(10.0 g, 0.042 mol) was distilled through a water-cooled condenser from a sand bath heated to 200°. The resulting liquid was heated over 2 g of sodium for 11 hr and then distilled at 65-72° (aspirator vacuum). The produced menthene (3.1 g, 55%) had a standard rotation of $[\alpha]^{23}\text{D}$ 113.7° (ether) [lit.[27] $[\alpha]^{14}\text{D}$ +114.1° (alcohol)] and contained (by glpc) *p*-menth-3-ene (70.0%), *trans-p*-menth-2-ene (23.2%), and unidentified components (6.8%). *trans-p*-Menth-2-ene was identified by mixed injection on glpc with an authentic sample of *trans-p*-menth-2-ene prepared by base-catalyzed elimination on menthyl *p*-toluenesulfonate.[28,29]

Gas Chromatography of Alkenes.—A 6 ft × 1/8 in. 5% SE-30 on 60/80 mesh, acid-washed, DMCS treated Chromosorb G column served to separate all alkene mixtures with the exception of the menthenes. A 1 m × 0.25 in. column packed with 30% silver nitrate in ethylene glycol (25%) on 60-80 mesh, acid-washed firebrick performed well in separating 2- and 3-*p*-menthenes. (Retention volumes for the 2- and 3-menthenes are 1.21 and 3.17, respectively, relative to toluene.)[30] The column was operated at room temperature with a helium flow rate of 60-90 ml/min. A 0.5-in.-o.d. version of this column was used to chromatograph the isomers preparatively.

Optical Purity of Camphene from Bornyl Diphenylphosphinate.—Ig was pyrolyzed by the standard method and the alkene products were taken up in ether. The ether solution was analyzed quantitatively by glpc and the concentration found to be 1.11 g of alkene/10.0 ml. The rotation due to the 1.4% bornylene (lit.[31] $[\alpha]^{18}\text{D}$ −21.69°) was assumed to be negligible. Thus from the observed rotation, $\alpha^{23}\text{D}$ −3.41°, of the alkene mixture, assuming all rotation due to the 78.2% camphene, a specific rotation, $[\alpha]^{23}\text{D}$ −39.4°, was calculated. Taking $[\alpha]^{17}\text{D}$ −104.7° (ether) for pure (−)-camphene,[32] an optical purity of 38% is calculated for the camphene.

Registry No.—Ia, 19639-45-3; Ib, 19639-46-4; Ic, 19639-93-1; Id, 19669-14-8; If, 19639-94-2; Ig, 19639-95-3.

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[28] N. Mori, *Nippon Kagaku Zasshi*, **78**, 36 (1957); *Chem. Abstr.*, **53**, 5320 (1959).

[29] A. K. MacBeth and W. G. P. Robertson, *J. Chem. Soc.*, 895 (1953).

[30] J. Herling, J. Shabtai, and E. Gil-Av, *J. Chromatogr.*, **8**, 349 (1962).

[31] J. Bredt and H. Sandkuhl, *Ann.*, **366**, 1 (1909).

[32] J. L. Simonsen, "The Terpenes," Vol. II, 2nd ed, University Press, Cambridge, 1949, p 289.

Bis(polyfluoroalkyl)acetylenes. VI. Thermal and Photochemical Additions of Perfluoro-2-butyne to Aromatic Compounds

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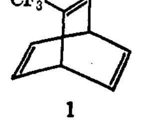
Received October 3, 1968

1,4 adducts have been isolated from thermal addition of perfluoro-2-butyne to benzene, toluene, and *o*-, *m*-, and *p*-xylenes. These thermal adducts are unstable at elevated temperatures. The photochemical addition of perfluorobutyne to aromatic compounds and the photosensitized rearrangement of the thermal adducts have also been investigated.

The high reactivity of bis(perfluoroalkyl)acetylenes as dienophiles was demonstrated in their addition to aromatic compounds to form 1,4 adducts.[2a] The addition to simple benzenoid compounds to form isolable 1,4 adducts was, however, limited to durene.[2a] We wish to report here the generality of the reaction as demonstrated by isolation of adducts from reactions of perfluoro-2-butyne (PFB) with benzene and other simple benzenoid compounds. The photochemical addition of PFB to several aromatic compounds and the photorearrangements of the thermal 1,4 adducts have also been investigated.[2b]

Results and Discussion

Thermal Addition Reactions.—The earlier investigation[2a] of the reaction of PFB with benzene at 250° under pressure did not result in detection of the 1,4 adduct 1. However, the isolation of 1,2-bis(trifluoromethyl)benzene strongly suggested the transient existence of 1. Compound 1 has now been isolated when the reaction is run under autogeneous pressure and at slightly lower temperatures (180-200°). Even at these temperatures, thermolysis of 1 and further reaction of 1 with PFB competes with formation of 1. Therefore, even under optimum conditions, 1 could be isolated in only 7-10% yield. The structural assignment of 1 was based on the chemical transformations shown in Scheme I. Elemental analyses and spectroscopic data agree with the assignment. Further, the assignment is supported by the excellent agreement between the observed and calculated 100-Mc proton magnetic resonance (pmr) spectra.[2b]



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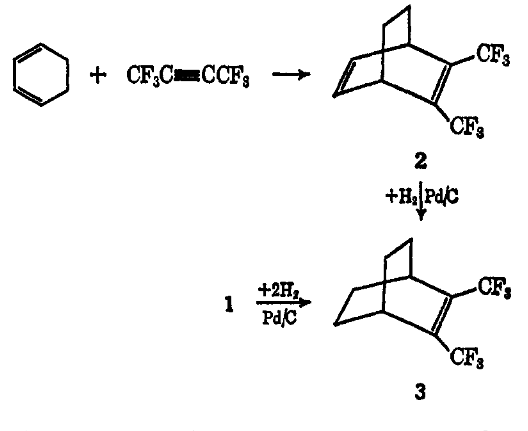
SCHEME I



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[1] To whom inquiries should be addressed: Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

[2] (a) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83**, 3428 (1961). (b) Part of this work was described previously in a preliminary report: R. S. H. Liu, *ibid.*, **90**, 215 (1968).

Table I

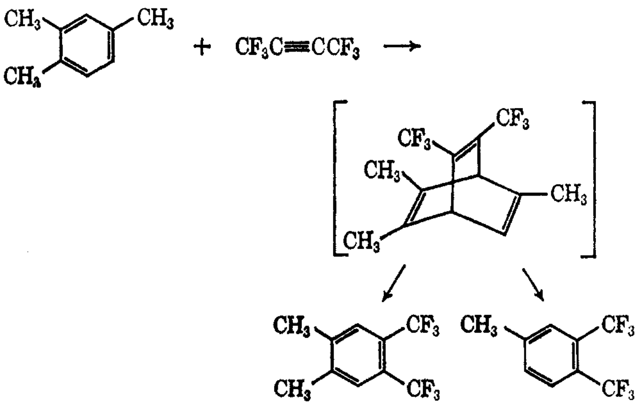
Reactions of Perfluoro-2-butyne with Benzenoid Compounds

Reactant	Reaction conditions,[a] temp in °C, time in hr	1,4 adduct (% yield)	Other products
Benzene	180, 20	2,3-Bis(trifluoromethyl)-bicyclo[2.2.2]octatriene (8)	*cis*-Hexafluoro-2-butene, 1,2-bis(trifluoromethyl)benzene, 1,2,4,5-tetrakis(trifluoromethyl)benzene, and 2,3,6,7-tetrakis(trifluoromethyl)naphthalene
	250, 12[b]		Above products plus 1,2,4-tris(trifluoromethyl)benzene and 1,4,6,7-tetrakis(trifluoromethyl)naphthalene
Toluene	180, 12	5-Methyl- (21)	Other products not identified
o-Xylene	200, 8	5,6-Dimethyl- (8)	1,2-Bis(trifluoromethyl)benzene plus other unidentified products
	250, 13		Same as above
m-Xylene	180, 10	5,8-Dimethyl- (6.7) 1,5-Dimethyl- (2.2)	Other products not identified
p-Xylene	200, 10	5,7-Dimethyl- (57) only	Other products not identified
1,2,4-Trimethylbenzene	220, 13	None isolated	1-Methyl-3,4-bis(trifluoromethyl)benzene, 1,2-dimethyl-4,5-bis(trifluoromethyl)benzene, and other unidentified products
Mesitylene	225, 10		Mixture of high-boiling materials
Durene[b]	200, 10	5,6,7,8-Tetramethyl- (41) only	

[a] Aromatic compound in excess. [b] Reference 2a.

1,4 adducts have also been isolated from reactions of PFB with benzene homologs. In general, better yields are obtained in these cases. The results are summarized in Table I. Structural assignments of these adducts were mainly based on the results of analyses of their pmr spectra. The spectra, together with data on several related compounds for comparison, are described in Table II. The major side reactions in these cases are again fragmentation of adducts and their further reaction with PFB. Thus, reactions at higher temperatures gave no 1,4 adducts (Table I). However, some of the identified products [*e.g.*, 1-methyl-3,4-bis(trifluoromethyl)benzene, **4**, and 1,2-dimethyl-4,5-bis(trifluoromethyl)benzene, **5**, from addition to 1,2,4-trimethylbenzene, Scheme II] again clearly indicate the intermediacy of such 1,4 adducts.

Scheme II

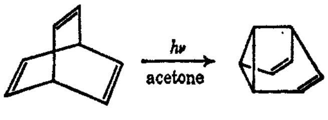


4 **5**

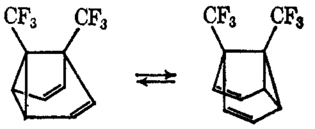
Because of these secondary reactions, no attempt was made to obtain quantitative data related to factors controlling the direction and efficiency of these addition reactions.

Photosensitized Reactions of the 1,4 Adducts.—All of the 1,4 adducts are photochemically labile and rearrange efficiently (quantum yield, 1)[3] in the presence of a high energy sensitizer (>60 kcal/mol). The product mixtures are generally complex and difficult to separate. However, in the case of **1**, the benzophenone-sensitized reaction produces a mixture of three products, as detected by glpc, in the approximate ratio of 4:2:1. The second major product has a much longer retention time and can be easily isolated by preparative glpc, while the remaining two products can be isolated only after repeated glpc separation.

All three compounds are colorless liquids. Their structures can be deduced from their nmr spectra and also by analogy with the known rearrangement of the parent bicyclo[2.2.2]octa-2,5-7-triene, **6**.[4] The pmr spectrum of the second major product (Figure 1a), having the longest retention time, consists of two peaks with some fine structures in a ratio of 2:1. The chemical shift of the major signal (4.72 ppm) has a value between those for tertiary and vinylic hydrogens normally observed for these compounds. This feature is reminiscent of that shown by compound **7**. The product is therefore assigned the symmetrical structure **8**, existing as a rapidly fluctuating system. The symmetrical feature is also noted in the ^{19}F nmr spectrum,[5] which shows only a singlet at 3545 Hz (from $CFCl_3$).



6 **7**



8

The pmr spectra of the two other products (Figure 1b and 1c) indicate their unsymmetrical structure.

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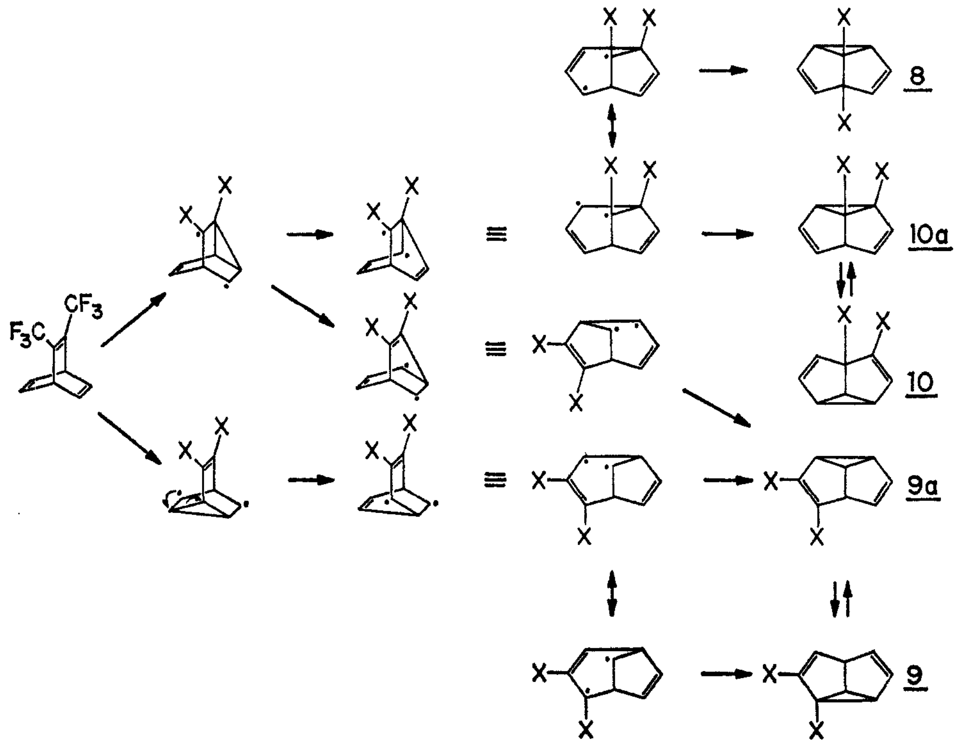
(3) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **90**, 213 (1968).

(4) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

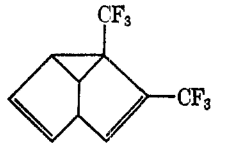
(5) Attempts to retard the dynamic equilibrium by scanning the sample at low temperature (−100°) failed. In our most extreme experiment a frozen propane solution of **8** was placed in the nmr probe. On warming, the ^{19}F spectrum, observable as soon as the sample began to thaw, was identical with the room temperature signal.

SCHEME III

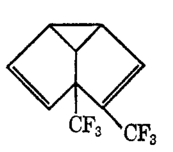
COMPLETE SCHEME OF REARRANGEMENT OF BIS(TRIFLUOROMETHYL)BICYCLO[2.2.2]OCTA-2,5,7-TRIENE (1).



They have been assigned structures **9** and **10** for the following reasons. The spectrum of **9** (1b) shows three saturated protons appearing as an A_2M structure with the A_2 part further split into doublets. There are three vinyl protons with two strongly coupled. The coupling constant (J = 5.7 Hz) suggests that they are both in a five-membered ring.[6] The ^{19}F spectrum shows two overlapping quartets centered at 3639 Hz. These features agree with the structure **9**. Compound **10** is the one formed in the least amount, thus most difficult to isolate. Its pmr spectrum (1c) again indicates the presence of three saturated hydrogen and three different vinyl protons. The ^{19}F spectrum shows two quartets at 3432 and 3954 Hz. Its structure is tentatively assigned as shown.

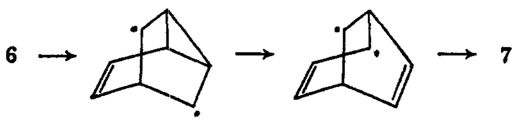


9



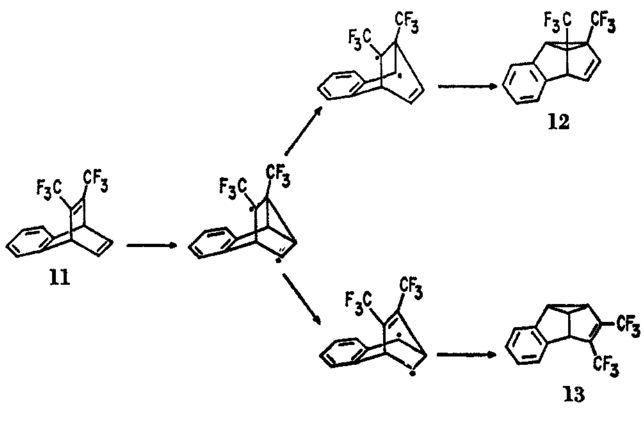
10

The mechanism of photosensitized rearrangement of bicyclo[2.2.2]octatriene, **6**, has been studied in detail by Zimmerman, *et al.*[7] Through labeling experiments, they showed that the pathway of rearrangement is that shown below. Following this mechanism, products **8–10** are indeed predicted from rearrangement of **1** (see Scheme III).[8] The absence of other products, *e.g.*, **9a** and **10a**, is probably due to their unfavorable energy content in comparison with their counter partners, compounds **9** and **10**, in the corresponding dynamic fluctuating equilibrium.



Other substituted 1,4 adducts were also found to undergo facile photosensitized rearrangements. The product mixtures were generally complex. In no case was isolation of product followed by definitive structural assignment possible. However, irradiation of the closely related compound **11** in the presence of acetophenone yielded two products, **12** and **13**, in a ratio of 9:1 (Scheme IV). The products, **12**, a colorless liquid, and **13**, a low-melting solid, were isolated by preparative glpc. The pmr spectrum of the major product shows five groups of signals. Two high-field protons

SCHEME IV



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[6] O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2017 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2018 (1963).

[7] H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

[8] We are grateful to Professor Howard Zimmerman for first pointing this out, and also communicating the results of his group to us prior to publication.

Table II
Assignments of Nmr Spectra of 1,4 Adducts[a]

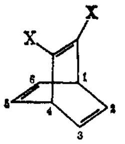
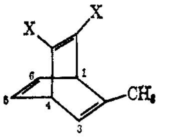
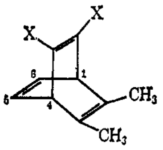
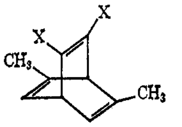
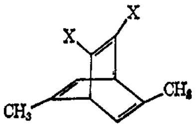
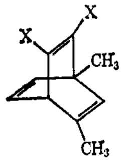
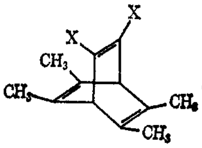
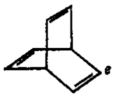
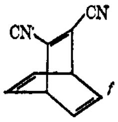
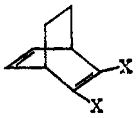
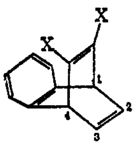
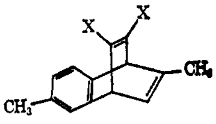
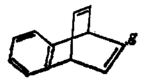
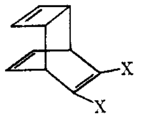
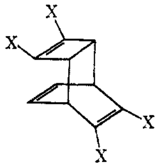
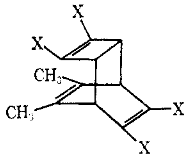
Compound ($X = CF_3$)	No.	Proton signal, structure (number of H)[b]			Fluorine signal,[c] $-CF_3$, Hz
		Methyl and methylene	Bridgehead	Olefinic and aromatic	
	1		5.08 m (2 H_1)	6.89 m (4 H_2)	3545
	19	1.90 d (3) (J = 1.8)	4.68 m (H_1) 4.90 m (H_4)	6.26 m (H_3) 6.85 sx (H_5, H_6)	3533
	20	1.77 s (6)	4.63 sx (2H_1)	6.80 sx (2 H_5)	3522
	21	1.93 d (6) (J = 1.8)	4.34 t (H_1) (J = 1.8) 4.73 t (H_4) (J = 5.8)	6.28 m (2 H_3)	3516
	22	1.90 d (6) (J = 1.6)	4.52 d,d (2 H_1) (J = 5.7, 1.7)	6.27 m (2 H_3)	3521
	23	1.91 s (3) 1.91 d (3) (J = 1.8)	4.67 m (H_4)	5.97 m (H_2) 6.52 d,d (H_6) (J = 6.5, 1.8) 6.82 t (H_5) (J = 6.2)	3349 (J = 11) 3398
 [d]		1.79 s (12)	4.23 s (2 H_1)		
 [e]			4.69 (2)	6.64 (6)	
 [f]			5.1 (2)	6.9 (4)	
	2	1.46 t (4) (J = 0.9)	4.05 broad (2)	6.38 sx (2)	3496
	11		5.17 sx (2 H_1)	7.23 sx (2 H_2) 6.8–7.1 m (4 H)	3516
	24	1.99 d (3) (J = 1.7) 2.21 s (3)	4.77 m (1 H_1) 4.97 d (1 H_4) (J = 5.8)	6.34 m (1 H_3)	
 [g]			4.62 m (2)	6.80 sx (4)	

TABLE II
(*Continued*)

Compound (X = CF_3)	No.	Proton signal structure (number of H)[b]			Fluorine signal[c] $-CF_3$, Hz
		Methyl and methylene	Bridgehead	Olefinic and aromatic	
	17		2.69 m (2) 3.85 m (2)	6.06 s (2) 6.11 sx (2)	3489
	16		2.92 m (2) 4.10 m (2)	6.30 sx (2)	3491 3504
	18	1.79 s (6)	2.88 broad (2) 3.73 broad (2)		3504 3685

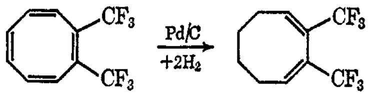
[a] All taken in CCl_4 unless specified, on A-60. [b] Tetramethylsilane as internal standard; chemical shift reported in parts per million (J = Hz): s, singlet; d, doublet; t, triplet; sx, sextet; m, multiplet; coupling constant in hertz. [c] $CFCl_3$ as internal standard; fluorine chemical shift reported in hertz upfield; taken on A-56. [d] Reference 2a. [e] Reference 4. [f] In $CDCl_3$: E. Ciganek, *Tetrahedron Lett.*, 3321 (1967). [g] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

appear as a singlet at 4.07 and a doublet (J = 2.3 Hz) at 4.35 ppm. Two coupled vinyl protons (J = 5.5 Hz) appear at 5.27 and 5.84 ppm, with the lower field one further splitting into doublets (J = 2.4 Hz), and four aromatic protons appear as a complex multiplet between 7.0 and 7.5 ppm. The coupling constant of the vinyl protons and the presence of one unique proton at 5.27 ppm agree with the structure **12**. The ^{19}F spectrum shows two coupled quartets (J = 8 Hz) centered at 3568 and 3725 Hz. The pmr spectrum of the minor compound shows a complex group of signals between 2.8 and 3.7 ppm (3 H), a doublet (J = 6 Hz) at 4.23 ppm, and signals for four aromatic protons between 7.1 and 7.5 ppm. The lack of signals in the regions for vinyl protons is most indicative of the structure. The ^{19}F spectrum shows two quartets (J = 8 Hz) at 3186 and 3501 Hz, the higher field quartet further splitting into doublets (J = 0.9 Hz). Based on this evidence, we have assigned the structure of **13** as shown.

The photosensitized rearrangement of compounds analogous to **11** has recently been reported.[9,10] It is interesting to note that products **12** and **13** are again predicted by the mechanism suggested by Zimmerman, *et al.*, in their study of the labeled parent hydrocarbon of **11**.[8,10]

Photoaddition of Perfluorobutyne to Aromatic Compounds in the Vapor Phase.—When a mixture of benzene and PFB vapor is irradiated in a Vycor tube with 2537-Å light, slow formation of at least eight compounds could be detected by glpc. Although the relative amounts of the minor products appear to vary from run to run and depend upon the irradiation period, the two major products usually comprise approximately 40 and 25%, respectively, of the product mixture. They have been isolated by preparative glpc.

The major product is a colorless liquid. Molecular weight measurement and elemental analysis indicate that it is a 1:1 adduct. Its pmr spectrum shows two singlets at 6.73 and 6.0 ppm with relative intensity 2:4, and it exhibits uv absorption with λ_{max} at 265 mμ (ϵ 700). These data agree with the structure 1,2-bis(trifluoromethyl)cyclooctatetraene, **14**. On hydrogenation over palladium/charcoal, **14** readily absorbs 2 mol of H_2 to give a compound of which the spectroscopic data agree with the structure of 2,3-bis(trifluoromethyl)-1,3-cyclooctadiene, **15**. This hydrogenation result is surprising, though not without precedent. Bryce-Smith, *et al.*, observed that cyclooctatetraene-1,2-dicarboxylic acid on hydrogenation absorbs 2 mol of H_2 to give a product[11] analogous to **15**. The second major product (25%) was shown to be identical with **9**, obtained from rearrangement of **1**. Among the minor products, compounds **8** and **10** have also been detected in relative yields of approximately 12 and 5%.



14 **15**

It is interesting to note that **1**, the 1,4 adduct, was as expected[12] not present in the product mixture. Further, that the relative amounts of **8**, **9**, and **10** obtained in this experiment are different from those from rearrangement of **1** clearly indicates that their formation does not involve the intermediacy of **1**.

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(9) J. P. N. Brewer and H. Henry, *Chem. Commun.*, 811 (1967).

(10) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191 (1968).

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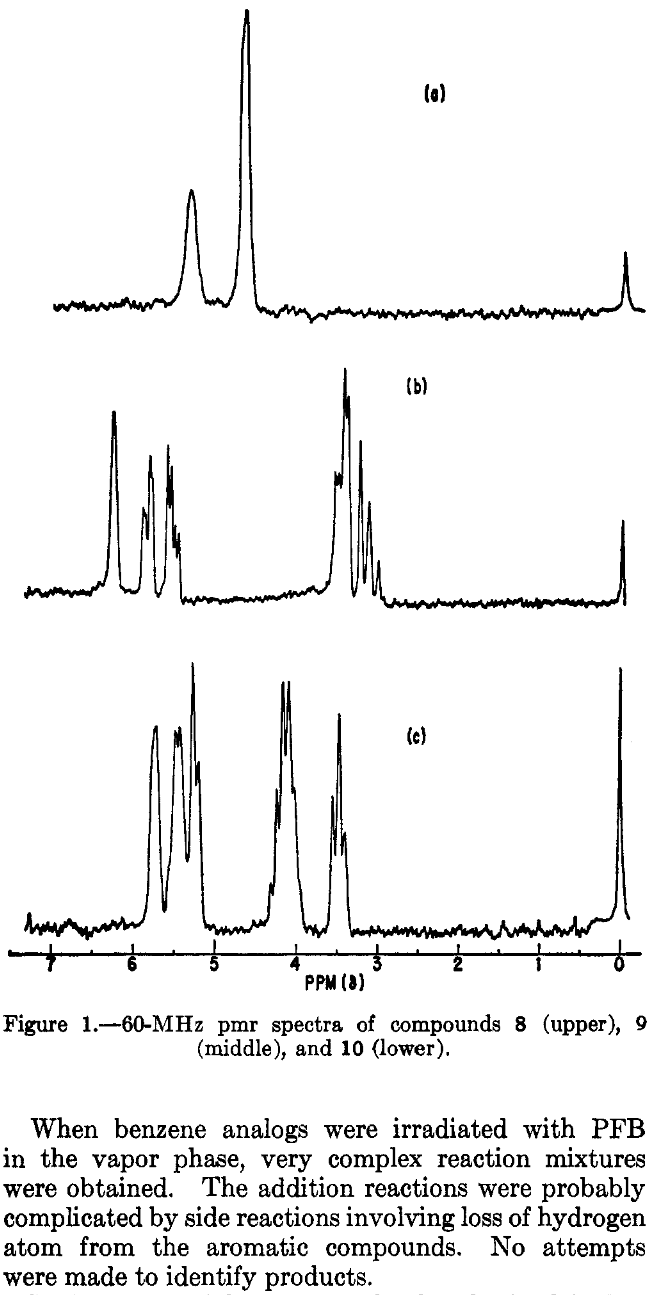
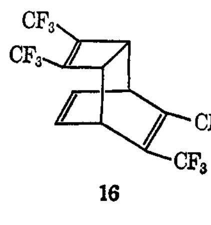


Figure 1.—60-MHz pmr spectra of compounds 8 (upper), 9 (middle), and 10 (lower).

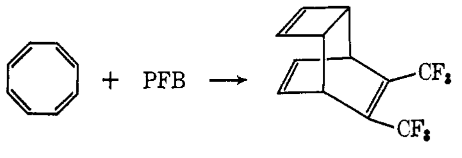
When benzene analogs were irradiated with PFB in the vapor phase, very complex reaction mixtures were obtained. The addition reactions were probably complicated by side reactions involving loss of hydrogen atom from the aromatic compounds. No attempts were made to identify products.

In Solution.—Adducts can also be obtained in low conversion on prolonged irradiation of a solution of benzene and PFB. The major product (73% relative yield) is a white solid, mp 110–111°. Elemental analysis and molecular weight suggest the molecular formula, $C_{14}H_6F_{12}$, a 2:1 adduct containing 2 mol of PFB. The mass spectrum has, besides the parent peak, a characteristic peak at 188, corresponding to $C_6H_2F_6$, possibly a bis(trifluoromethyl)cyclobutadiene fragment. The compound is therefore assigned the structure **16**. Nmr and ir data agree with the assignment. Among the minor products are **8** and **14** in relative amounts of 9 and 14%.



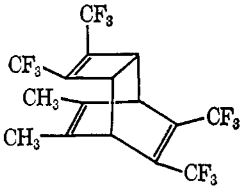
16

The formation of the 2:1 adduct is analogous to photochemical addition of benzene to maleic anhydride[13] and maleimide,[14] but differs from the addition of benzene to other acetylene compounds, where 1:1 adducts, the corresponding cyclooctatetraenes, were the only products.[15] However, based on the results of addition of PFB to cyclooctatetraene, it is likely that product **16** results from thermal addition of PFB to bis(trifluoromethyl)cyclooctatetraene.



17

Irradiation of PFB with other benzenoid compounds gave complex mixtures. No extensive effort was made to identify most products. However, in the case of *o*-xylene, a white solid was also obtained. Its spectroscopic properties show that it is an analogous 2:1 adduct, **18**.



18

Experimental Section

Thermal Addition of Benzene to Perfluorobutyne (PFB).—To a 400-ml high-pressure shaker tube was added 220 ml of benzene. After being cooled (−78°) and evacuated, the tube was charged with 25 g (0.15 mol) of PFB (Peninsular Chemical). The mixture was heated under autogenous pressure at 180° for 20 hr. The net decrease of pressure inside the tube was 20 psi. The yellowish product was distilled under atmospheric pressure. The fraction boiling at 32–39° (0.85 g) contained mostly *cis*-1,1,1,4,4,4-hexafluoro-2-butene, identified by its nmr spectrum. The next fraction contained only unreacted benzene. The pot residue, after concentration to approximately 40 ml, was distilled under vacuum. The fraction (5.6 g) boiling at 98–99° (210 mm) was collected. Analysis by glpc (silicon nitrile column) showed that it was a mixture of three components in an approximate ratio of 1:2:5. These were separated by preparative glpc. The minor product, mp 71.5–73°, was 1,2,4,5-tetrakis(trifluoromethyl)benzene (0.45 g, 1.7% yield), identified by melting point and nmr[16] and ir spectra. The major product, 1 (2.3 g, 6.6% isolated yield), a colorless liquid, was eluted next: uv (cyclohexane) λ_{max} 262 mμ (ε 144), shoulder at 220 (278).

Anal. Calcd for $C_{10}H_6F_6$: C, 50.01; F, 47.48; H, 2.52; mol wt, 240. Found: C, 49.58; F, 46.98; H, 2.65; mol wt, 240.[17]

The last product eluted was 1,2-bis(trifluoromethyl)benzene.

The pot residue solidified on standing. Recrystallization from methanol gave 7.8 g (23% yield) of 2,3,6,7-tetrakis(trifluoromethyl)naphthalene, mp 172.5–173.5°.

Reaction of 1,3-Cyclohexadiene with PFB.—A mixture of 1,3-cyclohexadiene (12 g) and PFB (26 g, 0.15 mol) was heated at 100° for 6 hr in a sealed tube in the presence of 0.15 g of hydroquinone. The yellowish product was distilled, and the fraction

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[13] H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, 326 (1959); G. O. Schenck and R. Steinmetz, *Tetrahedron Lett.*, 1 (1960); E. Grovenstein, D. V. Rao, and J. W. Taylor, *J. Amer. Chem. Soc.*, **83**, 1705 (1961).

[14] D. Bryce-Smith and M. A. Hems, *Tetrahedron Lett.*, 1895 (1966); J. S. Bradshaw, *ibid.*, 2039 (1966).

[15] See, *e.g.*, G. Schröder, "Cyclooctatetraene," Verlag Chemie, Weinheim, Germany, 1965, p 6.

[16] The nmr spectra of the cycloadducts are described in Table II.

[17] All molecular weights were determined by mass spectrometry.

boiling at 53–55° (20 mm), 16.7 g, 58%, contained the expected bicyclooctadiene, **2**.

Anal. Calcd for $C_{10}H_8F_6$: C, 49.59; H, 3.33; F, 47.08. Found: C, 49.43; H, 3.28; F, 47.48.

Hydrogenation of 2.—A solution of 2.0 g of the bicyclooctadiene in methanol (50 ml) containing a catalytic amount of palladium/charcoal was shaken under H_2 until the uptake stopped (~1 hr). The solution was filtered and extracted with 50 ml of petroleum ether and 50 ml of water. The organic layer was washed twice with water and dried over sodium sulfate. The solvent was evaporated leaving 1.34 g (66%) of **3**, a colorless liquid. Elemental analysis and nmr data showed that only 1 equiv of H_2 was absorbed.

Anal. Calcd for $C_{10}H_{10}F_6$: C, 49.18; H, 4.13; F, 46.69. Found: C, 49.82; H, 4.17; F, 46.92.

Hydrogenation of 1.—A methanol solution of 2.0 g of a 50:50 mixture of benzene and the bicyclooctatriene was subjected to catalytic (palladium/charcoal) hydrogenation. The product mixture was shaken with petroleum ether/water. Glpc analysis of the petroleum ether layer showed complete disappearance of the triene and the formation of one new product. The product was isolated from the petroleum ether layer by preparative glpc. Ir and nmr spectra of the product are identical with those of **3**, prepared previously.

Thermal Addition of Toluene to PFB.—A mixture of 220 ml of toluene and 16 g (0.1 mol) of PFB was used (Table I). The reaction mixture, after concentration to 25 ml by distillation under atmospheric pressure, was vacuum distilled. The fraction boiling at 66–67° (26 mm), 4.3 g, was found to contain essentially pure 2,3-bis(trifluoromethyl)-5-methylbicyclo[2.2.2]octa-2,5,7-triene, **19**: uv (*n*-hexane) λ_{max} 268 mμ (ϵ 170), 232 (350).

Anal. Calcd for $C_{11}H_8F_6$: C, 51.98; H, 3.17; F, 44.85. Found: C, 51.96; H, 3.56; F, 45.52.

A second fraction, bp 67–71° (26 mm), 1.9 g, was also obtained which contained (by nmr) approximately 50% bicyclic compound. No attempts were made to identify other products. However, the nmr spectrum of the mixture showed that the isomeric 1-methyl-2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene was not present in significant amounts.

Thermal Addition of *o*-Xylene to PFB.—A mixture of 40 ml of *o*-xylene and 33 g (0.2 mol) of PFB was used. The reaction mixture was distilled under vacuum, and the fraction of bp 52–55° (7 mm) (with major portion at 54–55°) was collected. Gc analysis (6-ft 20% TCEP column, 120°) showed that the mixture contained approximately 37% unreacted xylene, and the desired 1,4 adduct. The adduct (13.3 g, 21%) was isolated by preparative glpc, and its nmr spectrum agrees with the structure **20**: uv (cyclohexane) λ_{max} 275 mμ (ϵ 91), 230 (shoulder) (350).

Anal. Calcd for $C_{12}H_{10}F_6$: C, 53.74; H, 3.76; F, 42.51; mol wt 268. Found: C, 53.96; 53.74; H, 3.79, 3.74; F, 44.36, 43.45; mol wt, 268.

No extensive effort was made to identify other minor products. However, 1,2-bis(trifluoromethyl)benzene was found to be the second major product.

Thermal Addition of *p*-Xylene to PFB.—A mixture of *p*-xylene (220 ml), and PFB (29 g, 0.18 mol) was used. Glpc analysis (6-ft TCEP column 100°), showed the presence of one new product. The solution was concentrated to ~60 ml by distillation, and the yellow residue was distilled under vacuum. Three fractions [38–46, 46–50.5, and 50.5–52.5° (7.7 mm)] were collected which contained 60, 80, and 98%, respectively, of the 1,4 adduct, giving a total yield of 57% 2,3-bis(trifluoromethyl)-5,7-dimethylbicyclo[2.2.2]octa-2,5,7-triene, **22**: uv (*n*-hexane) λ_{max} 272 mμ (ϵ 109), 226 (334).

Anal. Calcd for $C_{12}H_{10}F_6$: C, 53.74; H, 3.76; F, 42.51. Found: C, 53.47; H, 3.87; F, 42.66.

Thermal Addition of *m*-Xylene to PFB.—A mixture of *m*-xylene (220 ml) and PFB (29 g, 0.18 mol) was used. Glpc analysis (6-ft TCEP column, 120°) showed two major new products. The reaction mixture was vacuum distilled, and two fractions were collected: one of bp 53–54° (1.6 mm), 4.3 g; and one of bp 54–55° (1.6 mm), 1.9 g. These contained essentially all of the desired 1,4 adducts plus some unreacted xylene. Based on glpc, 2,3-bis(trifluoromethyl)-5,8-dimethylbicyclo[2.2.2]octatriene, **21**, the major product, was formed in 6.7% yield and 2,3-bis(trifluoromethyl)-1,5-dimethylbicyclo[2.2.2]octatriene, **23**, in 2.2% yield. Other minor products were not identified.

Thermal Addition of 1,2,4-Trimethylbenzene to PFB.—1,2,4-Trimethylbenzene (12 g, 0.10 mol) and 24 g (0.15 mol) of PFB was used. From the product mixture was isolated a 10% yield of 1,2-dimethyl-4,5-bis(trifluoromethyl)benzene, mp 39–40°, identified by mixture melting point and ir, and 0.3% methylbis(trifluoromethyl)benzene, probably the 1,3,4 isomer.

Anal. Calcd for $C_9H_6F_6$: C, 47.38; H, 2.65. Found: C, 47.88; H, 2.86.

Thermal Addition of Cyclooctatetraene to PFB.—A mixture of 20 g of cyclooctatetraene, 0.2 g of hydroquinone, and 32 g (0.2 mol) of PFB was heated at 120° in an 80-ml shaker tube for 6 hr. A net pressure drop of 50 psi was noted. The brownish reaction mixture was vacuum distilled. A forerun of 3.1 g of unreacted cyclooctatetraene was recovered. The fraction of bp 56–56.5° (4.8 mm) was the 1:1 adduct **17**, 20.1 g (52% yield).

Anal. Calcd for $C_{12}F_6H_8$: C, 54.15; H, 3.02; F, 42.83. Found: C, 54.42; H, 2.98; F, 42.73.

Photosensitized Rearrangement of 1.—A deoxygenated benzene solution (100 ml) of the bicyclooctatriene (5.0 g) in a Pyrex immersion apparatus with benzophenone (0.2 g) as photosensitizer was irradiated with a Hanovia medium-pressure mercury lamp (200 W). The course of the reaction was followed by glpc analysis (3-ft silicone GE XE-60 column, 100°). Three products were detected almost immediately after irradiation was started. The reaction was complete within 1 hr.

The three products formed in the ratio of 4:1:2 (in the order of retention time) could be separated only by preparative glpc. The first two compounds, **9** and **10**, failed to separate cleanly; thus, the minor compound **10** was difficult to obtain in high purity. Compound **8**, with the longest retention time, was easily isolated. Structure assignments were based on spectroscopic information (see discussion).

The rearrangement can be sensitized efficiently with any sensitizer with energy greater than 60 kcal/mol, *e.g.*, benzophenone, anthraquinone, triphenylene, acetophenone, and xanthone. The relative amounts of the three products were not dependent upon sensitizer.

Photosensitized Reaction of 11.—An ether solution (120 ml) of the benzobicyclooctatriene (10.0 g) and 1.0 g of acetophenone in a Pyrex well was irradiated with a 450-W Hanovia lamp. Reaction was followed by glpc analysis (6-ft 20% silicon column, 150°). After 2 days the reaction was complete. Ether was evaporated and the residue was vacuum distilled at 99–101° (9.2 mm) yielding a mixture of compound **12** and **13** (55%). They were separated by preparative glpc.

Anal. Calcd for $C_{14}H_8F_6$: C, 57.94; H, 2.78; F, 39.28. Found for **12**: C, 58.18; H, 2.79; F, 39.96. Found for **13**: C, 57.61; H, 2.85; F, 40.54.

The relative amounts of **12** and **13** (9:1) do not depend on irradiation period. They can be sensitized only with sensitizers of energy greater than 70 kcal/mol. Benzophenone, therefore, failed to sensitize the reaction. With acetophenone, prolonged irradiation reduced the yield, probably owing to reaction of sensitizer with products.

Photochemical Addition of Benzene to PFB. A. In the Vapor Phase.—A mixture of 20 g of benzene and 15.2 g of PFB was sealed under vacuum (1 mm) in a large Vycor tube (18 × 2.5 in.). The lower portion of the tube was covered with black tape so that light did not reach the solution directly. The tube was placed in the Srinivasan–Griffin reactor and irradiated with low pressure mercury lamps. After 3 days the solution began to turn slightly yellow and small amounts of polymeric material began to coat the tube. Irradiation was continued for a total of 7 days. Unreacted butyne was removed by distillation, and the benzene solution of the product mixture was concentrated by distillation under vacuum to approximately 5 ml, containing 50% benzene.

Preparative gc (Carbowax 20M column) was used for separation of the product mixture. At least eight peaks were detected. The three major components (40, 25, and 12%) were isolated. The major product (40%), **14**, was a colorless liquid: uv (cyclohexane) λ_{max} 265 mμ (ϵ 700).

Anal. Calcd for $C_{10}H_6F_6$: C, 50.01; H, 2.52; F, 47.47; mol wt, 240. Found: C, 50.22; H, 2.70; mol wt, 240.

The second major product (25%) was also a colorless liquid and identical with **9**, a photorearranged product of **1**: uv (cyclohexane), no absorption maxima, ≥220 mμ.

Anal. Found: C, 49.56, 50.25; H, 2.53, 2.69; F, 46.80; mol wt, 240.

The third major product, a colorless liquid, was identical with **4**, the major photorearranged product from **1**.

Anal. Found: C, 49.37; H, 2.65; F, 47.57; mol wt, 240.

B. In Solution.—A deoxygenated solution of 2 ml of benzene and 8 ml of PFB was irradiated in a sealed quartz tube (15 × 180 mm) for 3 days. The solution turned slightly yellow. Unreacted PFB was removed by distillation and the residual benzene solution was analyzed by gc. A mixture of compounds similar to that obtained in the vapor phase was found, but, in different relative amounts and the conversion was low (~5%). Three products are predominant (73, 14, and 9%). The two minor ones (14 and 9%) have retention times identical with those of **9** and **14**. Evaporation of the solution gave a yellow crystalline residue. After one recrystallization from methanol, 150 mg of a white crystalline solid, **16**, mp 110–111°, was obtained.

Anal. Calcd for $C_{14}H_6F_{12}$: C, 41.81; H, 1.50; F, 56.69; mol wt, 402. Found: C, 42.10, 42.43, 42.50; H, 1.38, 1.88, 1.74; F, 55.49; mol wt, 402.

Hydrogenation of 9.—A sample of 0.1037 g of the cyclooctatetraene in ethanol was hydrogenated over palladium/charcoal. Rapid uptake of H_2 was observed, and the reaction was complete after 14 min; 0.0175 g H_2 was absorbed (2.08 mol equiv).

From a separate preparative hydrogenation run, a pure sample of the hydrogenated product, **3**, was obtained by gc separation (5-ft Carbowax column): ^1H nmr (CCl_4), a triplet centered at 6.67 (J = 8.0 Hz) (2 H) and complex multiplets between 0.9 and 2.6 ppm (8 H); ^{19}F nmr (CCl_4), a singlet at 3656 Hz; uv (methanol), no maxima above 220 mμ, 218 (ε 2.0 × 10⁴), 225 (1.1 × 10⁴).

Anal. Calcd for $C_{10}H_{10}F_6$: C, 49.18; H, 4.13; F, 46.69. Found: C, 49.42; H, 4.04; F, 47.57.

Photochemical Addition of *o*-Xylene to PFB.—A sealed quartz tube containing 8 ml of *o*-xylene and 1 g of PFB was irradiated with 2537-Å light for 5 days. Glpc analysis of the yellowish irradiation solution showed the formation of at least three new products in low yield. One major component isolated by glpc (silicone X-60 column) was a white solid, mp 72–73°, mol wt 430, thus in agreement with the formula $C_{18}H_{10}F_{12}$ (compound **18**).

Registry No.—PFB, 692-50-2; **1**, 781-13-5; **2**, 19640-15-4; **3**, 19640-16-5; **8**, 19640-17-6; **9**, 19640-18-7; **10**, 19640-19-8; **11**, 1580-25-2; **12**, 19640-21-2; **13**, 19640-22-3; **14**, 19640-23-4; **16**, 19640-24-5; **17**, 19640-25-6; **18**, 19640-26-7; **19**, 19669-17-1; **20**, 1554-49-0; **21**, 19640-28-9; **22**, 19640-29-0; **23**, 19640-30-3; **24**, 19640-31-4; 1,2,4,5-tetrakis(trifluoromethyl)benzene, 320-23-0; 2,3,6,7-tetrakis(trifluoromethyl)naphthalene, 2559-74-2.

Fluorinated Cyanates and Isocyanates. A New Type of Rearrangement

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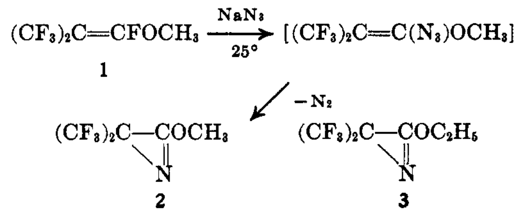
Three isomeric compounds, 2,2-bis(trifluoromethyl)-3-methoxy-2H-azirine (**2**), α-methylhexafluoroisopropyl cyanate (**12**), and α-methylhexafluoroisopropyl isocyanate (**7**), have been prepared. While the normal isomerization of cyanate **12** to isocyanate **7** did not occur, the novel rearrangement of azirine **2** to isocyanate **7** proceeded readily at 95°. α-Phenylhexafluoroisopropyl cyanate did rearrange, but with migration of the isocyanate group to the benzene ring.

Alkoxyfluoroazirines.—Direct syntheses of fluoroazirines starting from fluoro olefins and azide salts were examined earlier with unpromising results.[1] Best results were obtained by isolating the intermediate α,β-unsaturated azide and decomposing it in a separate second step, both in our work with hexafluoropropylene and triethylammonium azide[1] and in other work with sodium azide.[2]

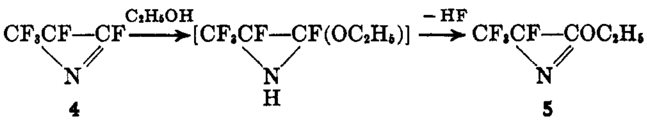
A successful one-step synthesis has now been accomplished starting with a fluoro olefin containing only one readily replaceable halogen and employing diglyme–water as solvent. Reaction of methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propenyl ether (**1**) with sodium azide at 0–25° gave an 11% isolated yield of 2,2-bis(trifluoromethyl)-3-methoxy-2H-azirine (**2**). Azirine **2** is much less reactive than the related perfluoroazirines, particularly in its stability toward polymerization and addition of active hydrogen compounds. This lowered reactivity accounts for the ability of **2** to survive in part the reaction conditions. Azirine **2** does exhibit the expected[1] ir absorption for fluoroazirine C═N at short wavelength (5.48 μ).



$$(CF_3)_2C{=}CFOCH_3 \xrightarrow[25°]{NaN_3} [(CF_3)_2C{=}C(N_3)OCH_3] \xrightarrow{-N_2} (CF_3)_2C{-}COCH_3\ (=N)\quad (CF_3)_2C{-}COC_2H_5\ (=N)$$

1 **2** **3**

The ethoxy compound **3** corresponding to **2** may have been the product obtained in unspecified yield by Knunyants and Bykhovskaya from sodium azide and octafluoroisobutylene in ethanol solution, although the ir band for C═N is indicated to be at 5.80 μ.[3] Azetene structures have been proposed by these workers for several such compounds, including **3** and **4**, structures which have not been confirmed in separate work.[1,2] Another product, derived by Knunyants and Bykhovskaya from the compound now known to be azirine **4**, can also be assigned one of two isomeric ethoxyazirine structures (probably **5**) rather than an azetene structure. Formation of **5** by addition of ethanol to the C═N bond and elimination of HF is in accord with known additions of other active hydrogen compounds to **4**.[1]



$$CF_3CF{-}CF(=N) \xrightarrow{C_2H_5OH} [CF_3CF{-}CF(OC_2H_5)(NH)] \xrightarrow{-HF} CF_3CF{-}COC_2H_5(=N)$$

4 **5**

A similar addition of water across the azirine C═N in **2** is indicated in the present work by the isolation of carbamate **6** as a by-product. The actual step of cleavage of the ring occurs at the carbon–carbon bond, and must be facilitated by the ability of the *gem*-trifluoromethyl groups to stabilize a negative charge. This mode of ring scission is abnormal for unfluorinated azirines and is also different from that postulated by

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[1] C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965).

[2] R. E. Banks and G. J. Moore, *J. Chem. Soc.*, 2304 (1966).

[3] I. L. Knunyants and E. G. Bykhovskaya, *Proc. Acad. Sci. USSR, Chem. Sect.*, **131**, 411 (1960).