkenes, leading to adducts that are useful precursors to many functional groups as well as to small and larger ring heterocycles.² A study of allene substrates with these reagents is of interest not only from the point of view of defining regiochemical and mechanistic factors³ governing such additions to cumulative double bonds but also as potential synthetic routes to methyleneazirines and methyleneaziridines.⁴ For instance, ionic addition of halogen azide XN_3 to allene 1, if analogous to Br_2 addition to this substrate,⁵ should lead to 2, which might be a precursor to allenic azide 4 and hence to methyleneazirine 5. On the other hand free radical addition of XN_3 to 1 could lead to 2, which as an allylic halide is expected to be converted by reduction or treatment with a phosphine⁶ to a methyleneaziridine 6. Since we have shown that IN_3 usually adds to olefins via a three-membered iodonium ion intermediate,⁷ while BrN_3 can add either in an ionic or a free radical fashion, the latter being favored by nonpolar solvents,^{2b} we decided to examine the behavior of these halogen azides toward some allenes.

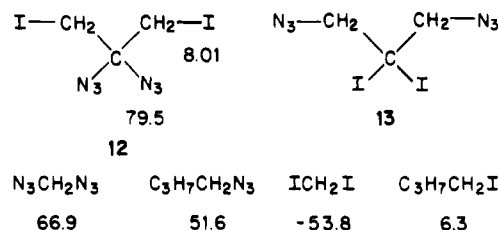


Allenes 7-11 were chosen as substrates in order to establish how alkyl substituents affect the regiochemistry

of addition. Allene itself (7) was found to react with IN_3 in acetonitrile at room temperature (ionic conditions) to produce 12, as a crystalline white solid in 60% yield. The



general structure as a 2:1 adduct (either 12 or 13 was evident from the mass spectrum, a strong azide band at 2140 cm^{-1} and an NMR H singlet at $\delta\ 3.65$. Mass spectrum fragmentation ($m/e\ 141$, $^+\text{CH}_2\text{I}$) and its lack of reactivity with base favor structure 12. Further corroboration was



provided by ^{13}C NMR and X-ray studies. The two methylene carbons appear at 8.01 ppm (higher intensity) while the quaternary carbon is found at 79.5 ppm, indicative of structure 12 but not of 13. Structure 12 is also consistent with ^{13}C values and substituent effects in azido and iodoalkanes^{8a} (see above).

X-ray diffraction data collected on 12, although insufficient for a complete structure assignment, due to the instability of 12 under X-ray irradiation, revealed an I-I intramolecular distance of 5.82 Å. This is in agreement with a 1,3-diiodo structure since geminal diiodo compounds have contact distances of approx. 3.56 Å.^{8b}

The formation of 12 in the presence of an excess of allene was surprising since electrophilic additions to allenes usually give only 1:1 adducts,⁹ unless forcing conditions are employed. The result can be rationalized, if a vinyl azide monoadduct 14 is formed first, because the azido function may be expected to activate the olefin to further attack by IN_3 . Indeed under milder reaction conditions (-30°C , 1 h, 20 mol excess of 7) a 1:1 adduct 14 was formed (ratio of 14-12 was 75:25). The large chemical shift difference between the vinyl protons in 14 (0.45 ppm) is

(1) Synthetic Methods. 21. For paper 20, see: Hassner, A.; Fibiger, R.; Andisik, D. *J. Org. Chem.* 1984, 49, 4237.

(2) (a) Hassner, A. *Acc. Chem. Res.* 1971, 4, 9. (b) Hassner, A.; Boerwinkle, F. *Tetrahedron Lett.* 1969, 3309. (c) Anderson, D. J.; Hassner, A. *Synthesis* 1975, 493. (d) Nair, V. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, Part 1, pp 215-332.

(3) (a) Stang, P. J. *Prog. Phys. Org. Chem.* 1973, 10, 205. (b) Smadja, W. *Chem. Rev.* 1983, 83, 263.

(4) (a) Burgess, E. M.; Sanchez, J. P. *J. Org. Chem.* 1974, 39, 940. (b) Bottini, A. T.; Roberts, J. D. *J. Am. Soc.* 1957, 79, 1462. (c) Bleiholder, R. F.; Schechter, H. *Ibid.* 1968, 90, 2131. (d) Quast, H.; Risler, W. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 414.

(5) (a) Peer, H. G. *Recl. Trav. Chim. Pays-Bas* 1962, 81, 113. (b) Taylor, D. R. *Chem. Rev.* 1967, 67, 317. (c) Caserio, M. C. In *Selective Organic Transformation*; Thyagarajan, B. S., ed.; Wiley: New York, 1970; Vol. 1, pp 239-299.

(6) Hassner, A.; Galle, J. E. *J. Am. Chem. Soc.* 1970, 92, 3733.

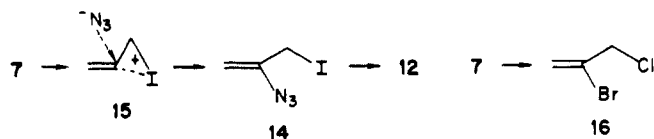
(7) Hassner, A.; Boerwinkle, F.; Levy, A. B. *J. Am. Chem. Soc.* 1970, 92, 4879.

(8) (a) The effect of increasing iodine substitution on the same carbon atom is upfield, namely, opposite to that shown by most other atoms: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C -NMR Spectroscopie*; G. Thieme Verlag: Stuttgart, 1984; p 150. (b) Bjorwatten, T. *Acta Chem. Scand.* 1962, 16, 749; 1963, 16, 2292.

(9) Banks, R.; Raseldine, R.; Taylor, D. *J. Chem. Soc.* 1965, 978.

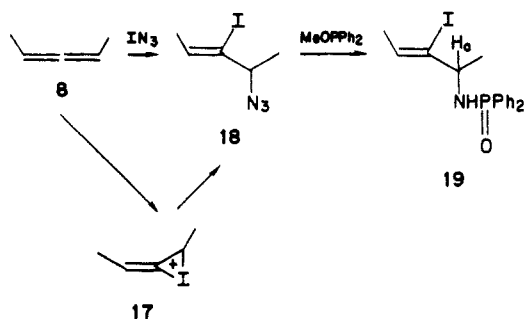
consistent with the vinyl azide structure, since deshielding of a cis proton (by ca. 0.4 ppm) is a known phenomenon in vinyl azides.¹⁰ Indeed, 14 was converted to 12 in the presence of IN_3 .

The regiochemistry of addition of IN_3 to allene 7, although in consonance with protonation of 7,¹¹ is unexpected in view of the fact that BrCl adds⁵ in a different regiochemical sense to give 16 (assuming ionic addition via three-membered ring halonium ions in both cases). Ad-

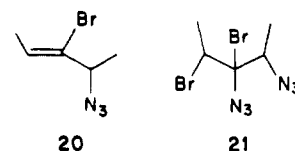


dition of bromine to substituted allenes has been shown to proceed through a bridged ion, by employing an optically active substrate.⁵ Possibly due to the good nucleophilicity of the azide ion the transition state for IN_3 addition to the unsubstituted allene 7 resembles 15. Unfortunately, a comparison with free radical addition of BrN_3 to 7 was not possible because no addition occurred in the reaction of BrN_3 with allene in pentane at -65°C and at room temperature an unstable oil resulted which decomposed too rapidly to obtain structural data.

The symmetrically substituted 2,3-pentadiene 8 reacted readily with IN_3 in acetonitrile to give exclusively 3-iodo-4-azido-2-pentene 18 in 80% yield after chromatography on silica gel. Its general structure was apparent from mass spectra (m/e 195), IR, and NMR data. The regiochemistry, that is placement of the azido function on the saturated carbon, was also established by conversion of 18 with diphenylmethoxyphosphine to the phosphoramidate 19. The latter exhibited three-bond P-H_α coupling of 9.5 Hz after exchanging the N-H proton with D_2O and irradiating the methyl protons at 1.25 ppm. Four-bond P-H coupling as found in a regioisomer of 19 is expected to be only 2-3 Hz.¹² Ring closure to a phosphorylated methylene aziridine⁶ had not occurred presumably because the iodo function is vinylic. The regiochemistry of 18 indicates that the additional alkyl substituent on the three-membered iodonium ion 17 (compared to 15) favors opening at the sp^3 carbon.

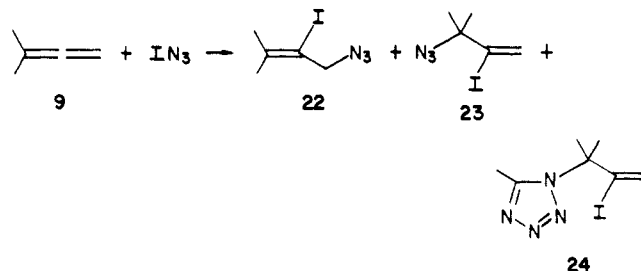


Addition of BrN_3 to 8 at -65°C either in pentane or dichloromethane led, apparently via an ionic addition, to 3-bromo-4-azido-2-pentene 20, the bromo analogue of 18, as evidenced by IR, NMR, and mass spectrum data. However, when BrN_3 in pentane was allowed to react at 20°C with 2,3-pentadiene an unstable product resulted which evolved gas rapidly in solution and exploded when the solution was concentrated. We tentatively assign structure 21 to this unstable adduct, on the assumption

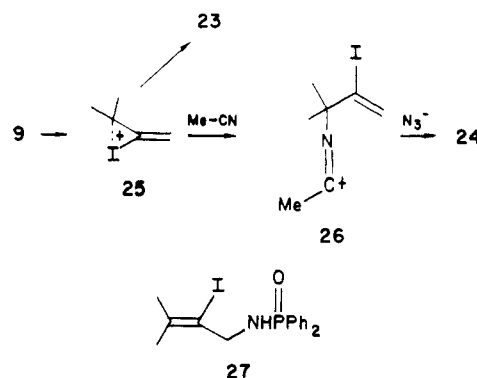


that a free radical addition of BrN_3 to 8 had taken place (see below) and because a number of vicinal diazides have previously reported to be explosive or unstable,¹³ while we find geminal and 1,3-diazides not to have such properties.

The geminally dimethylated allene 9 reacted with IN_3 in acetonitrile to produce three products of which the terminal azide 22 was the major product (ratio of 22-23-24 was 8:1:1). Formation of tetrazole 24 is the result of attack by acetonitrile on iodonium ion intermediate 25 followed by capture of the resulting nitrilium species 26 by azide ion. Tetrazole formation has previously been observed and can be anticipated when very stable carbenium ions (e.g., tertiary) can be intermediates in XN_3 additions.¹⁴ After



separation of the tetrazole 24, the remaining mixture of allyl azides 22 and 23 (in a ratio of 85:15) was heated to 70°C for 5 min in deuteriochloroform, which caused an isomerization to a 95:5 ratio of the two isomers. Separation of chromatography afforded pure 22, which was converted into the phosphoramidate 27 by reaction with MeOPPh_2 . The latter again showed three-bond P-H coupling of 8.5 Hz in agreement with the assigned structure. In view of the known facile [3,3]-rearrangement of allyl azides¹⁵ favoring the isomer with the more substituted double bond it seems reasonable that in addition to 24, the primary product of IN_3 addition to 9 is either 23 or contains a large proportion of this allyl azide and that during the course of the reaction 23 undergoes allylic rearrangement to 22. The regiochemistry of 23 is consistent with a three-membered ring^{16a} iodonium ion intermediate 25 and is analogous to INCO and $\text{Hg}(\text{OAc})_2$ additions to 9,¹⁶ although an iodoallyl cation cannot be excluded.



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(11) Jacobs, T. L. *J. Am. Chem. Soc.* 1960, 82, 6397.

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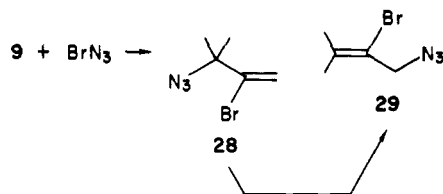
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(14) Mehta, G. *Tetrahedron Lett.* 1975, 445. Hassner, A.; Matthews, G., unpublished results.

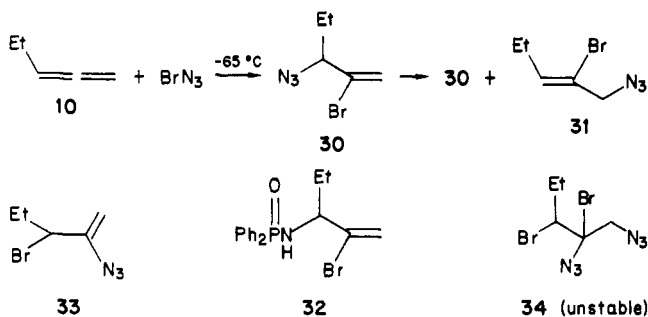
(15) (a) Winstein, S.; Gagneux, A.; Young, W. *J. Am. Chem. Soc.* 1960, 82, 5946. (b) Hassner, A.; Teeter, S. *J. Org. Chem.* 1971, 36, 2176.

(16) (a) Okuyama, T.; Ohashu, K.; Izawa, K.; Fueno, T. *J. Org. Chem.* 1974, 39, 2255. (b) Greibrokk, T. *Acta Chem. Scand.* 1973, 27, 3368. (c) Walters, W. L.; Kiefer, E. F. *J. Am. Chem. Soc.* 1967, 89, 6261.

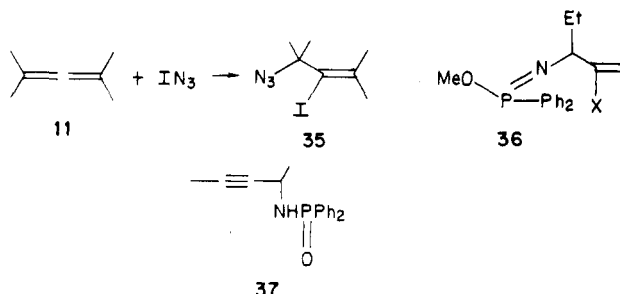
Bromine azide addition to 3-methyl-1,2-butadiene (**9**) at -65°C yielded a 45:55 mixture of 2-bromo-3-azido-3-methyl-1-butene (**28**) and 1-azido-2-bromo-3-methyl-2-butene (**29**) as determined by NMR. Heating of this mixture at 70°C in CDCl_3 for 20 min caused isomerization to a 5:95 mixture of **28**–**29**. This is completely analogous to the behavior of the iodo azides **23** and **22** and suggest again an ionic path for BrN_3 addition at -65°C .



Addition of BrN_3 to 1,2-pentadiene (**10**) at -65°C led almost exclusively to attack on the more substituted double bond in what amounts to ionic addition of BrN_3 to afford 3-azido-2-bromo-1-pentene (**30**). The latter **30** was converted to the phosphoramidate **32** with methoxydiphenylphosphine. Heating of **30** at 70°C led to a 33:67 mixture of **30** and **31**, an allyl azide equilibration analogous to that shown by adducts **23** and **28**. On the other hand addition of BrN_3 to **10** at room temperature provided an unstable oil that readily decomposed, and according to its NMR and IR spectra appears to be vicinal diazide **34**. Free radical additions to allene show a preference for radical attack at the central carbon.¹⁷ With BrN_3 such reactions may proceed by N_3^{\cdot} attack via **33**. Apparently, the resulting vicinal diazides decompose at room temperature.



Tetramethylallene **11** reacted readily with IN_3 at room temperature and led to isolation of adduct **35** in 70% yield after chromatography; no tetrazole formation was observed in this case.



When the XN_3 -allene adducts **18**, **22**, and **30** were treated with methoxydiphenylphosphine under exclusion of moisture the phosphine imines (e.g., **36**) formed could not be induced to cyclize to methyleneaziridines even by prolonged heating in refluxing toluene or by addition of catalytic amounts of iodide. Instead conversion to phos-

phoramidates **19**, **27**, and **32** was carried out in wet ether. On the other hand, treatment of **19** with potassium *tert*-butoxide in THF at reflux led to acetylene **37**. The same product was obtained with sodium amide in liquid ammonia. Since it has been shown¹⁸ that anti elimination of hydrogen halide from a vinyl halide to give an acetylene is much faster than syn elimination, we tentatively assign the *Z* stereochemistry (H and I trans on the olefinic bond) to **19** and hence to adduct **18**.¹⁹

In conclusion IN_3 and BrN_3 were shown to undergo addition to allenes. Ionic addition of IN_3 to alkyl-substituted allenes proceeds regioselectively favoring formation of an allyl azide, which can undergo [3,3]-rearrangement. Allene itself is an exception in that it adds IN_3 to form a vinyl azide and hence a bisadduct. BrN_3 tends to behave as an ionic reagent in additions to allenes at -65°C , but at room temperature it adds as a free radical reagent leading to bisadducts which are unstable at room temperature and can decompose explosively.

Experimental Section

Melting points (Fisher-Johnsblock) are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 457 instrument. NMR spectra were recorded on a Varian EM-360 or HA-100 spectrometer with Me_4Si as internal standard. Due to the lability of the iodo function and the instability of vicinal diazides and vinyl azides elemental analysis was not always possible. All recorded analysis were performed by Atlantic Microlab, Inc., Atlanta, GA. Mass spectra were recorded on a Varian M.A.T. CH-5 instrument. Skelly F refers to petroleum ether with bp 35–60 $^{\circ}\text{C}$; skelly B refers to petroleum ether with bp 60–90 $^{\circ}\text{C}$.

1,3-Diiodo-2,2-diazidopropane (12). Allene (8 g, 200 mmol) dissolved in acetonitrile (600 mL) was added to solution of IN_3 ¹⁰ (20 mmol) in CH_3CN at 20°C . The reactants were allowed to stir overnight and then worked up in the normal fashion.¹⁰ After removal of solvent in vacuo 2.64 g of a red oil was obtained. This oil was dissolved in cyclohexane (75 mL) at reflux and upon standing at room temperature deposited white crystals. Recrystallization from skelly B produced needles, mp 41–42 $^{\circ}\text{C}$: ^1H NMR (CDCl_3) δ 3.65 (s); ^{13}C NMR 8.01, 79.05 ppm; IR (CCl_4) 2140 cm^{-1} ; mass spectrum, *m/e* (relative intensity) 378 (M^+ , 4.5), 336 (60.2), 237 (21.5), 181 (100), 141 (95), 127 (98.1). Anal. Calcd for $\text{C}_3\text{H}_4\text{N}_6\text{I}_2$: C, 9.52; H, 1.05; I, 67.95. Found: C, 9.60; H, 1.15; I, 67.29. X-ray diffraction data on **12** indicate an I–I intramolecular distance of 5.82 Å.

Reaction of Allene with IN_3 at -30°C . Allene (20 g, 0.5 mol) in 50 mL of acetonitrile at -30°C was added to a solution of IN_3 (0.025 mol) at -30°C , and the reaction was allowed to proceed for 1 h. Normal workup followed by chromatography on neutral alumina (skelly F) yielded a mixture (1.5 g) of 1,3-diiodo-2,2-diazidopropane (**12**) and 2-azido-3-iodopropene (**14**) in a ratio of 1:3 by NMR: ^1H NMR (CDCl_3) δ [**12**] 3.65 (s), [**14**] 4.05 (s, 2), 6.0 (br s, 1), 6.45 (d, $J = 0.5$ Hz, 1); IR 2140 cm^{-1} . This mixture was converted to **12** upon further reaction with IN_3 .

Reaction of 2,3-Pentadiene with IN_3 . The diene **8** (1.36 g, 20 mmol) was dissolved in 100 mL of acetonitrile and then added to a prepared slurry of IN_3 and NaN_3 (20 mmol) in acetonitrile.¹⁰ The reaction was allowed to proceed for 4 h followed by workup to give 3.6 g of a pale yellow oil identified as **18**: IR (CCl_4) 2140 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.4 (d, $J = 7$ Hz, 3), 1.85 (d, $J = 7$ Hz, 3), 3.85 (q, $J = 7$ Hz, 1), 5.95 (q, $J = 7$ Hz, 1).

Reaction of **18 with Methoxydiphenylphosphine.** To a solution of **18** (2.0 g) in wet ether (100 mL) at 25°C was added the phosphine (2.17 g). Boiling chips were added to facilitate gas

(18) Staley, S.; Doherty, R. *Chem. Commun.* 1969, 288.

(19) Iodophosphoramidate **27** remained unchanged on treatment with NaNH_2 in liquid ammonia or with KH or potassium *tert*-butoxide. The failure to eliminate HI to form an allenic phosphoramidate may be due to reluctance for abstraction of the α -proton after the more acidic NH was removed to create an amidate ion. Attempts to prepare allenic azides of type **4** have so far likewise been unsuccessful; thus treatment of **18** with potassium *tert*-butoxide or of **22** with LDA gave only starting iodo azide and unidentified tarry material.

(17) Jacobs, T. L.; Illingworth, G. E. *J. Org. Chem.* 1963, 28, 2692. Taylor, D. R. *Chem. Rev.* 1967, 67, 317.

evolution. After 4 h, gas evolution had ceased, and the solvent was removed in vacuo, yielding 3.6 g of a yellow oil. The oil was dissolved in CH_2Cl_2 and pentane was added to precipitate a white solid identified as **19**, recrystallized twice from skelly B- CHCl_3 (8:2), mp 134–135 °C: $^1\text{H NMR}$ (CDCl_3) δ 1.25 (d, $J = 6$ Hz, 3), 2.9–3.8 (m, 2) [one proton exchanges with D_2O], 5.5 (q, $J = 6$ Hz, 1), 7.3–8.2 (m, 10); mass spectrum, m/e 411 (M^+), 396, 284, 245. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{INOP}$: C, 49.60; H, 4.62; N, 3.40. Found: C, 49.58; H, 4.62; N, 3.42.

Reaction of BrN_3 with 2,3-Pentadiene (8) at -65 °C. 2,3-Pentadiene (0.85 g, 12.5 mmol) was dissolved in 50 mL of pentane and cooled to -65 °C. To this solution was added BrN_3 (12.5 mmol) prepared at 25 °C in 100 mL of pentane.⁷ The reaction was allowed to proceed for 30 min, and after workup, the solvent was removed in vacuo to yield 1.8 g of a yellow oil identified as 3-bromo-4-azido-2-pentene (**20**): IR 2140 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.42 (d), 1.9 (d).

Reaction of 2,3-Pentadiene with BrN_3 at 20 °C. 2,3-Pentadiene (1.36 g, 20 mmol) was dissolved in pentane (100 mL), and to this solution was added BrN_3 (20 mmol) previously prepared in pentane (100 mL). Reaction was allowed to proceed until all color had been discharged. The solvent was then removed in vacuo to yield a yellow oil. This oil immediately began to evolve gas (N_2), and within a short time complete decomposition had occurred: IR (CCl_4) 2130 cm^{-1} . $^1\text{H NMR}$ was difficult to obtain (due to rapid decomposition in the tube); However, a rapid scan in CCl_4 indicated no vinyl protons and broad aliphatic absorptions.

Reaction of 3-Methyl-1,2-butadiene (9) with IN_3 . 3-Methyl-1,2-butadiene (2.04 g, 30 mmol) was added to an acetonitrile solution (150 mL) of IN_3 (30 mmol). The reaction was allowed to proceed for 10 h, after which time the reaction mixture was worked up in the normal fashion. The resulting oil (5.5 g) was dissolved in dichloromethane and skelly F was added to precipitate a white solid (0.52 g) identified as the tetrazole **24**: $^1\text{H NMR}$ (CDCl_3) δ 2.1 (s, 6), 2.74 (s, 3), 6.28 (d, $J = 2.5$ Hz, 1) 6.6 (d, $J = 2$ Hz, 1); m/e 278 (M^+). Anal. Calcd for $\text{C}_7\text{H}_{11}\text{IN}_4$: C, 30.21; H, 3.95; N, 20.14. Found: C, 30.30; H, 4.02; N, 20.04.

The filtrate from above was examined by NMR and was shown to be an 85:15 mixture of **22** and **23**, respectively. Heating this mixture for 5–10 min at 70 °C (CDCl_3) resulted in conversion to a 95:5 mixture of **22** and **23**, which on separation by preparative-layer chromatography on alumina (9:1 skelly F-ether) furnished 1-azido-2-iodo-3-methyl-2-butene (**22**) [$^1\text{H NMR}$ (CDCl_3) δ 1.85 (s, 3), 1.8 (s, 3), 3.2 (s, 2)] and 2-iodo-3-azido-3-methyl-1-butene (**23**) (lower R_f) [$^1\text{H NMR}$ (CDCl_3) δ 1.4 (s, 6), 5.85 (d, $J = 2$ Hz, 1), 5.5 (d, $J = 2$ Hz, 1)].

Reaction of 3-Methyl-1,2-butadiene (9) with BrN_3 at -65 °C. 3-Methyl-1,2-butadiene (1.7 g, 25 mmol) was dissolved in 100 mL of pentane and cooled to -78 °C. To this solution was added a solution of BrN_3 (25 mmol) prepared at 20 °C in 100 mL of pentane. The reaction was allowed to proceed for 1 h at -65 °C, and the solvent was removed in vacuo, yielding 5.1 g of a yellow oil: IR 2140 cm^{-1} . NMR indicated a 45:55 mixture of 2-bromo-3-azido-3-methyl-1-butene (**28**) and 1-azido-2-bromo-3-methyl-2-butene (**29**): $^1\text{H NMR}$ (CDCl_3) δ [28] 1.5 (s, 6), 5.95 (d, $J = 2$ Hz, 1), [29] 1.95 (s, 3), 1.98 (s, 3), 4.25 (s, 2). By heating at 70 °C in CDCl_3 for 20 min this mixture was converted to a 95:5 mixture of **29** and **28**, respectively.

Reaction of 1-Azido-2-iodo-3-methyl-2-butene (22) with Methoxydiphenylphosphine To Give 27. The iodine azide adduct **22** (2.0 g) was dissolved in wet ether (100 mL) and to this solution was added dropwise 2.2 g of methoxydiphenylphosphine until the evolution of gas had ceased. The solution was allowed to sit for an additional hour at 25 °C, and then the solvent was removed in vacuo, resulting in a yellow oil. This oil was dissolved in dichloromethane and skelly F was added to precipitate **27** as a white solid (2.52 g, 73.5%), recrystallized twice from acetone-skelly B (3:7), mp 128–130 °C: $^1\text{H NMR}$ (CDCl_3) δ 1.55 (s, 3), 1.85 (s, 3), 3.7–3.9 (m, 2), 3.2–3.65 (m, 1) [exchanges with D_2O], 2.5–1.8 (m, 10); mass spectrum, m/e (relative intensity) 411 (M^+), (3.5), 384 (92), 283 (98), 215 (50), 201 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{INOP}$: C, 49.60; H, 4.62; N, 3.40. Found: C, 49.60; H, 4.80; N, 3.45.

Reaction of 1,2-Pentadiene (10) with BrN_3 at -65 °C. A pentane solution of BrN_3 (25 mmol) was added to a solution of

1,2-pentadiene (1.5 g, 22 mmol) at -65 °C in 100 mL of pentane. Complete discharge of color occurred within 25 min. The resulting solution was warmed to room temperature, and the solvent was removed in vacuo. The resulting oil (3.9 g) was purified by passage over Woelm neutral alumina (skelly F) and was identified as 2-bromo-3-azido-1-pentene (**30**): $^1\text{H NMR}$ (CDCl_3) δ 1.9 (t, $J = 6$ Hz, 3), 1.7 (m, 2), 3.75 (t, $J = 8$ Hz, 1), 5.6 (s, 1), 5.85 (s, 1); IR (CCl_4) 2135, 910 cm^{-1} ; mass spectrum, m/e (relative intensity) 189 (M^+ , 40), 191 (40), 147 (70), 149 (70).

Isomerization of 30. The bromine azide adduct **30** (0.2 g) was dissolved in CDCl_3 and placed in a 3-mm NMR tube. The tube was sealed and placed in a water bath at 70 °C. After 1 day, no further change in the NMR spectra was observed, resulting in a 67:33 ratio of 1-azido-2-bromo-2-pentene (**31**) to 2-bromo-2-azido-1-pentene (**30**): $^1\text{H NMR}$ (CDCl_3) δ [31] 1.1 (t, $J = 8$ Hz, 3), 2.25 (q, d, $J = 8$ Hz, 2), 4.05 (s, 2), 6.1 (t, $J = 8$ Hz, 1).

Reaction of 2-Bromo-3-azido-1-pentene (30) with Methoxydiphenylphosphine. To a solution of the bromine azide adduct **30** (1.0 g) in wet ether (100 mL) was added 1.09 g of methoxydiphenylphosphine. After 4 h at 25 °C all gas evolution had ceased, and the solvent was removed in vacuo, yielding 1.6 g of a yellow oil. The oil was dissolved in dichloromethane (20 mL) and pentane was added to precipitate **32** as a white solid. Recrystallization from skelly B- CHCl_3 (6:4) gave an analytical sample of **32**, mp 121–122 °C: $^1\text{H NMR}$ (CDCl_3) δ 1.9 (t, $J = 7$ Hz, 3) 1.8 (q, $J = 7$ Hz, 2), 3.1–3.7 (m, 2), 5.5 (dd, $J = 2$ Hz, 2), 8.3–9.2 (m, 10); mass spectrum, m/e (relative intensity) 363 (M^+ , 11.8), 334 (18.6), 284 (29), 201 (199), 155 (13.8), 77 (72.8), 51 (33). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{BrNOP}$: C, 56.10; H, 5.23; N, 3.84. Found: C, 56.02; H, 5.27; N, 3.82.

Reaction of 1,2-Pentadiene (10) with BrN_3 at 20 °C. 1,2-Pentadiene (2 g, 29 mmol) dissolved in 150 mL of pentane was added to a solution of BrN_3 (29 mmol) in pentane at 20 °C. The reaction was allowed to proceed for 20 min, and then the solvent was removed in vacuo but replaced by CCl_4 . Slow evolution of gas was observed to occur and rapid evolution soon followed, which ultimately led to detonation in an NMR tube. However, by keeping the solution very dilute it was possible to obtain a spectrum of **34**: $^1\text{H NMR}$ (CCl_4) δ 1.1 (t, $J = 7$ Hz, 3), 1.8 (m, 3), 4.2 (s, 2); IR (CCl_4) 2120 cm^{-1} .

Reaction of Tetramethylallene (11) with Iodine Azide. Tetramethylallene (1.92 g, 20 mmol) dissolved in acetonitrile (100 mL) was added to a prepared slurry of iodine azide (20 mmol) in acetonitrile. The reaction was allowed to proceed for 5 h, and then the reaction was worked up in the normal fashion to give 4.2 g of a yellow oil identified as **35**. Chromatography on silica with pentane gave 3.7 g (70%) of pure **35** as an oil: $^1\text{H NMR}$ (CDCl_3) δ 1.55 (s, 6), 2.11 (s, 3), 2.28 (s, 3); IR (CCl_4) 2140 cm^{-1} .

Reaction of 18 with Sodium Amide in Liquid Ammonia. Formation of *N*-[2-(3-Pentynyl)]diphenylphosphonamide (37). Iodo azide **18** (1.0 g, 2.5 mmol) was added to a suspension of sodium amide (3.0 mmol) in liquid ammonia at -78 °C. The reaction was then allowed to proceed for 5 h after which time 0.3 g of ammonium chloride was added. The reaction mixture was poured into 250 mL of ether, the ether was washed with water (2 \times 50 mL), dried, and removed in vacuum to give 0.5 g of a pale yellow oil. This oil was dissolved in skelly B-acetone (2:1) from which white crystals were deposited (0.3 g, 25%) identified as the acetylene **37**; mp 82–84 °C; $^1\text{H NMR}$ (CDCl_3) δ 1.5 (d, $J = 6$ Hz, 3), 1.75 (d, $J = 2$ Hz, 3), 3.15 (m, 1) [exchanges with D_2O], 4.0 (m, 1), 7.4–7.6 (m, 10); IR (CCl_4) 3350, 2250 cm^{-1} ; mass spectrum m/e (relative intensity) 283 (M^+ , 65), 268 (70), 201 (100), 97 (50). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{PNO}$: C, 72.08; H, 6.36; N, 4.94. Found: C, 71.93; H, 6.44; N, 4.92.

Under the same conditions 90% of the iodo azide **22** was recovered unchanged.

Registry No. 8, 591-96-8; 9, 598-25-4; 10, 591-95-7; 11, 1000-87-9; 12, 102586-55-0; 14, 102586-56-1; 18, 102586-57-2; 19, 102586-58-3; 20, 102586-59-4; 22, 102586-60-7; 23, 102586-61-8; 24, 102613-56-9; 27, 102586-64-1; 28, 102586-62-9; 29, 102586-63-0; 30, 102586-65-2; 31, 102586-66-3; 32, 102586-67-4; 33, 102586-68-5; 35, 102586-69-6; 37, 102586-70-9; MeOP(Ph)₂, 4020-99-9; IN_3 , 14696-82-3; BrN_3 , 13973-87-0; allene, 463-49-0.