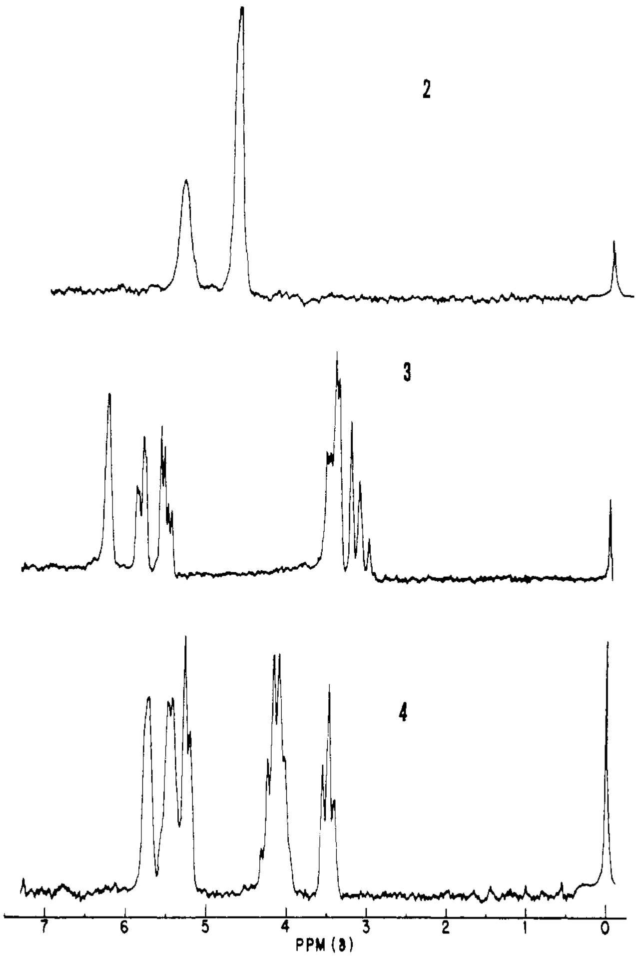


Figure 2. Nmr spectra (60 Mc, ^{1}H) of 2–4.

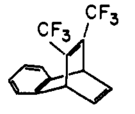
yields of 4:2:1. These compounds have been separated by glpc. Based on nmr data and by analogy with the known rearrangement of the parent bicyclo[2.2.2]-octa-2,5,7-triene,[4] the three products are believed to be isomers of bis(perfluoromethyl)tricyclo[$5.1.0.0^{4,8}$]octa-2,5-diene.

Table I. Diels–Alder Reaction of Perfluorobutyne with Benzenoid Compounds

Reactant	Reaction conditions	1,4 Adduct (yield, %)
Benzene	180°, 20 hr	(8)
Toluene	180°, 12 hr	2-Methyl (21)
o-Xylene	200°, 8 hr	2,3-Dimethyl (18)
m-Xylene	180°, 10 hr	3,5-Dimethyl (6.7) 1,3-Dimethyl (2.2)
p-Xylene	200°, 10 hr	2,5-Dimethyl (57)
Durene[1]	200°, 10 hr	2,3,5,6-Tetramethyl (41)

The ^{1}H nmr spectra of the photoproducts are shown in Figure 2. The symmetrical spectrum of 2 is reminiscent of that described for the parent hydrocarbon,[4] and for similar reasons it suggests that 2 exists as a rapidly fluctuating system.[5] On the other hand, those of 3 and 4,[6] each showing three vinyl protons, correspond only to nonequilibrating systems.[7] The ^{19}F spectrum of **2** shows a singlet at 3853 cps; **3**, two overlapping quartets centered at 3639 cps; and **4**, two quartets at 3432 and 3954 cps. The assignments are also supported by results of elemental analyses, molecular weight, and ir and uv data.

Other substituted bicyclooctatrienes were also found to undergo facile photosensitized rearrangements. The product mixtures are generally too complex to attempt product isolation. However, in the case of the closely related compound **5**,[1] only one photoproduct was obtained in essentially quantitative yield. Definitive structural proof of the photoproduct is underway.[8]



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(4) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. G. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

(5) A sample of propane solution of 2 was cooled to liquid N_2 temperature. On warming, no significant change of the F spectrum was observed.

(6) The coupling constants between two of the vinyl protons in **3** and **4** are 5.1 and 4.1 cps, respectively, suggesting the presence of five-membered rings.

(7) Probably steric interaction makes the other extreme structure of **3** and **4** energetically unfavorable.

(8) Professor H. E. Zimmerman has kindly informed us of his unpublished results on the parent hydrocarbon. In his case, the only photoproduct is believed to be benzosemibullvalene.

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Received August 29, 1967

Ionic and Free-Radical Addition of Bromine Azide to Olefins[1]

Sir:

In connection with our work on the stereospecific introduction of nitrogen functions into organic molecules through pseudo-halogen addition reactions,[2,3] we decided to try the addition of bromine azide (BrN_3) despite its reported explosive properties.[4] Whereas iodine azide reacted as an I^+ source, the more electronegative bromine in bromine azide might facilitate homolytic cleavage of the reagent. We wish to report that under our conditions BrN_3 not only adds to olefins but can undergo both a facile ionic and a free-radical addition, giving rise to opposite orientation in the products. Moreover, the ionic addition proceeds stereospecifically *trans*. The ionic additions are carried out in dichloromethane–nitromethane mixed solvent and the free-radical additions are carried out in oxygen-free pentane. Table I summarizes the results obtained.

Unlike iodine isocyanate or iodine azide, BrN_3 cannot be generated *in situ* in the presence of olefin, and special experimental conditions are required.[5] Evi-

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(1) (a) Stereochemistry. XXIX. For paper XXVIII see A. Hassner and F. W. Fowler, *Tetrahedron Letters*, 1545 (1967); (b) this investigation was supported by Petroleum Research Fund Grant 2004A from the American Chemical Society.

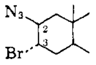
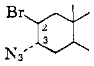
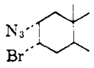
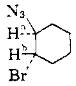
(2) A. Hassner, M. Lorber, and C. H. Heathcock, *J. Org. Chem.*, **32**, 540 (1967), and previous papers.

(3) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Am. Chem. Soc.*, **89**, 2077 (1967).

(4) D. A. Spencer, *J. Chem. Soc.*, **127**, 216 (1925).

(5) For example, 8.0 g of bromine is added to an ice-cooled and stirred mixture of 32.5 g of sodium azide, 100 ml of either methylene chloride or pentane, and 25 ml of 30% HCl. The mixture is stirred for 30 min to 1 hr and the organic layer containing the bromine azide is decanted and used as is. We use an excess of hydrazoic acid to decrease the formation of dibromo adduct. Using our experimental procedures we have had no explosions.

Table I. Ionic and Free-Radical Addition of Bromine Azide to Olefins

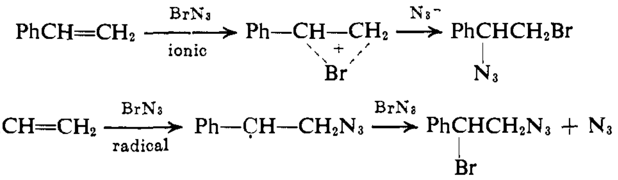
Olefin	Type of addition	Yield, %	Product[a]	Nmr
Styrene	Ionic	95	$C_6H_5CH^a(N_3)CH_2{}^bBr$ I	H_a, τ 5.34, triplet H_b, τ 6.56, doublet J_{ab} = 7 cps; CCl_4
Styrene	Radical	100	$C_6H_5CH^aBrCH_2{}^bN_3$ II	H_a, τ 5.12, triplet H_b, τ 6.33, doublet J_{ab} = 7 cps; CCl_4
2-Cholestene	Ionic	52	 III	H_2 τ 5.70, half-width 6 cps H_3 τ 5.93, half-width 8 cps C-19, τ 9.01, CCl_4
2-Cholestene	Radical	37	 IV	H_2 τ 5.71, half-width 8 cps H_3 τ 5.93, half-width 7 cps C-19, τ 8.91, CCl_4
		27	 V	H_2 τ 5.76, half-width 21 cps H_3 τ 6.03, half-width 7 cps C-19, τ 9.2; CCl_4
Cyclohexene	Ionic	45[b]	 VI	H_a multiplet H_b at τ 6.33; CCl_4
trans-2-Butene	Ionic	35[b]	$CH_3{}^aCH^bBrCH^c(N_3)CH_3{}^d$ VII, *erythro*	H_a τ 8.32; H_b τ 5.88 H_d τ 8.63; H_c τ 6.38, $CDCl_3$ $J_{ab} = J_{cd}$ = 7 cps, J_{bc} = 5 cps
cis-2-Butene	Ionic	35[b]	$CH_3{}^aCH^bBrCH^c(N_3)CH_3{}^d$ VIII, *threo*	H_a τ 8.30; H_b τ 5.89 H_d τ 8.62; H_c τ 6.40; $CDCl_3$ $J_{ab} = J_{cd}$ = 7 cps, J_{bc} = 4 cps
Chalcone	Ionic	48	$C_6H_5CH^b(N_3)CH^aBrCOC_6H_5$ IX	H_a H_b broad singlet, τ 4.73

[a] Satisfactory analyses were obtained for II–IX. [b] Based on amount of bromine used.

dence for the presence of BrN_3 rather than of bromine in solution is provided by the failure of the reagent to brominate acetone, a process that occurs very readily with free bromine in the presence of olefins.

The bromine azide reagent can play a dual role depending upon the polarity of the solvent. Thus in nitromethane–methylene chloride ionic addition of BrN_3 to styrene proceeds in a regiospecific[6] manner and in essentially quantitative yield to produce adduct I. If the reaction is carried out in chloroform the product consists of *ca.* 80% free-radical adduct II and 20% ionic adduct I. The free-radical process becomes the sole pathway (by nmr) if air is excluded by purging with nitrogen. In agreement with this scheme is the fact that the ratio of ionic to free-radical product increases if the BrN_3 addition is carried out in chloroform in the presence of oxygen as a free-radical inhibitor.

The ionic adduct to styrene, prepared by a different route, and the corresponding vinyl azide, α-azidostyrene (J_{vinylic} = 2 cps), have been reported.[7] The radical adduct to styrene (II) has a markedly different nmr (see Table I) and elimination of hydrogen bromide by means of potassium *t*-butyl alchoholate gives β-azidostyrene (J_{vinylic} = 14 cps; infrared 2110 cm^{-1}). It should be noted that this vinyl azide is difficult to obtain by other routes. These results are consistent with an ionic addition that proceeds by attack of electrophilic bromine and a radical addition that occurs through initial attack of azide radical. Both additions are regiospecific[6] and controlled by electronic factors.



$$PhCH{=}CH_2 \xrightarrow[\text{ionic}]{BrN_3} Ph-\underset{\overset{+}{Br}}{CH-CH_2} \xrightarrow{N_3^-} \underset{N_3}{PhCHCH_2Br}$$

$$PhCH{=}CH_2 \xrightarrow[\text{radical}]{BrN_3} Ph-\underset{\cdot}{C}H-CH_2N_3 \xrightarrow{BrN_3} \underset{Br}{PhCHCH_2N_3} + N_3$$

The addition of BrN_3 to 2-cholestene under ionic conditions gives only the *trans* diaxial product III. This points to the possible intermediacy of a bromonium ion which is opened stereospecifically *trans* by azide ion. The configuration and orientation of III are assigned on the basis of nmr evidence. The protons at C-2 and C-3 show a half-width of 6 and 8 cps indicative of equatorial protons,[8] and the C-19 methyl protons occur at τ 9.01, compared with τ 9.22 for cholestane, and close to where the C-19 methyl hydrogens in the iodine azide adduct occur (τ 9.02).[3] When the addition is performed under free-radical conditions, two 1:1 adducts are isolated. One is diaxial and the other is axial,equatorial, assigned again on the basis of the half-width of the C-2 and C-3 protons in the nmr. In the diaxial isomer, the C-19 methyl protons absorb at τ 8.91, similar to 2β-chloro-3α-iodocholestane (τ 8.89)[9] and 2β,3α-dibromocholestane (τ 8.86), and we assign to it the configuration IV with the 2β (axial) bromine. The axial,equatorial isomer has the C-19 methyl at τ 9.19 indicating the absence of a halogen or azide substituent at the 2β position, and is tentatively assigned structure V.

Bromine azide adds stereospecifically to *cis*- and *trans*-2-butenes under ionic conditions. Thus when the respective adducts are eliminated with potassium *t*-butyl alcoholate the isomeric vinyl azides formed are consistent with *trans* addition of BrN_3 followed by a regiospecific[6] and *trans* elimination of hydrogen bromide,

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(6) We suggest the term *regiospecific* (latin *regio*: direction) to describe direction or orientation in additions to multiple bonds (as well as in elimination reactions).

(7) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

(8) A. Hassner and C. H. Heathcock, *ibid.*, **29**, 1350 (1964).

(9) G. Matthews, University of Colorado, unpublished data.

i.e., *cis*-2-butene leads to *trans*-2-azido-2-butene and *trans*-2-butene leads to *cis*-2-azido-2-butene. The vinyl azides were identified by spectral comparison with authentic materials.[3]

The ionic addition of BrN_3 to cyclohexene gives one adduct by vpc which is presumed to be *trans* on the basis of the results with the butenes and 2-cholestene. Bromine azide adds very slowly to chalcone under the ionic conditions; however acid catalysis allows the reaction to proceed at a useful rate. Further work on these and other systems are currently in progress.

[10] NASA Predoctoral Fellow, 1965–1967.

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Boron–Nitrogen Cage Structures. 1,2,4,5-Tetraaza-3,6-diborine Dimers

Sir:

Considerable interest in polyhedral boron hydrides and carboranes[1] has been evident in recent years. Boron–nitrogen compounds have also received much attention.[2] Although there are reports of bicyclic[3] and tricyclic[4] compounds containing boron and nitrogen, no polyhedral cage structures have been described. We wish now to present evidence for such structures.

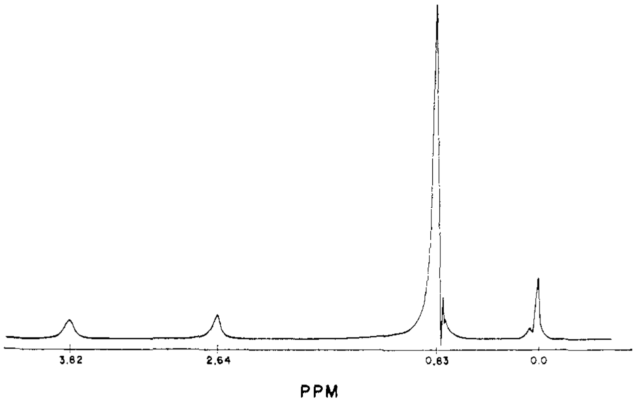


Figure 1.

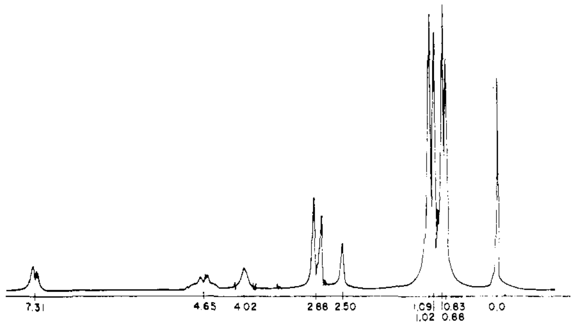
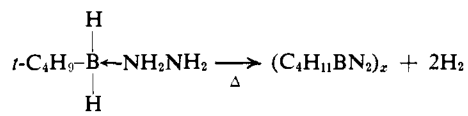


Figure 2.

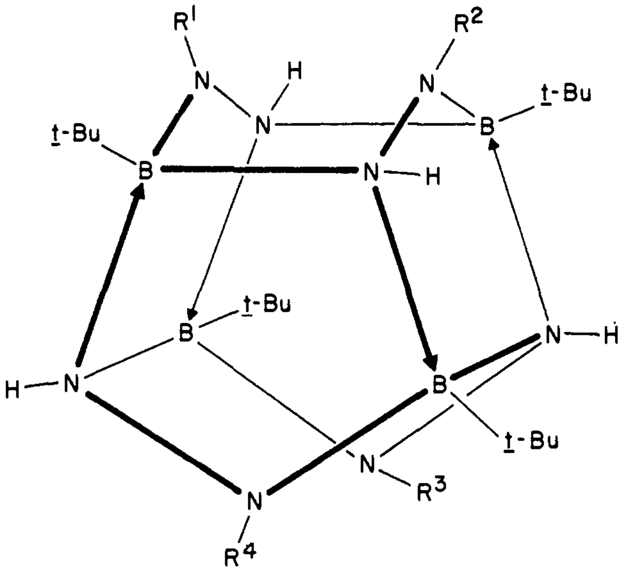
Thermal decomposition of hydrazine *t*-butylborane at 140° causes evolution of hydrogen in amounts consistent with the following reaction and provides a white solid product, **1**, mp 161–163°. Elemental analysis of **1** is



$$t\text{-}C_4H_9\text{-}\underset{H}{\overset{H}{B}}\leftarrow NH_2NH_2 \xrightarrow[\Delta]{} (C_4H_{11}BN_2)_x + 2H_2$$

compatible with the empirical formula depicted, and infrared shows the presence of N–H bonds and the absence of B–H. Thermal tensimetry and mass spectral data indicate that the material is tetrameric. The proton nuclear magnetic resonance spectrum (Figure 1) shows that there are equal numbers of two types of hydrogen on nitrogen, and that all of the *t*-butyl groups are equivalent. All borons are also equivalent according to the B^{11} spectrum. Hydrolysis of **1** with aqueous acid gives *t*-butylboronic acid and hydrazine, thus demonstrating that no rearrangements occur.

Treatment of **1** with excess methyl isocyanate under mild conditions provides a new compound, **2**, mp 184–185°, which is composed of 2 equiv of the isocyanate and 1 equiv of compound **1**. The proton nmr spectrum of compound **2** (Figure 2) shows four separate peaks for the *t*-butyl groups and four types of hydrogen on nitrogen. There are at least seven separate H^1 shifts under suitable conditions. Spectra at 40 and 60 Mc demonstrate that the "splitting" of *t*-butyl resonances is the result of differences in chemical shift and not coupling. The structures shown below are proposed; these may be described as two six-membered rings in the boat form bonded to each other through four coordinate covalent nitrogen–boron bonds thus forming four five-membered rings. Only conventional kinds of bonds and bond angles are required in these structures and maximum coordination of boron and nitrogen is achieved. Dreiding models which approximate the



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^3 = H$; $R^2 = R^4 = \text{-CONHCH}_3$
3, $R^2 = R^3 = R^4 = \text{-CONHCH}_3$; $R^1 = H$
4, $R^1 = R^2 = R^3 = R^4 = \text{-CONHCH}_3$

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[1] Leading references to the chemistry of these systems can be found in M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 5.

[2] A recent survey of boron–nitrogen chemistry is available: H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1966.

[3] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

[4] N. N. Greenwood, J. H. Morris, and J. C. Wright, *J. Chem. Soc.*, 4753 (1964).