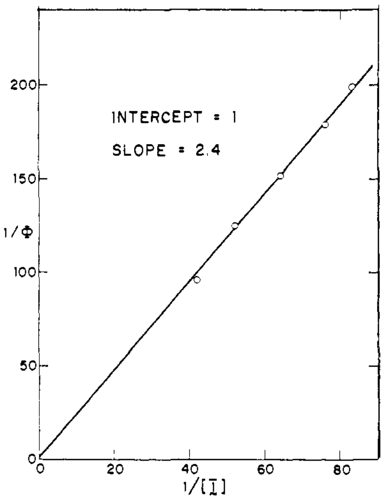

Figure 2. A Stern–Volmer plot of the 9,10-dibromoanthracene-sensitized reaction of **1**.

mole^{-1} sec^{-1}, the calculated diffusion rate constant in hexane at 20°).[15] The average lifetime of the T_2 state of 9,10-dibromoanthracene is, therefore, 2×10^{-11} sec.

Although the present evidence does not rule out completely "relay" mechanisms, suggested by Schenck[16] for other systems, our results require a relay mechanism involving a state other than T_1 and S_1.

From Table I it is obvious that parallel arguments can be presented for compounds **2**, **3**, and **4**, with the proviso that their corresponding triplet-state energies are higher than that of **1**. These systems, however, confirm that in **1** we are not observing an isolated effect. Studies have been expanded to less rigid molecules, where nonvertical excitations are more likely to occur. The results will be reported in the future.

Acknowledgment. The authors wish to thank Drs. R. Kellogg, R. G. Bennett, and H. E. Simmons of Du Pont and Professor G. S. Hammond of California Institute of Technology for helpful discussions and critical comments.

(15) F. Wilkinson, *Advan. Photochem.*, **3**, 248 (1964).

(16) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

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Received August 29, 1967

2,3-Bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,7-trienes and Their Photorearrangement Reactions

Sir:

The thermal 1,4 cycloaddition of perfluoro-2-butyne to aromatic compounds was reported by Krespan, *et al.*[1] Successful examples of addition to simple benzenoid rings, however, were limited to durene. We wish now to report the isolation of other 1,4 adducts and their photosensitized reactions.

When a mixture of benzene (220 ml) and perfluorobutyne (40.5 g) was heated in a 400-ml high-pressure shaker tube at 180° under autogenous pressure, a gradual decrease of pressure was noticed; after 20 hr a mixture of products was obtained. Glpc analysis of the mixture and comparison of retention times showed, in addition to the previously reported volatile products, 1,1,1,4,4,4-hexafluoro-2-butene, 1,2-bis(perfluoromethyl)benzene, and 1,2,5,6-tetrakis(perfluoromethyl)benzene, the presence of one additional major product. After fractional distillation and glpc separation, the product was isolated in 8% yield.

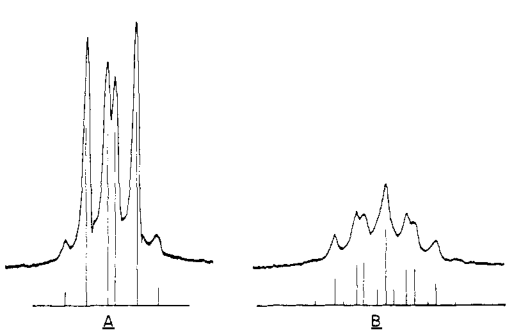
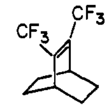


Figure 1. Observed (upper) and calculated (lower) 100-Mc ^{1}H nmr spectrum of bis(perfluoromethyl)bicyclooctatriene.

The compound is a colorless liquid, $\lambda_{\max}^{n\text{-hexane}}$ 262 mμ (ϵ 144), 220 mμ (sh) (ϵ 278). Based on the following evidence, it has been assigned the structure 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene. Results of elemental analysis and molecular weight determination show that the compound is a 1:1 adduct. The 100-Mc ^{1}H nmr spectrum[2] (Figure 1) shows two groups of signals centered at 685 (A) and 504 cps (B) with relative intensities of 2:4. The 56.4-Mc ^{19}F nmr spectrum shows only a singlet at 3545 cps from Freon 11.[2] On hydrogenation over Pd–charcoal, the compound absorbed 2 moles of hydrogen, giving a product (**1**)



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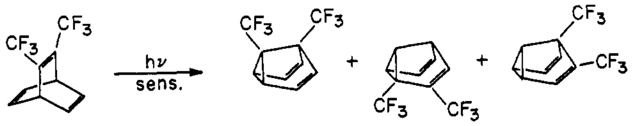
identical (ir, nmr) with the hydrogenation product obtained from reaction of 1,3-cyclohexadiene and perfluorobutyne.

The assignment is further supported by the calculated proton spectrum of **1b** (Figure 1, lower) using the following parameters:[3] $J_{1,2}$ = 5.8 cps, $J_{2,3}$ = 6.2 cps, $J_{1,3}$ = 1.7 cps, $\delta(H_1,H_2)$ = 174.1 cps. The agreement is obviously good.

Corresponding adducts were also obtained from the reaction of toluene and *o*-, *m*-, and *p*-xylenes with perfluorobutyne (Table I). Structural assignments of the products were mainly based on spectroscopic data.

When irradiated with a photosensitizer (acetophenone, benzophenone, or triphenylene), bis(perfluoromethyl)bicyclo[2.2.2]octatriene undergoes a facile rearrangement to give three products, **2–4**. With benzophenone as sensitizer, **2**, **3**, and **4** are formed in relative



2 **3** **4**

(1) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

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(2) All nmr spectra were taken in CCl$_4$, tetramethylsilane, and Freon 11 as internal standard.

(3) The calculation was based on the assumption that the H–F couplings are zero. Judging by the width of the absorption peaks, this assumption may not be entirely valid.

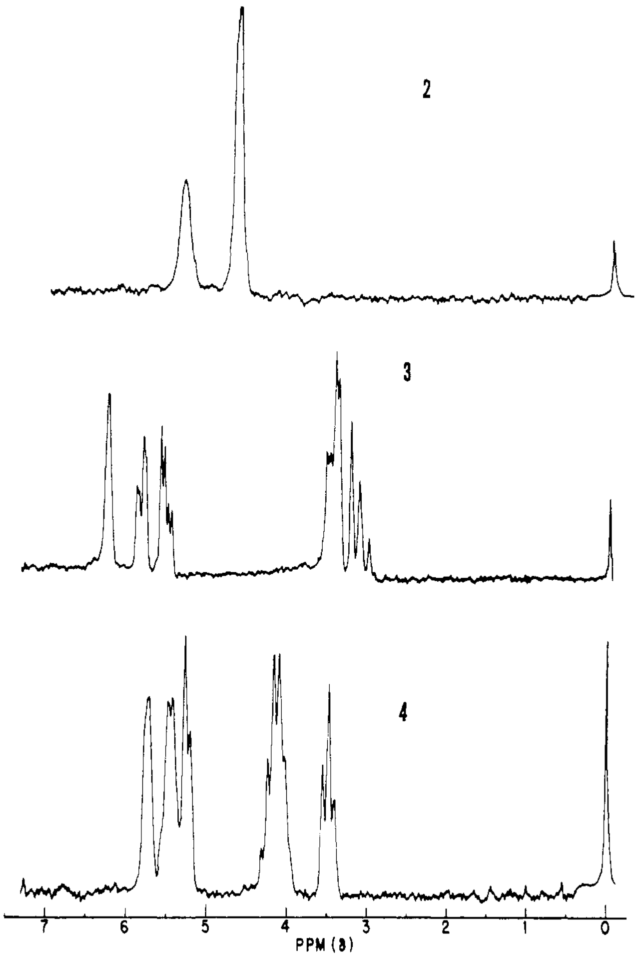


Figure 2. Nmr spectra (60 Mc, ^{1}H) of **2**–**4**.

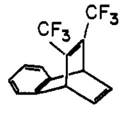
yields of 4:2:1. These compounds have been separated by glpc. Based on nmr data and by analogy with the known rearrangement of the parent bicyclo[2.2.2]octa-2,5,7-triene,[4] the three products are believed to be isomers of bis(perfluoromethyl)tricyclo[5.1.0.0^{4,8}]octa-2,5-diene.

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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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.