run compared to the scatter observed in the mass spectral analyses indicated that the latter method was more precise. The differences between the overall averages for the mass spectral and nmr data are, however, well within experimental accuracy: the results are summarized in Table I.

Phenylacetylene-d_1. In a 100-ml round-bottomed flask equipped with stirring bar and reflux condenser was placed 22.0 g of phenylacetylene and a suspension of 3 g of calcium oxide in 20 ml of deuterium oxide. The material was stirred for 24 hr at 40°. The organic layer was decanted, the aqueous suspension was extracted with ether, the combined organic phases were dried over magnesium sulfate and filtered, and the ether was removed under vacuum. Analysis by nmr spectroscopy indicated that the material was 85% d_1. The exchange was repeated and the phenylacetylene was distilled to give 20.4 g (93% recovery) of 97–98% d_1 material.

***cis*-β-Deuteriostyrene.** A 500-ml three-necked round-bottomed oven-dried flask was fitted with reflux condenser, addition funnel, magnetic stirring bar, nitrogen inlet, and thermometer. The flask was flushed with dry nitrogen and kept under a nitrogen atmosphere during the reaction. A mixture of 100 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride), 37.4 g (0.535 mol) of 2-methyl-2-butene (Aldrich, distilled), and 6.82 g (0.180 mol) of sodium borohydride was placed in the flask and cooled to 0° in a Dry Ice–isopropyl alcohol bath. A mixture of 38.0 g (0.244 mol) of freshly distilled boron trifluoride etherate in 40 ml of tetrahydrofuran was added over a period of 1.5 hr while the reaction temperature was held at 0°. The mixture was stirred for 2 hr at 0°, and then 22.7 g (0.222 mol) of freshly distilled phenylacetylene-d_1 (97–98% deuterated) in 20 ml of tetrahydrofuran was added as rapidly as possible while keeping the temperature between 0 and 5°. The mixture was allowed to warm to room temperature and stirred for 1 additional hr; the excess hydride was decomposed with a few milliliters of ethylene glycol. After dropwise addition of 50 ml of glacial acetic acid, the mixture was stirred overnight and poured into 200 ml of ice water. The organic layer was separated, washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled, employing a trace of Dow Antiform A and a 12 cm Vigreux column. The crude product was redistilled to give 5.9 g (26%) of *cis*-β-deuteriostyrene, bp 52–53° (30 mm), 95–96% isotropic purity by 100-MHz nmr.

2,2,3-Triphenylcyclobutanol. In a three-necked, round-bottomed flask equipped with magnetic stirring bar, reflux condenser with drying tube, and addition funnel was placed 0.10 g (2.6 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether. A solution of 1.0 g (3.3 mmol) of 2,2,3-triphenylcyclobutanone in 100 ml of anhydrous ether was added dropwise to the stirred suspension. The mixture was heated under reflux with stirring for 20 hr and decomposed by the addition, in succession, of 0.1 ml of aqueous 10% sodium hydroxide and 0.3 ml of water. The solids were removed by filtration and washed with several portions of ether. The combined organic materials were dried over magnesium sulfate, filtered, and concentrated under vacuum. Three recrystallizations of the crude material (0.90 g, 90%) gave white crystals, mp 100–101°, from petroleum ether (bp 60–69°).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.16; H, 6.72.

The nmr spectrum of the alcohol exhibited absorptions at τ 2.4–3.2 (m, 15 H), 5.2 (d, 1 H), 6.05 (d of d, 1 H), 6.9–7.5 (m, 2 H), and 2.4 (broad s, 1 H). The absorption at τ 2.4 ppm disappeared when the deuteriochloroform solution of the adduct was shaken with deuterium oxide. The detailed analysis of the nmr spectrum is given in the discussion.

The relative alcohol, 2,2,3-triphenylcyclobutanol-1-*d*, was prepared in an identical manner but substituting lithium aluminum deuteride for lithium aluminum hydride.

A recent paper[49] gives mp 144–146° from methanol for the undeuterated alcohol.

(49) R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391 (1969). The five following articles by Huisgen and coworkers contain additional material on diphenylketene cycloadditions.

Stereochemistry of Halogen Azide Additions to Olefins. The Stability of Three-Membered Iodonium *vs.* Bromonium Ions[1]

Alfred Hassner, Fred P. Boerwinkle, and Alan B. Levy

Contribution from the University of Colorado, Department of Chemistry, Boulder, Colorado 80302. *Received October 18, 1969*

Abstract: The reaction of iodine azide and bromine azide with olefins in polar solvents was studied with a view toward the stereochemistry of the addition. Specifically, *cis*-β-deuteriostyrene (**6**) was used as a substrate to elucidate the properties of three-membered ring iodonium and bromonium ion intermediates. Thus, addition of IN_3 proceeded stereospecifically to **6** as evidenced by the exclusive formation of α-azido-*trans*-β-deuteriostyrene **10** on elimination of HI from the adduct. Though stereospecific *anti* addition of bromine azide was observed with *cis*- and *trans*-2-butene as well as with 2-cholestene, BrN_3 addition to **6** led to a 1:1 mixture of *cis*- and *trans*-α-azido-β-deuteriostyrene, indicating the involvement of a benzylic cation. The free-radical addition of BrN_3 to **6** indicates the reaction to be stereorandom and hence to involve no bridging of the intermediate radical by the azide group.

The addition of iodine azide (IN_3) to unsaturated compounds has been shown to be a highly regioselective[2] as well as stereoselective method of introduction of azide functions into organic molecules.[3] This selectivity has been explained in terms of the formation of the three-membered ring halonium ion intermediate which is opened regiospecifically and from the backside by azide ions. With phenyl-substituted olefins **1** opening of the iodonium ion always occurs at the benzylic carbon suggesting the possibility that equilibration of **2** with an open benzyl cation **3** may be occurring. Whereas iodonium ion **2** would be opened with inversion to the *erythro* isomer of **4**, carbonium ion **3** could become planar and convert to **5** by rotation, in which case a mixture of diastereomers should result.

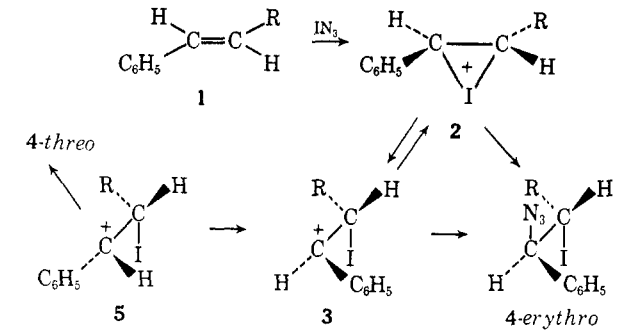
The *anti*[4] stereochemistry observed in IN_3 additions to β-substituted styrenes[3] can be explained as proceeding

(1) (a) Stereochemistry. LIII. For the preceding paper in the series see A. Hassner, *Intra-Sci. Chem. Rep.*, **4**, in press; (b) presented in part before the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968, Paper P-81.

(2) *Regio* is used to denote directive effects in bond making or breaking: A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

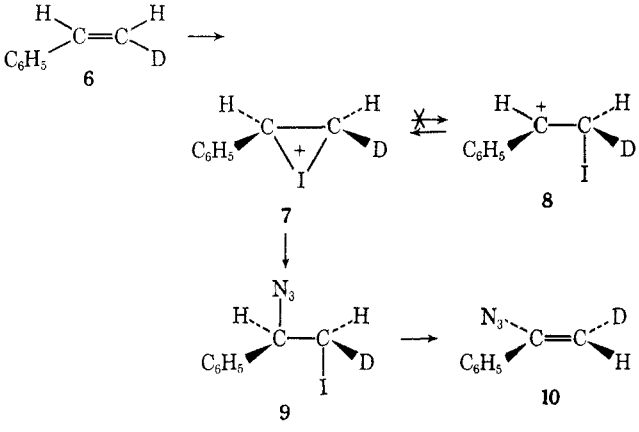
(3) (a) F. W. Fowler, A. Hassner and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); (b) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

(4) We prefer to use *cis* and *trans* for configurational assignments and *syn* and *anti* describing transformations during chemical processes.



through ion **2**, but it is also possible to attribute this specificity to hindrance of free rotation by the R group in an intermediate such as **3**. This work describes the influence of substituents on the stability and opening of three-membered iodonium and bromonium ion intermediates.

Iodonium Ions. To minimize steric inhibition to free rotation in a carbonium ion such as **3**, we chose β-deuteriostyrene as a substrate. We considered the *cis*-isomer **6** more appropriate than *trans*-β-deuteriostyrene since any resulting ion **8** might have a propensity to produce the more stable *erythro* adduct, while **7** would lead solely to the *threo* compound **9**. Olefin **6** was prepared from phenylacetylene by deuteration and reduction with disiamylborane in a modification of the reported procedure.[5] The styrene **6** contained 85% deuterium as determined by nmr.



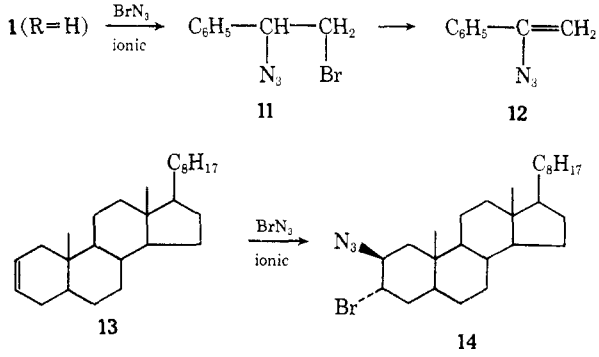
Iodine azide was added to **6** under conditions previously reported[3] to favor *anti* addition to olefins. Elimination from **9** with potassium *t*-butoxide in ether gave α-azido-*trans*-β-deuteriostyrene (**10**) in 96% yield. The structure of **10** was evident from the singlet absorption of the proton *cis* to phenyl at τ 4.69. In these compounds the proton *cis* to phenyl absorbs at lower field (4.69) than the *trans* proton (5.17). These results clearly indicate that both the addition of IN_3 in acetonitrile as well as the elimination of HI had proceeded in an *anti* fashion. Hence, even in the polar solvent used, the iodonium ion **7** does not open to a benzylic cation prior to reaction with azide ions. These conclusions are in agreement with the reported *anti* stereochemistry in the addition of INCO to **6** in ether solution.[6]

(5) A. Streitwieser, L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

(6) A. Hassner and C. C. Heathcock, *Tetrahedron Lett.*, 1125 (1964); A. Hassner, R. P. Hoblitt, C. Heathcock, E. Kropp, and M. Lorber, *J. Amer. Chem. Soc.*, **92**, 1326 (1970).

Bromonium Ions. The ionic addition of bromine to olefins has been extensively studied and shown to be a kinetically rather complicated reaction.[7] Though in most cases the reaction proceeds stereoselectively *anti*, there are many examples of *syn* or nonselective additions.[8] Since azide ion is very similar to bromide ion in size and nucleophilicity[9] it was expected that ionic addition of BrN_3 to olefins should be feasible and give comparable results. In analogy with the chemistry of IN_3, we were able to show that bromine azide (BrN_3) can likewise react with olefins. Unlike IN_3 the reagent BrN_3 is most conveniently prepared by addition of bromine to a solution of NaN_3 in methylene chloride in the presence of hydrochloric acid and the resulting organic layer is used in additions to olefins.[10]

The reaction of BrN_3 with styrene in dichloromethane–nitromethane proceeds regiospecifically and leads to isolation of α-azido-β-bromoethylbenzene (**11**) in 95% yield. The assigned regiochemistry of the product is consistent with its nmr spectrum which showed a triplet (J = 7 Hz) for the α proton at τ 5.34 and a doublet for the β protons at 6.56. By comparison, the IN_3 adduct **4** (R = H) shows nmr absorptions at τ 5.40 and 6.74. Final proof came from treatment of **11** with potassium *t*-butoxide which led to α-azidostyrene **12** in 83% yield. The formation of **11** is best explained by an ionic addition of BrN_3 proceeding by attack of electrophilic bromine on the double bond.



Consistent with this interpretation as well as with the formation of a three-membered ring bromonium ion intermediate is the formation of the *trans*-diaxial product **14** from addition of BrN_3 to 2-cholestene (**13**) in dichloromethane–nitromethane. The stereo- and regiochemistry of **14** are assigned on the basis of nmr evidence. The protons at C-2 and C-3 show half-widths of 6 and 8 Hz, respectively, indicative of equatorial protons,[11] thus placing the Br and N_3 groups axially. The shift of the C-19 protons by 0.21 ppm to lower field as compared to cholestane is characteristic of an axial azido group but not of an axial halogen at C-2.[11b]

Ionic addition of BrN_3 to *cis*- and *trans*-butene **15a** and **15b** gives rise cleanly to the *threo* and *erythro* adducts **17a** and **17b**, respectively. The low yield in these

(7) R. C. Fahey, *Top. Stereochem.*, **3**, 280 (1968).

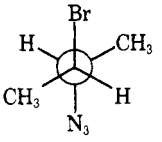
(8) (a) J. P. Snyder and D. G. Farnum, *J. Org. Chem.*, **31**, 1699, (1966); (b) O. Tsuge, K. Yanagi, and S. Fukuhara, *Kogyo Kagaku Zasshi*, **69**, 932 (1966); *Chem. Abstr.*, **65**, 13474f (1966).

(9) (a) A. E. Alexander, *J. Amer. Chem. Soc.*, **61**, 177 (1939); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

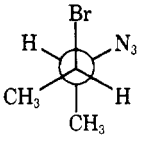
(10) A. Hassner and F. Boerwinkle, *ibid.*, **90**, 216 (1968).

(11) (a) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964); (b) A. Hassner, J. E. Kropp, and G. J. Kent, *ibid.*, **34**, 2628 (1969).

additions (35%) appears to be due to the high volatility of adducts **17a** and **17b** causing their loss during the removal of nitromethane from the reaction mixture. The ir and nmr spectra of the two diastereomers are similar but distinct. The coupling constants for the C-2 and C-3 hydrogens in **17a** and **17b** are 4 and 5 Hz, respectively. This can be interpreted as signifying that a greater proportion of the molecules have the hydrogens in the *anti*-conformation **19b** of the *erythro*-isomer **17b** than in conformation **19a** of the *threo*-isomer **17a**. The C–Br and C–N dipoles are in an unfavorable alignment in conformer **19a**, thereby destabilizing this conformation.

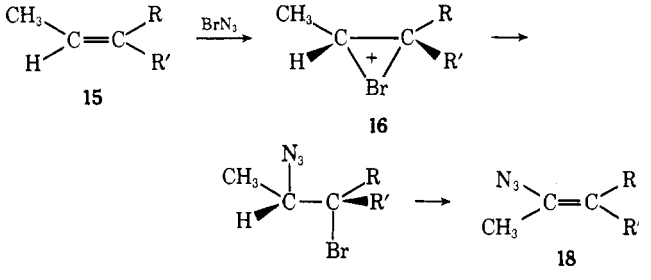


erythro-conformer **19b**



threo-conformer **19a**

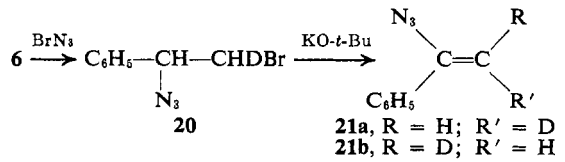
The isomeric purity of **17a** and **17b** was indicated by their clean conversion to vinyl azides **18a** and **18b**, respectively, on treatment with potassium *t*-butoxide. The vinyl azide derived from *cis*-2-butene (**15a**) was identical with authentic[8] 2-azido-*trans*-2-butene (**18a**), whereas 2-azido-*cis*-2-butene (**18b**) was obtained from the BrN_3 addition product to **15b**. It is interesting to note that the nmr spectra of these vinyl azides indicate long-range coupling by the methyl protons (J = 1–1.5 Hz) through five bonds. The stereochemical results are consistent with the formation of discrete three-membered ring bromonium ion intermediates **16a** and **16b** which are opened in an *anti* manner, followed by *anti* elimination of HBr.



15 **16** **17** **18**

a series, R = CH_3; R′ = H
b series, R = H; R′ = CH_3

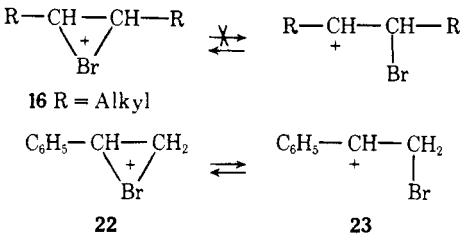
On the other hand when BrN_3 was added to *cis*-β-deuteriostyrene (**6**) at 0° in methylene chloride–nitromethane and the resulting adduct was treated with potassium *t*-butoxide in ether a 1:1 mixture of *cis*:*trans* deuterated vinyl azides **21a** and **21b** was found. This was indicated by the integration of the proton signals in the nmr of the product at τ 5.17 and 4.69.



20 **21a**, R = H; R′ = D
21b, R = D; R′ = H

By analogy with the elimination of HI from **9** it is reasonable to assume that HBr elimination from **20** has likewise proceeded in an *anti* manner. That in fact no reversible abstraction of the benzylic proton from **20** had taken place was shown by the lack of H–D exchange in unreacted bromo azide **11** during the *t*-butoxide-induced conversion of **11** and **12**. Hence, the BrN_3 addition to *cis*-β-deuteriostyrene (**6**) involves the formation of a benzylic cation prior to reaction with azide ions.

Our results indicate that a three-membered ring iodonium ion intermediate (*i.e.*, **2**) does not equilibrate readily to a carbonium ion regardless of whether the substituent on each carbon of the ring is alkyl or phenyl. On the other hand in the corresponding three-membered ring bromonium ion this is only true for the alkyl-substituted cases (see **16**), whereas even a monophenyl-substituted bromonium ion **22** will equilibrate to a benzylic cation **23** before it is trapped by azide ions. These conclusions agree in general with those of Fahey and Schneider,[12] who found that ionic bromine addition to *cis*- and *trans*-1-phenylpropene in CCl_4 proceeded preferentially (*ca.* 80%) *anti* but not 100% stereospecifically. This was interpreted in terms of a weakly bridged bromonium ion intermediate resembling a benzylic cation and which can undergo rotation at least to a certain extent. It would not be surprising that in the more polar solvent acetonitrile employed in our study the open benzylic ion **23** should be further stabilized relative to the bridged ion **22**.



16 R = Alkyl

22 **23**

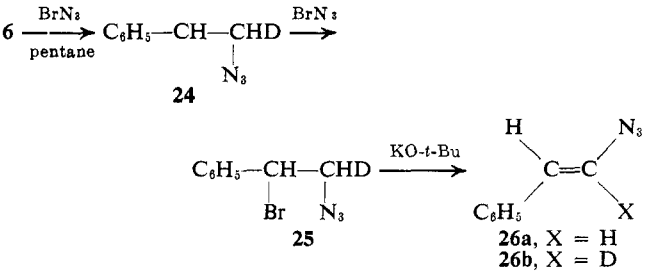
Stereochemistry of Free-Radical Addition of BrN_3. Bromine azide can also undergo a facile free-radical addition leading to opposite regiochemistry in the products as compared to the ionic additions.[10,13] Favorable free-radical conditions include pentane as a solvent, purging the solution with nitrogen, and performing the reaction in the presence of light. Under these conditions styrene gave α-bromo-β-azidoethylbenzene (**25**) in essentially quantitative yield.[13] The radical addition can be rationalized by initial attack of azide radical and subsequent reaction of the benzyl radical **24** with BrN_3 to give **25** in a chain process.

The radical addition of BrN_3 to *cis*-β-deuteriostyrene (**6**) was carried out to determine if there was any preferential stereochemistry in the reaction of the intermediate radical **24**, which might reflect neighboring group participation by the azide function in radical reactions. Treatment of the adduct **25** with potassium *t*-butoxide and subsequent nmr analysis of the product showed it to be a 1:1 mixture of *trans*-β-azidostyrene **26a** and *trans*-β-azidostyrene-2-*d* (**26b**). This indicated that the radical addition of BrN_3 to **6** was nonselective.

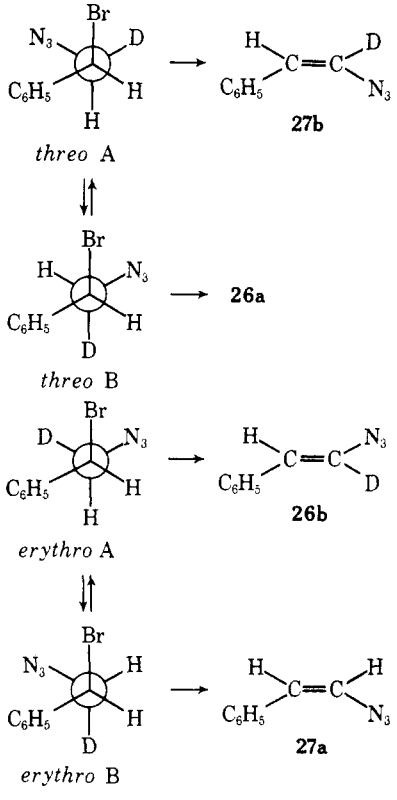
The fact that no *cis*-vinyl azide **27** was found suggests that the steric interactions in the transition state leading to the *cis* isomer override the deuterium isotope effect. Thus of the two *threo* conformers of **25** favorable for

(12) R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).

(13) Further details about the free-radical addition of BrN_3 will be reported separately.



anti elimination of HBr or DBr only *threo* B produces an elimination product. These results are consistent with the elimination of mesitoic acid from *erythro*- and *threo*-1,2-diphenyl-2-*d*-ethyl mesitoate by potassium *t*-butoxide, which gave 100% retained and 93% lost deuterium, respectively, in the resulting *trans*-stilbene.[14]



Since the radical addition of BrN_3 to *cis*-deuteriostyrene gave a mixture of *syn* and *anti* adducts, it follows that the azide function showed no tendency toward bridging with a β radical in this system.

Experimental Section

All solvents used were reagent grade or distilled. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were taken of liquid films unless otherwise noted on a Beckman IR-5 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 204-2b gas chromatograph with a flame ionization detector. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Phenyldeuterioacetylene. Phenyldeuterioacetylene (30.9 g) (59%) was obtained from 51 g (0.50 mol) of phenylacetylene on treatment with ethylmagnesium bromide followed by quenching with D_2O (99%). It contained 88 atom % of deuterium (by nmr): bp 30–34° (7 mm); nmr τ 2.58 (m).

(14) D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, 75, 6011 (1953).

***cis*-β-Deuteriostyrene (6).** This compound was made by modification of a procedure of Streitwieser, *et al.*[5] To 100 ml of tetrahydrofuran, containing 0.1 mol of B_2H_6, was added 14.0 g (0.20 mol) of 2-methyl-2-butene at 0°. The solution was stirred for 4 hr, then 7.73 g (0.075 mol) of phenyldeuterioacetylene (88% D) dissolved in 5 ml of ether was added. The mixture was stirred overnight and after 10 ml of methanol and 30 ml of *n*-hexanoic acid was added, it was stirred and let stand at 0° for 3 days. Attempted distillation of the mixture under vacuum gave rise to evolution of gas causing variable pressure with rising pot temperature, but 1.66 g (21%) of styrene was isolated as a condensate, containing 85% of *cis*-β-deuteriostyrene (**6**) by nmr: τ 4.87 (d, 1, J = 11 Hz), 3.37 (d, 1, J = 11 Hz, of t, J = 2.5 Hz), 2.75 (m, 5).

α-Azido-β-iodo-β-deuterioethylbenzene (9). The addition was performed according to the reported procedure.[5] From 0.52 g (5 mmol) of *cis*-β-deuteriostyrene (**6**), 1.14 g (83%) of α-azido-β-iodo-β-deuterioethylbenzene (**9**) was formed.

***trans*-α-Azido-β-deuteriostyrene (10).** The elimination was performed as reported.[3] From 1.14 g (4.2 mmol) of α-azido-β-iodo-β-deuterioethylbenzene (**9**), 0.59 g (96%) of crude *trans*-α-azido-β-deuteriostyrene (**10**) was formed: nmr τ 4.69 (s, 1), 2.62 (m, 5).

Preparation of Bromine Azide. (1) For Ionic Additions. To a suspension of 32.5 g (0.5 mol) of sodium azide in 100 ml of methylene chloride cooled to 0° was added 20 ml of 37% hydrochloric acid and 5 ml of water at 0°. This heterogeneous mixture was stirred for 10 min with a mechanical stirrer in a 500-ml three-necked, Morton-type flask immersed in an ice bath. Then 8.0 g (0.05 mol) of bromine was added and stirring was continued for an additional 20–30 min, after which time the solution had lightened considerably in color. The methylene chloride solution was separated from the water phase and used in the addition.

(2) For Radical Additions. The same procedure was used as for ionic additions except that pentane purged with nitrogen was used (400 ml) instead of methylene chloride.

α-Azido-β-bromoethylbenzene (11). A solution of bromine azide (25 mmol), prepared as in procedure 1, was added to 100 ml of nitromethane at room temperature containing 2.3 g (22 mmol) of styrene and the mixture stirred and let stand 5 min. The solution was then evaporated under reduced pressure to yield 5.0 g (100%) of an oil. The oil was placed on 100 g of Merck acid-washed alumina and washed through with 100 ml of dichloromethane to give 4.75 g (95%) of an oil which was 94% pure α-azido-β-bromoethylbenzene (**11**) by nmr integration of characteristic aliphatic to aromatic protons (a small amount of impurity, absorbing at 6.1 (m), was present): nmr (CCl_4) τ 6.54 (d, 2, J = 7 Hz), 5.34 (t, 1, J = 7 Hz), 2.69 (s, 5); ir 3040, 2976, 2924, 2110, 1546, 1495, 1453, 1252, 962, 917, and 699 cm^{-1}.

α-Azidostyrene (12). To a solution of 2.26 g (10 mmol) of α-azido-β-bromoethylbenzene (**11**) in 75 ml of anhydrous ether at 0° was added 1.35 g (12 mmol) of potassium *t*-butoxide. The mixture was stirred overnight and allowed to warm to room temperature. It was then washed with two 100-ml portions of cold water, dried ($MgSO_4$), and evaporated to a yellow liquid. The latter was diluted with 75 ml of pentane and filtered through 20 g of Merck alumina to give 1.20 g (82%) of α-azidostyrene after removal of the solvent at room temperature. The nmr and ir spectra were identical with that reported for α-azidostyrene.[3]

The above reaction is essentially complete in 15 min. When the reaction was quenched after 1 min with 10 ml of D_2O, the product contained 38% of α-azidostyrene (**12**) and 62% of α-azido-β-bromoethylbenzene (**11**) in which no deuterium had been incorporated (by nmr).

α-Azido-β-bromo-β-deuterioethylbenzene (20). The reaction was performed as for α-azido-β-bromoethylbenzene (**11**). From 0.52 g (5 mmol) of *cis*-β-deuteriostyrene (**6**), 1.06 g (93%) of crude α-azido-β-bromo-β-deuterioethylbenzene (**20**) was formed.

α-Azido-*cis*- and -*trans*-β-deuteriostyrene (21a and 21b). The reaction was performed as for α-azidostyrene. From 0.78 g (3.4 mmol) of α-azido-β-bromo-β-deuterioethylbenzene (**20**), 0.368 g (90%) of crude α-azido-β-deuteriostyrene was formed, containing a 47:53 mixture of *cis*:*trans* deuterium respectively, as determined by nmr: (*trans*-H) τ 5.17 (s), (*cis*-H) 4.69 (s), 2.65 (m, 5).

2β-Azido-3α-bromocholestane (14). A solution of bromine azide (25 mmol), prepared as in procedure 1, was added to 3.21 g (8.68 mmol) of 2-cholestene (**13**) dissolved in 50 ml of dichloromethane and 150 ml of nitromethane at 0°. The mixture was stirred for 5 min, then evaporated to a black oil at room temperature. The oil was filtered through 100 g of Merck acid-washed alumina with 200 ml of dichloromethane. The resulting solution was evaporated to an oil (4.83 g) under reduced pressure. Chromatography on 300 g

of Merck acid-washed alumina (CH_2Cl_2–Skellysolve F, 1:1) gave 2.22 g (52%) of 2β-azido-3β-bromocholestane (**14**): mp 88–89° (from CH_2Cl_2–acetone); nmr (CCl_4) τ 5.70 (s, 1, half-width 6 Hz), 5.93 (s, 1, half-width 8 Hz), 9.01 (C-19); ir 2941, 2882, 2110, 1468, 1447, 1385, 1250, 1215, 960, and 758 cm^{-1}. *Anal.* Calcd for $C_{27}H_{46}BrN_3$: C, 65.83; H, 9.41. Found: C, 65.85; H, 9.40.

erythro-**2-Azido-3-bromobutane (17b).** A solution of bromine azide (50 mmol), prepared as in procedure 1, was added to 200 ml of nitromethane containing 4.0 g (excess) of *trans*-2-butene (**15b**) at 0°. The dichloromethane was removed under reduced pressure at room temperature and the remaining 200 ml of nitromethane removed by distillation through a 12-in. Vigreux column at room temperature. The residue was distilled to give 3.11 g (35%) of *erythro*-2-azido-3-bromobutane (**17b**): bp 56–58° (15 mm); nmr τ 8.63 (d, 3, J = 7 Hz), 8.32 (d, 3, J = 7 Hz), 6.38 (q, 1, J = 7 Hz, of d, J = 5 Hz), 5.88 (q, 1).

cis-**3-Azido-2-butene (18b).** To a cooled (−10°) and stirred solution of 0.655 g (3.68 mmol) of *erythro*-2-azido-3-bromobutane (**17b**) in 20 ml of anhydrous ether was added 0.5 g (4.46 mmol) of potassium *t*-butoxide. The reaction was stirred for 16 hr and allowed to warm to room temperature. The mixture was poured into 20 ml of ether and 30 ml of water. The ether layer was washed once with 30 ml of water, separated, and dried ($MgSO_4$). Evaporation of the ether under reduced pressure gave 0.223 g (57%) of crude *cis*-3-azido-2-butene (**18b**). The low yield was presumably due to the volatility of the vinyl azide. The nmr was identical with that reported.[3]

threo-**2-Azido-3-bromobutane (17a).** The adduct was prepared from *cis*-2-butene (**15a**), exactly as for the *erythro* adduct: yield, 3.14 g (35%); bp 54–59° (15 mm); nmr τ 8.62 (d, 3, J = 7 Hz), 8.30 (d, 3, J = 7 Hz), 6.40 (q, 1, J = 7 Hz, of d, J = 4 Hz), 5.89 (q, 1, J = 7 Hz, of d, J = 4 Hz); ir 3021, 2950, 2110, 1449, 1387, 1316, 1253, 1209, 1122, 1075, 1063, 1021, 1008, 962, and 883 cm^{-1}.

Anal. Calcd for $C_4H_8BrN_3$: C, 26.99; H, 4.52. Found: C, 27.09; H, 4.46.

trans-**3-Azido-2-butene (18a).** This compound was prepared from *threo*-2-azido-3-bromobutane (**17a**) similar to the formation of *cis*-3-azido-2-butene (**18b**): yield, 0.190 g (48%). The low yield was presumably due to the volatility of the vinyl azide. The nmr was identical with that reported.[3]

α-Bromo-β-azido-β-deuterioethylbenzene (25). To a solution of 0.52 g (5 mmol) of *cis*-β-deuteriostyrene (**6**) in 13 ml of pentane (purged with N_2) was added 13 ml of 0.5 *M* bromine azide solution (6.5 mmol), prepared as in procedure 2, with irradiation by a 100-W incandescent lamp. The solution was allowed to stand 30 min, then evaporation of the pentane under reduced pressure gave 1.17 g (100%) of crude α-bromo-β-azido-β-deuterioethylbenzene (**25**).

Treatment of α-Bromo-β-azido-β-deuterioethylbenzene (25) with Base. To a Dry Ice cooled solution of 1.7 g (5 mmol) of impure α-bromo-β-azido-β-deuterioethylbenzene in 20 ml of anhydrous ether was added 0.62 g (5.5 mmol) of potassium *t*-butoxide. The mixture was allowed to come to room temperature and let stand for 30 min with occasional stirring. The reaction was then extracted with two 25-ml portions of H_2O, dried ($MgSO_4$), and evaporated to give 0.69 g (95%) of crude vinyl azide. Nmr analysis, corrected for nondeuterated product, showed β-azidostyrene (**26**), with an H:D ratio of 1:1: nmr (β-deuterio-β-azidostyrene) τ 3.83 (t, J = 2 Hz; J = 7 Hz, of d, J = 5 Hz); ir 2985, 2941, 2110, 1449, 1385, 1252, 1160, 1054, 1010, 990, 970, and 883 cm^{-1}.

Anal. Calcd for $C_4H_8BrN_3$: C, 26.99; H, 4.52. Found: C, 27.13; H, 4.54.

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Cyclopropane Participation and Degenerate Rearrangement in the Solvolysis of 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-Nitrobenzoate[1]

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Abstract: The synthesis of pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-ol (**4a**) has been accomplished by ultraviolet irradiation of 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (**5**). The latter is conveniently prepared by reaction of deltacyclene epoxide with hydrobromic acid followed by dehydrobromination of the resulting rearranged bromohydrin (**10a**). The rate of hydrolysis of the pentacyclic *p*-nitrobenzoate **4b** in 65% aqueous acetone (7.00×10^{-5} sec^{-1}, 125°) is enhanced by 10^{10}–10^{12} compared to 7-norbornyl derivatives. Hydrolysis of the deuterium-labeled analogs, **4b**-9-*d* and **4b**-*anti*-4-*d*, revealed a degenerate rearrangement which specifically interchanges the 9 with the *anti*-2,3 positions and the *anti*-4 with the 1,8 positions. These data demonstrate effective and exclusive participation by the *anti*-cyclopropane ring in the hydrolysis of **4b**. The formation of a relatively stable, threefold symmetric trishomocyclopropenyl-type cation (**24**), which reacts with water faster than it undergoes bridge inversion, best explains the reactivity and scrambling results.

The extent and consequences of remote cyclopropane participation in carbonium ion reactions have received considerable attention in the recent literature.[3–7] Although the analogy with remote double bond participation has provided a useful basis for comparison, it is now evident that the influence of these two groups

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