and $C_4F_9IF_2$ and confirmed many of the observations reported herein. I want to express particular appreciation to Walter G. Barber for his assistance throughout this work. His intrepid handling of ClF_3 demonstrated that even the most dangerous work can be performed safely. Mr. Barber also built the fluorine-handling equipment, with assistance and advice from Edward Hancock, our resourceful mechanic.

Thomas E. Beukelman performed the nmr studies, and I owe a great deal to his imaginative examination of the spectra. Dr. James Proctor conducted the X-ray study of solid $C_{10}F_{21}IF_2$.

Fluorocyclopropanes. III. 1,4-Cycloaddition Reactions of Perfluorocyclopropene and 1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene

Peter B. Sargeant[1]

Contribution No. 1460 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received January 29, 1969*

Abstract: Perfluorocyclopropene and 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene undergo (a) Diels–Alder reaction with cyclopentadiene to yield *endo*-2,3,3,4-tetrafluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene and *exo*- and *endo*-2,4-bis(trifluoromethyl)-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-enes, and with furan to yield 2,3,3,4-tetrafluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene and 2,4-bis(trifluoromethyl)-3,3-difluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene; (b) cycloaddition with quadricyclane to provide 3,4,4,5-tetrafluorotetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]dec-8-ene and 3,5-bis(trifluoromethyl)-4,4-difluorotetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]dec-8-ene; and (c) homoconjugate Diels–Alder reaction with norbornadiene to provide 4,5,5,6-tetrafluoropentacyclo[5.3.0.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$]decane and 4,6-bis(trifluoromethyl)-5,5-difluoropentacyclo[5.3.0.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$]decane. The perfluorocyclopropene adducts undergo facile cyclopropyl-allyl rearrangement to yield the corresponding unsaturated fluorocarbons. The 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene adducts are more stable; however, the cyclopentadiene adduct undergoes cyclopropylallyl-homovinylcyclopropyl rearrangement. Proton and fluorine nmr spectra are reported and discussed.

Cyclopropenes react with 1,3-dienes to give Diels–Alder adducts.[2-4] Perfluorocyclopropene[5,6] yields a Diels–Alder adduct with 1,3-butadiene, and a 1,2 cycloadduct with tetrafluoroethylene.[6] In this paper we report additional Diels–Alder reactions of perfluorocyclopropene (**1**) and 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (**2**),[7,8] as well as cycloaddition reactions with tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (quadricyclane) and norbornadiene.

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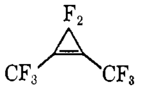

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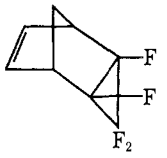
Results

Perfluorocyclopropene and cyclopentadiene gave *endo*[9]-2,3,3,4-tetrafluorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**3**) which readily underwent cyclopropyl–allyl rearrangement to 2,2,3,4-tetrafluorobicyclo[3.2.1]octa-3,6-diene (**4**). Cyclopropene **2** and cyclopentadiene gave both *exo*- and *endo*-2,4-bis(trifluoromethyl)-3,3-difluorotricyclo[3.2.1.$0^{2,4}$]oct-6-enes (**5** and **6**). The *exo* isomer **5** isomerized to the more stable *endo* isomer **6** on mild heating (65°); at 200° the cyclopropyl–allyl rearrangement did not occur, rather a cyclopropyl–allyl–homovinylcyclopropyl rearrangement gave 2,4-bis(trifluoromethyl)-3,3-difluorotetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (**7**). Furan gave 2,3,3,4-tetrafluoro-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-one (**8**) with **1** and 2,4-bis(trifluoromethyl)-3,3-



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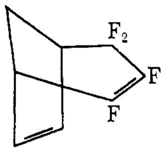

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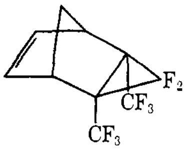

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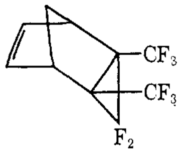

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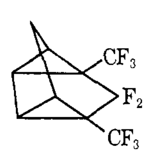

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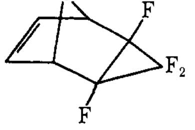

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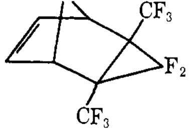

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(2) F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

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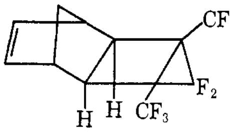
(8) P. B. Sargeant, to be published.

(9) We designate the isomer with the *endo*-substituted cyclopropane ring as the *endo* isomer in this and subsequent compounds.

difluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**9**) with **2**. Quadricyclane and **2** gave 3,5-bis(trifluoromethyl)-4,4-difluorotetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (**10**); with **1** the product was 3,4,5,5-tetrafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**11**), presumably resulting from cyclopropyl–allyl rearrangement of the intermediate tetracycle corresponding to **10**.



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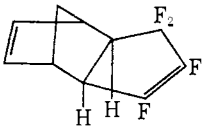

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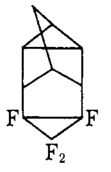
Norbornadiene and **1** gave 4,5,5,6-tetrafluoropentacyclo[5.3.0.0^{2,10}.0^{3,8}.0^{4,6}]decane (**12**) which underwent cyclopropyl–allyl rearrangement to 4,4,5,6-tetrafluorotetracyclo[5.3.0.0^{2,10}.0^{3,8}]dec-5-ene (**13**). With **2** the product was 4,6-bis(trifluoromethyl)-5,5-difluoropentacyclo[5.3.0.0^{2,10}.0^{3,8}.0^{4,6}]decane (**14**).



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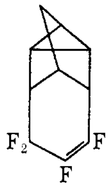

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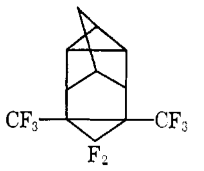
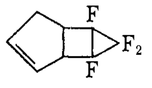


14

Discussion

The structure and stereochemistry, where assigned, of the cycloaddition products were established by a combination of chemical and spectroscopic methods. The nmr spectra of norbornane and norbornene derivatives have been shown[10–23] to have characteristic form, chemical shift relationships, and coupling constants. The proton and fluorine nmr spectral parameters observed in this study are reported in Table I. Similarities will be discussed in detail for the appropriate reaction products. Products retaining the cyclopropane ring were identified from their geminal F–F coupling constant (~170 Hz);[8] indivdual fluorine substituents were identified since *cis* F–F or CF$_3$–F coupling constants are generally larger than *trans* coupling constants.[8] Ring-opened products were identified by their characteristic fluorine-substituted double-bond absorptions in the infrared spectrum and their geminal F–F coupling constants (~260 Hz), as well as by obvious changes in the fluorine chemical shifts. Mass spectra gave molecular weights, elemental analyses, and cracking patterns consistent with the assigned structures. The mass spectra are complex; some characteristic ions for each product are reported in the Experimental Section.

Perfluorocyclopropene and Cyclopentadiene. Cyclopentadiene and **1** at room temperature for 24 hr gave **3**. The ^{1}H nmr spectrum showed the characteristic[10,11,22] olefinic proton triplet at 6.72 ppm. The bridgehead protons were at 3.23 ppm, and the bridge protons were an AB pattern at 1.19 and 1.75 ppm (J = 10.5 Hz). The ^{19}F nmr spectrum showed the cyclopropane ring was intact with tertiary fluorine resonance at 221 ppm and the geminal fluorines at 128.1 and 134.8 ppm (AB pattern) with 177 Hz coupling constant. Alternative 1,2 cycloadducts or their rearrangement products such as **15–18** are inconsistent with the nmr spectra. The stereochemistry of the cyclopropane ring is assigned *endo* in adducts **3** and **6** because the chemical shift of the bridge hydrogen *syn* to the double bond (proton F in Table I) is relatively constant at 1.8–2.0 ppm, whereas the chemical shift of the bridge hydrogen *anti* to the double bond is dependent on the substituents at carbons 2 and 4. When the cyclopropane ring is *exo*, as in **5**, the *anti* bridge proton is sterically compressed by fluorine at carbon 3 and the chemical shift falls at lower field than the chemical shift of the *syn* hydrogen. Deshielding by steric compression has been observed in cage molecules[24,25] and in norbornyl systems.[11–14,17,18] The A fluorine (Table I) is long-range coupled to the bridgehead protons A,B (4.3 Hz) through the extended W conformation, but the B fluorine is not. The A fluorine is also coupled to the olefinic C,D protons (1.8 Hz) through five bonds. Frequency sweep double resonance indicates the tertiary fluorines are coupled by 6.3 Hz with the bridge proton E; in this case, the extended W conformation does not hold, but the coupled atoms are in close proximity.[26] Double resonance experiments also indicate a small coupling between the C,D protons and the E proton, consistent with the assignment.[22]



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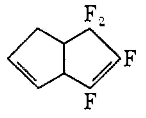

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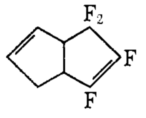

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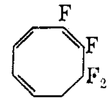

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On standing at room temperature 6 days or on attempted distillation, **3** rearranged quantitatively to **4**. Such cyclopropyl–allyl rearrangements have been observed with cyclopentadiene–tetrachloro (or bromo) adducts,[4] as well as with 3,3-dichloro- and 3,3-dibromotetracyclo[3.2.1.0^{2,4}]octanes and -oct-6-ene.[18–20,27] The infrared spectrum of **4** had strong FC=CF absorption at 1738 cm^{-1}. The ^{1}H nmr spectrum showed two olefinic protons at 6.78 and 6.10 ppm, two bridgehead protons at 3.17 ppm, and two bridge protons at 2.23 ppm. The vinyl coupling constant J_{CD} is 5.6 Hz; the origin of the other couplings is not clear. The ^{19}F

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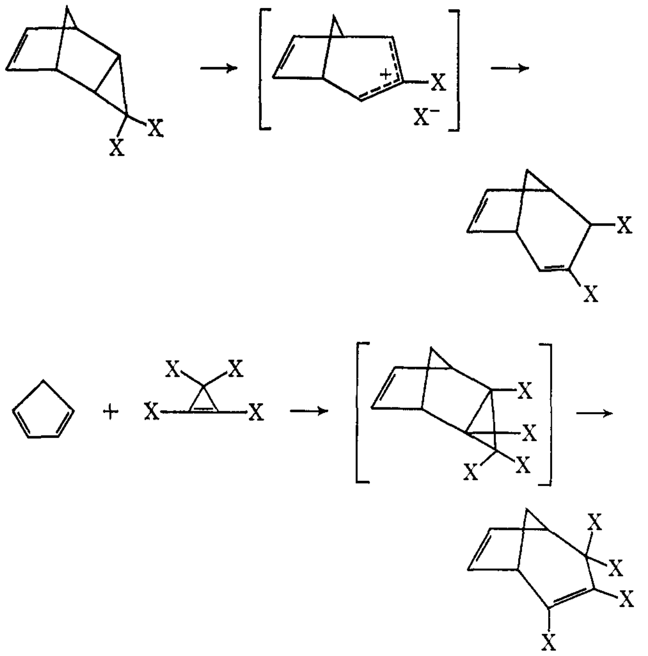
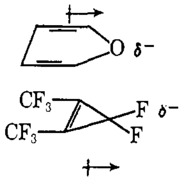


X = Cl or Br

nmr spectrum showed the secondary fluorines as an AB pattern at 100.3 and 117.4 ppm with J_{AB} = 263 Hz and the olefinic fluorines at 127.8 and 174.5 ppm. The olefinic fluorines were coupled to several other atoms, but the spectrum was not further analyzed. The mass spectrum had a large parent ion (*m/e* 178, RA = 95) and was consistent with the assigned structure.

1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene and Cyclopentadiene. Cyclopentadiene and **2** reacted at −78° to give, after ether was removed at 0°, 69% *exo* adduct **5** and 31% *endo* adduct **6** in 90% yield. Distillation or heating at 65° converted the *exo* isomer to the thermodynamically more stable *endo* isomer. Molecular models indicate there is considerable steric compression between a methylene-bridge hydrogen and a methylene fluorine in the *exo*, but not the *endo*, isomer; the *exo* isomer would also be expected to be less stable because of bond opposition of the cyclopropane ring with the methylene bridge. The infrared spectra of both isomers had weak carbon–carbon double bond stretching at 1560–1580 cm^{-1}. The ^{1}H nmr spectrum of the *endo* isomer showed the olefinic protons at 6.72 ppm, the bridgehead protons at 3.57 ppm, and the bridge protons as an AB pattern (J = 8.6 Hz) at 2.01 and 1.15 ppm. The similar bridge proton chemical shifts in **3** and **6** have previously been noted. The ^{19}F nmr spectrum showed the trifluoromethyl groups at 59.9 ppm and the secondary fluorines have an AB pattern at 113.7 and 129.9 ppm. The geminal fluorine coupling constant (J = 178 Hz) showed the cyclopropyl ring was intact. The ^{1}H nmr spectrum of the *exo* isomer had olefinic protons at 6.27 ppm, bridgehead protons at 3.57 ppm, and an AB pattern (J = 8.4 Hz) for the bridge protons at 2.36 and 1.84 ppm. The ^{19}F nmr spectrum had trifluoromethyl groups at 61.7 ppm and the secondary fluorines as an AB pattern (J = 177 Hz) at 109.4 and 136.0 ppm. The A fluorine had a strong (8.5 Hz) coupling with one of the bridge hydrogens; double resonance did not clearly distinguish which. The mass spectrum of each isomer showed a parent ion (*m/e* 278) and similar fragmentation patterns.

This is the first example in which an *exo* adduct is isolated from reaction of a cyclopropene with cyclopentadiene. With furan, **2** yields only *endo* adduct **9**. Present visualization of the transition state[4] suggests the reactants are oriented to each other in a geometry closely resembling the carbon skeleton of the adduct. Furan and cyclopropene **2** have dipole moments which would strongly oppose the mutual orientation required for *exo* adduction (I). Furthermore, close contact between two electronegative elements leads to enhanced van der Waals repulsions. On the other hand, the analogous interaction of **2** with cyclopentadiene is favored by molecular dipole–dipole interaction, and possibly by a favorable interaction between the methylene hydrogen (δ^+) and the methylene fluorine (δ^-) in the developing transition state (II). Once formed, however, adduct **5** can readily isomerize to **6**, possibly *via* allylic cation **6a**.[28]



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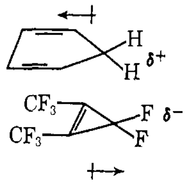

II

A mixture of the *exo* **5** and *endo* **6** isomers and a little dicyclopentadiene was heated in a sealed tube at 65°. Periodic examination of the ^{1}H nmr spectrum showed nearly quantitative conversion of the *exo* to the *endo* isomer (Table II). The constancy of the (*endo*-**6** + *exo*-**5**)/dicyclopentadiene ratio indicates geometrical isomerization and not preferential isomer destruction. Retro-Diels–Alder reaction followed by preferential addition to yield the *endo* isomer seems unlikely. In an open system, isomerization was quantitative; under these conditions free cyclopropene would be rapidly expelled. At 200°, the initial reaction was conversion of *exo* to *endo* isomer (~20 min); after 1 hr a third isomer, tetracycle **7**, was obtained in quantitative (by vpc) yield. The infrared spectrum of **7** had absorptions at 2940, 2880 (sat. CH), and 1170 (CF) cm^{-1}, but no unsaturated CH or C=C stretch. The mass spectrum had a parent ion at *m/e* 278, and the fragment ion pattern was significantly different from the previous two isomers, **5** and **6**, and was consistent with the assigned structure. The ^{1}H nmr spectrum had a multiplet (two hydrogens) at 2.57 ppm and a multiplet (four hydrogens) at 2.29 ppm. The ^{19}F nmr spectrum showed the trifluoromethyl groups at 65.8 ppm and the secondary fluorines as an AB pattern at 101.1 and 108.3 ppm. The geminal fluorine coupling constant (J = 242 Hz) indicated the cyclopropane ring was no longer intact. Photochemical isomerization of other tricyclo-[3.2.1.0^{2,4}]oct-6-enes to this tetracyclic system has been previously observed.[29] Reported infrared and ^{1}H nmr spectra are consistent with ours. We could not, however, effect the isomerization photochemically. We postulate the rearrangement proceeds initially through the cyclopropyl–allyl rearrangement path outlined for the tetrafluoro-substituted tricyclic compound **3**, but

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(28) We are indebted to a referee for suggesting this rationale.

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Table I. Proton and Fluorine Nmr Spectral Parameters

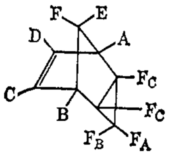
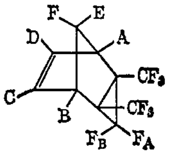
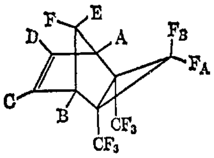
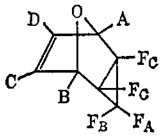
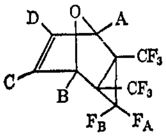
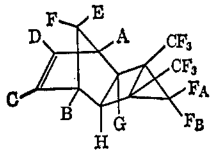
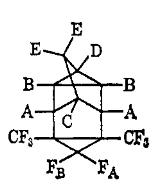
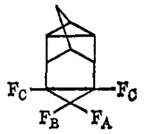
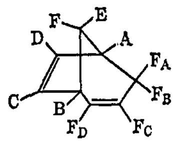
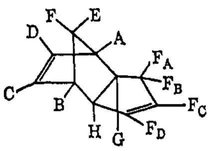
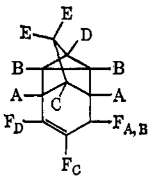
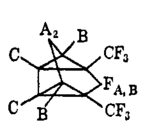
	δ_H, ppm[a]	Mult[b]	Splittings, Hz	Assignment[c]	Coupling constants, Hz
 **3**	6.71	3	1.4	C,D	
	3.23	7	1.8, $W_b \sim 14^d$	A,B	
	1.75	M	$W_{1/2} \sim 4.5^e$	F	EF = 10.5
	1.19	M (3 × 3 × 2)	6.0, 2.1, 2.1	E	$EF_C = 6.3^f$
	$\delta_F{}^g$				
	128.1	7	0.4, $W_{1/2} \sim 6$	B	$F_AF_B = 177$
					$F_AH_{C,D} = 1.8$
	134.8	3 × 3 × 3	24.3, 4.3, 1.8	A	$F_AF_C = 24.3$
					$F_AH_{A,B} = 4.3$
	221	2 × 2 × 3 × 2	24.4, 6.3, 2.3, 1.4	C	$F_CH_{A,B} = 2.3$
					$F_BF_C = 1.4$
 **6**	δ_H				
	6.72	1	$W_{1/2} \sim 5.5$	C,D	
	3.57	1	$W_{1/2} \sim 6.5$	A,B	
	2.01	1	$W_{1/2} \sim 4$	F	EF = 8.6
	1.15	1	$W_{1/2} \sim 8$	E	
	δ_F				
	59.9	2 × 2	19.0, 2.6	CF_3	$F_ACF_3 = 19.0$
					$F_BCF_3 = 2.6$
	113.7	7	19.0	A	$F_AF_B = 178$
	129.9	2 × 7	2.8, 2.6	B	$H_?F_B = 2.8$
 **5**	δ_H				
	6.27	2 × 3	3.0, 2.0	C,D	
	3.57	1	$W_{1/2} \sim 6.5$	A,B	
	2.36	1	$W_{1/2} \sim 5$	E	EF = 8.4
	1.84	1	$W_{1/2} \sim 7$	F	
	δ_F				
	61.7	2 × 2	19.0, 2.6	CF_3	$CF_3F_A = 19.0$
					$CF_3F_B = 2.6$
	109.4	7 × 2	19.0, 8.5	A	$F_AF_B = 177$
	136.0	7	2.6	B	$H_?F_A = 8.5$
 **8**	δ_H				
	6.32	M	$W_b \sim 4$	C,D	
	4.60	2 × M	3.4, $W_b \sim 8$	A,B	
	δ_F				
	129.9	2	0.3	F_B	$F_AF_B = 175$
					$F_BF_C = 0$
	139.3	3 × 3	23.3, 3.2	F_A	$F_AF_C = 23.4$
					$H_{A,B}F_A = 3.2$
	227.8	2	23.4	F_C	
 **9**	δ_H				
	6.62	1	$W_{1/2} \sim 3.8$	C,D	
	5.17	1	$W_{1/2} \sim 3.8$	A,B	
	δ_F				
	59.7	2 × 2	16, 2.2	CF_3	$CF_3F_A = 16$
					$CF_3F_B = 2.2$
	116.7	7	15.9	F_A	$F_AF_B = 166$
	137.0	7 × 3	2.2, 1.2	F_B	$H_{A,B}F_B = 1.2$
 **10**	δ_H				
	6.20	3	1.8, $W_b \sim 6$	C,D	
	3.24	1	$W_{1/2} \sim 5.8$, $W_b \sim 16$	A,B	
	2.11	1	$W_{1/2} \sim 3.2$, $W_b \sim 5$	G,H	
	2.10	1		F	EF = 10.4
	1.55	1		E	
	δ_F				
	61.8	2 × 2	11.4, 5.6	CF_3	$CF_3F_A = 11.5$
					$CF_3F_B = 5.6$
	140.2	7	11.6	F_A	$F_AF_B = 172$
	142	7 × 2	5.6, 1.8	F_B	$H_?F_B = 1.8$

Table I (*continued*)

	δ_H, ppm[a]	Mult[b]	Splittings, Hz	Assignment[c]	Coupling constants, Hz
	2.67	1	$W_{1/2} \sim 5.9$	A,A	
	2.16	2 × M	5.4, $W_b \sim 18$	C	
	1.57	M	Asymmetrical	B,B,D,E,E	
	δ_F				
	59.8	2 × 2	18.6, 4.0	CF_3	$CF_3F_A = 18.6$
					$CF_3F_B = 4.0$
14	127.3	7 × 2	4.0, 2.3	F_A	$F_AF_B = 176$
	133.2	7	18.4	F_B	
	δ_F				
	142.7	3 × M	22.7, 0.2	F_A	$F_AF_C = 22.7$
	152.4	1		F_B	$F_AF_B = 179$
	218	2	22.7	F_C	$F_BF_C = 0$
12					
	δ_H				
	6.78	2 × 2 × 2	5.6, 3.9, 3.1	C	$H_CH_D = 5.6$
	6.10	2 × 2 × 2	5.6, 3.3, 1.3	D	
	3.17	M	$W_b \sim 40$, AB?	A,B	
	2.23	M	$W_b \sim 14$	E,F	
	δ_F				
	100.3	M		F_A	$F_AF_B = 263$
4	117.4	M		F_B	
	127.8	4 × 2 × 2	13.3, 5.0, 3.4	F_D	
	174.5	2 × 2 × 2 × 2 × 2	19.8, 16.6, 7.5, 6.4, 5.0	F_C	
	δ_H				
	6.07	2 × 2	2.3, 1.5	C,D	
	2.90	M	$W_b \sim 9$	A	
	2.80	M	$W_b \sim 10.8$	B	
	2.3	M	AB?	G,H	
	1.38	M (7?)	0.8, $W_{1/2} \sim 4$, $W_b \sim 8$	E,F	
	δ_F				
	88.0	M		F_A	$F_AF_B = 251$
11	108.1	M		F_B	
	132.1	3	9.2	F_D	
	160.0	3 × 2	14, 7	F_C	
	δ_H				
	2.33	M		A,A	
	2.08	M		C	
	1.40	M		B,B,D,E,E	
	δ_F				
	85.6	2 × 3	21.5, 13.2	F_A	$F_AF_B = 266$
	107.8	3	15	F_B	
	128.8	3 × 2 × 2	14.6, 13.8, 7.6	F_D	
13	173.7	2 × 3 × 2	17.2, 14, 7.2	F_C	
	δ_H				
	2.57	M		A,A	
	2.29	M		B,B,C,C	
	δ_F				
	65.8	2 × 2	10.1, 3.1	CF_3	$CF_3F_A = 10.1$
7					$CF_3F_B = 3.1$
	101.1	7 × 3	10.1, 3.0	F_A	$F_AF_B = 242$
					$H_7F_A = 3.0$
	108.3	7	3.1	F_B	

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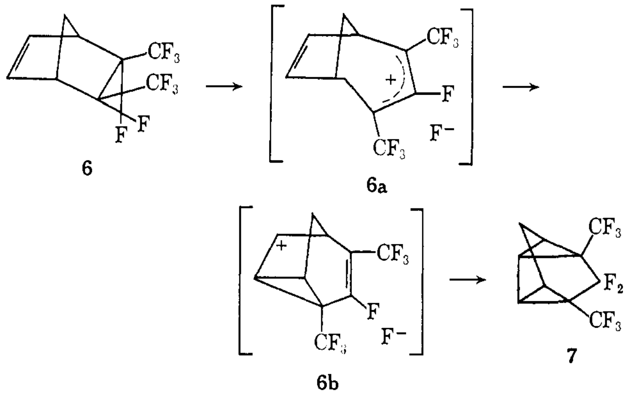
[a] Neat liquid referenced to internal TMS. [b] 1 = singlet, 2 = doublet, 3 = triplet, etc., M = multiplet; arranged in order of decreasing separations. [c] Integration of both the ^1H and ^{19}F spectra are consistent with the assignments. [d] W_b = width of resonance at base. [e] $W_{1/2}$ = width of resonance at half-height. [f] Established by frequency sweep double resonance. [g] Referenced to external trichlorofluoromethane.

Table II. Isomerization of *exo*-2,4-Bis(trifluoromethyl)-3,3-difluorotricyclo[3.2.1.0^{2,4}]oct-6-ene (5)

Time, hr	*endo*/*exo*^{a}	(*endo* + *exo*)/ dicyclopentadiene^a
0	42/58	92/8
0.5	44/56	92/8
1.5	45/55	92/8
18.5	77/23	92/8
22.5	81/19	92/8
6 days	99/1	93/7

^{a} Average of five integrations of the ^{1}H nmr spectrum.

because the allyl cation **6a** is destabilized by the electronegative trifluoromethyl substituents, further cyclopropyl–allyl–homovinylcyclopropyl rearrangement yields tetracycle **7**. Products corresponding to the collapse of ion **6b** have also been observed during thermal rearrangements of Diels–Alder adducts of type **6**.[5,18]



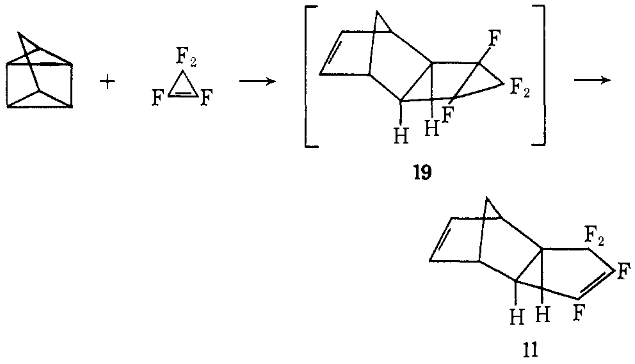
Perfluorocyclopropene and Furan. Perfluorocyclopropene and furan at room temperature for several days (heating gave resinification) gave **8** in 30% yield. The ^{1}H nmr spectrum had olefinic hydrogens at 6.32 ppm and bridgehead hydrogens at 4.60 ppm. The ^{19}F nmr had tertiary fluorines at 227.8 ppm and the secondary fluorines as an AB multiplet at 129.9 and 139.3 ppm. The geminal coupling constant (J = 175 Hz) indicates the cyclopropane ring is intact. The stereochemistry cannot be assigned with certainty, but the cyclopropane ring is presumed *endo* by analogy with the cyclopentadiene adduct **3** and the similarity of the fluorine chemical shifts. The mass spectrum had a parent ion (*m*/*e* 180) and was consistent with the assigned structure.

1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene and Furan. Furan and **2** reacted instantly at room temperature to give **9** in quantitative yield. The ^{1}H nmr spectrum showed olefinic protons at 6.62 ppm and bridgehead protons at 5.17 ppm. The ^{19}F nmr spectrum had the trifluoromethyl groups at 59.7 ppm and the geminal fluorines as an AB pattern (J = 166 Hz) at 116.7 and 137.0 ppm. The stereochemistry is not certain from the nmr spectra; but unlike the corresponding reaction with cyclopentadiene, apparently only the *endo* isomer is produced. The mass spectrum had a *p*-2H (*m*/*e* 278) ion, but no parent ion, and was consistent with the assigned structure.

We note that the above Diels–Alder reactions of **2** proceed at lower temperatures and to higher yields than the corresponding reactions of perfluorocyclopropene. Similar results are observed in the Diels–Alder reactions with 1,4-butadiene.[6,30] Also, replacing chlorine or bromine with fluorine decreases the reactivity of the cyclopropene.[4] The results obtained in this work are consistent with the assertion of Tobey and Law[4] that fluorine substitution relieves cyclopropene strain energy, possibly through a change in σ bond hybridization, and lowers cyclopropene ground-state energy.

Perfluorocyclopropene and Quadricyclane. Perfluorocyclopropene and quadricyclane at 100° for 21 hr gave **11**. The ^{1}H nmr spectrum had olefinic absorption at 6.07 ppm; the 1,7-bridgehead protons were assigned to overlapping multiplets at 2.90 and 2.80 ppm; the 2,6-bridgehead protons were at 2.3 ppm and the bridge protons were at 1.38 ppm. The ^{19}F nmr spectrum had the secondary fluorines as an AB pattern at 88.0 and 108.1 ppm. The geminal coupling constant was 251 Hz, which is similar to that for **4**, and indicates a ring-opened product. The olefinic fluorines were at 132.1 and 160.0 ppm. The mass spectrum had a parent ion (*m*/*e* 204), a large retro-Diels–Alder ion (C_5H_6), and was consistent with the assigned structure.

The reaction is believed to proceed through the intermediate tetracycle **19** (see below) which by analogy with the previously discussed Diels–Alder adducts would be expected to rapidly undergo cyclopropyl–allyl rearrangement at the reaction temperature. Quadricyclane has been previously observed to yield similar cycloadducts with ethylenic and acetylenic dienophiles.[31] The stereochemistry has been exclusively that of *exo* attack by the dienophile.[31,32] Although the nmr spectrum does not allow identification of the 1,2 or 6,7 coupling constants for stereochemical assignment,[31] we tentatively assign the 2,6 hydrogens to the *endo* position by analogy with the results of Smith.[31] Molecular models indicate the apparent chemical shift equivalence of the olefinic hydrogens at C-8 and C-9 would not be expected for the *endo* isomer which has the C-3 double bond near the C-9 hydrogen; however, the C-3 double bond is remote from both the C-8 and C-9 hydrogens in the *exo* isomer and might not influence the chemical shift. Compare for example the nonequivalence of the C-6 and C-7 protons in **4**. Furthermore, the bridge hydrogens at C-10 would be expected to give an AB pattern for the *endo* isomer since only H_F is shielded by a double bond, but both hydrogens are shielded by double bonds in the *exo* isomer and might not exhibit different chemical shifts.



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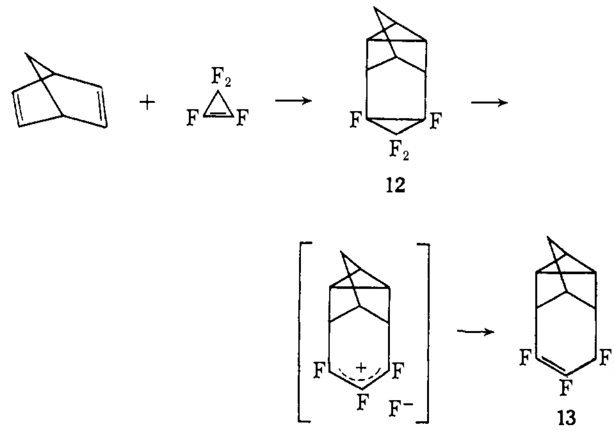
[30] W. Mahler, private communication.

[31] C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

[32] C. D. Smith, private communication.

1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene and Quadricyclane. Quadricyclane and **2** reacted at room temperature to give **10** in 76% yield. The ^1H nmr spectrum had olefinic hydrogens at 6.20 ppm, the C-1, C-7 bridgehead hydrogens at 3.24 ppm, the C-2, C-6 bridgehead hydrogens at 2.11 ppm, and the bridge hydrogens as an AB pattern (J = 10.4 Hz) at 2.10 and 1.55 ppm. The ^{19}F nmr spectrum had the trifluoromethyl groups at 61.8 ppm and the secondary fluorines as an AB pattern at 140.2 and 142 ppm. The geminal coupling constant (J = 172 Hz) and the evident symmetry of the molecule indicated the cyclopropane ring was still intact. The mass spectrum had a parent (*m/e* 304) ion and a large retro-Diels–Alder ion (C_5H_6) and was consistent with the assigned structure. Although analogy with the previous reactions of quadricyclane[31] and examination of molecular models (which indicates considerable strain in all isomers but that depicted in Table I) would suggest *exo* addition of the cyclopropene, we have not assigned the stereochemistry with confidence.

Perfluorocyclopropene and Norbornadiene. Perfluorocyclopropene and norbornadiene at 90° for 22 hr gave a major product, tetracycle **13**, and a small amount of pentacycle **12**. The ^1H nmr spectrum of tetracycle **13** had multiplets at 2.33 and 2.08 ppm assigned to the tertiary hydrogens and a multiplet at 1.40 ppm assigned to the cyclopropyl and bridge hydrogens. The ^{19}F nmr spectrum had the secondary fluorines as an AB pattern at 85.6 and 107.8 ppm. The coupling constant (J_{AB} = 266 Hz) indicated the ring-opened structure was present. The olefinic fluorines appeared as multiplets at 128.8 and 173.7 ppm. The ^{19}F nmr spectrum is similar to that for the previously discussed ring-opened products **4** and **11**. The infrared spectrum had strong fluorine-substituted carbon–carbon double-bond stretch at 1750 cm^{-1}; the mass spectrum had a parent ion (*m/e* 204) and a pattern consistent with the assigned structure. The minor product, pentacycle **12**, was identified by the ^{19}F nmr spectrum which had the secondary fluorines as an AB pattern at 142.7 and 152.4 ppm, J_{AB} = 179 Hz indicating a cyclopropyl ring, and tertiary fluorines at 218 ppm. Pentacycle **12** is believed to be the initial product which, at the reaction temperature, undergoes the now-familiar cyclopropyl-allyl rearrangement to **13**. This homoconjugate Diels–Alder addition of norbornadiene has been previously observed with a number of negatively substituted olefins and acetylenes,[33-38] as well as tetrachloro- and 1,2-dichloro-3,3-difluorocyclopropene.[4] Our spectral data are consistent with those previously reported.[4,33-38]



1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene and Norbornadiene. Norbornadiene and **2** at room temperature gave a quantitative (by nmr) yield of pentacycle **14**. The ^1H nmr spectrum had absorptions at 2.67 and 2.16 ppm assigned to the tertiary hydrogens and at 1.57 ppm assigned to the cyclopropyl and bridge hydrogens. The ^{19}F nmr spectrum had the trifluoromethyl groups at 59.8 ppm and the secondary fluorines as an AB pattern at 127.3 and 133.2 ppm. The geminal coupling constant J_{AB} = 176 Hz indicated the cyclopropyl ring was still intact. The mass spectrum had a *p*-H ion (*m/e* 303) and a pattern consistent with the assigned structure.

The cycloadditions of the bis(trifluoromethyl)cyclopropene with both quadricyclane and norbornadiene occur at lower temperatures and give higher yields than the corresponding perfluorocyclopropene cycloadditions. These results coupled with the similar reactivity relationships observed for Diels–Alder additions support the concept of ground-state stabilization of perfluorocyclopropene compared to chloro-, bromo-, or trifluoromethyl-substituted cyclopropenes. We have commented elsewhere on the unusual stability of perfluorocyclopropene compared to the hydrocarbon cyclopropene.[6]

Experimental Section

General. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer; fluorine nmr spectra were obtained with Varian Associates HR-60 and A-56/60 spectrometers operating at 56.4 Hz. Chemical shifts are referenced to internal TMS ^1H and externally substituted trichlorofluoromethane (^{19}F). Spectral parameters are reported in Table I. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer calibrated with polystyrene. Mass spectra were obtained on a Bendix Time-of-Flight mass spectrometer at 70 eV ionizing voltage, 0.125 trap voltage, and 25° inlet temperature. Perfluorocyclopropene was prepared as described elsewhere.[6]

1,2-Bis(trifluoromethyl)-3,3-difluorocyclopropene (2). Hexafluoro-2-butyne (162 g, 1.0 mol) and hexafluoropropylene oxide (332 g, 2.0 mol) were charged to a 1-l. stainless steel bomb and heated at 185° for 5 hr. The product mixture was distilled to give trifluoroacetyl fluoride (bp −53 to −40°, 103 g), cyclopropene **2** (bp 11–12°, 59 g, 0.28 mol, 28% yield),[7] a mixture of perfluoro-1,3-dimethylbicyclo[1.1.0]butane and perfluoro-1,3-dimethylcyclobutene (bp 37°, 32 g, 0.12 mol, 12% yield),[7] and perfluoro-2,3-dimethylbutadiene (bp 47–51°, 14.6 g, 0.05 mol, 5% yield).[7] This reaction was first run by Dr. W. Mahler with essentially identical results.[30] The ^{19}F nmr spectrum of cyclopropene (**2**) has not been previously reported; it has a triplet (J_{FCF_3} = 2.4 Hz) at 63.0 ppm due to the trifluoromethyl groups and a septet (J_{FCF_3} = 2.4 Hz) at 107.2 ppm due to the secondary fluorines.

***endo*-2,3,3,4-Tetrafluorotricyclo[3.2.1.0^{2,4}]oct-6-ene (3) and 2,2,3,4-Tetrafluorobicyclo[3.2.1]octa-3,6-diene (4).** Cyclopentadiene (freshly distilled, 6.6 g, 0.1 mol) was dissolved in deuteriochloroform (20 ml) and cooled to −78° in a three-necked, round-bottomed flask equipped with a gas addition tube, Dry Ice condenser, and magnetic stirrer. Perfluorocyclopropene (11.2 g, 0.1 mol) was slowly added above the surface of the stirring solution. Reaction did not occur at −80 or 0°; after 24 hr at room temperature the

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(33) E. F. Ullman, *Chem. Ind.* (London), 1173 (1958).

(34) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(35) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960).

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

(37) S. J. Cristol, E. L. Allred, and D. L. Wetzel, *J. Org. Chem.*, **27**, 4058 (1962).

(38) P. D. Bartlett, G. E. H. Wallbillich, and L. K. Montgomery, *ibid.*, **32**, 1290 (1967).

only product by ^{1}H and ^{19}F nmr was *endo* isomer **3**. Periodic nmr examination showed the original pattern decreased in intensity while a new pattern developed. After 2 months the new spectrum completely replaced the old spectrum. After 7 days, distillation of the product mixture gave only **4** (8.4 g, 0.05 mol, 50% yield, bp 75° (44 mm)). The infrared spectrum had absorptions at 3020 (unsat. CH), 2980, 2920 (sat. CH), 1738 (FC═CF), 1675 (HC═CH), 1445 (CH_2), and 1200 (CF) cm^{-1}. The mass spectrum had a large parent ion (*m/e* 178, RA = 95) and a *p*-F (*m/e* 159, RA = 23) ion.

***exo*- and *endo*-2,4-Bis(trifluoromethyl)-3,3-difluorotricyclo[2.2.1.0^{2,4}]oct-6-enes (5 and 6).** Cyclopentadiene (5.62 g, 0.085 mol) was dissolved in ether (50 ml) and cooled to −78° in a 100-ml, three-necked, round-bottomed flask equipped with a gas addition tube, Dry Ice condenser, and magnetic stirrer. Cyclopropene **2** (17.5 g, 0.082 mol) was introduced slowly above the stirring solution. After 1 hr at −78° no unreacted cyclopropene was present. Two products were observed by ^{1}H and ^{19}F nmr and by vpc. Distillation gave only *endo* isomer **6** (bp 74–76° (43 mm), 20.5 g, 0.074 mol, 90% yield). The infrared spectrum had absorptions at 3030 (unsat. CH), 2950 (sat. CH), 1560 (HC═CH), 1475 (CH_2), and 1200 (CF) cm^{-1}. In a second experiment the ether was removed in a rotary evaporator at 0°. The destruction of the less stable product did not occur. The ^{1}H and ^{19}F nmr spectra identified the less stable product as *exo* isomer **5**. Integration of the vapor phase chromatogram and ^{1}H and ^{19}F nmr spectra all gave a 69:31 *exo*:*endo* ratio before and 63:37 *exo*:*endo* ratio after ether removal. The infrared spectrum of the isomer mixture is similar to that for the *endo* isomer with a few additional bands and some broadening of the 1560–1580-cm^{-1} area. The mass spectrum of each isomer showed parent (*m/e* 278, RA ∽ 10), p-F (*m/e* 259, RA *exo* = 13, RA *endo* = 8), and CF_3 (*m/e* 69, RA *exo* = 80, RA *endo* = 70) ions and similar fragmentation patterns.

2,4-Bis(trifluoromethyl)-3,3-difluorotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (7). A mixture of *exo*-**5** and *endo*-**6** (10.0 g, 0.036 mol) was heated at 200° in a 50-ml, round-bottomed flask equipped with a reflux condenser and magnetic stirrer. After 20 min vpc showed quantitative conversion of *exo* to *endo* isomer; after 1 hr vpc showed quantitative conversion to a new product. Distillation gave tetracycle **7** (bp 77° (10 mm), 8.0 g, 0.029 mol, 80% yield). The infrared spectrum had absorptions at 2960, 2880 (sat. CH), and 1200 (CF) cm^{-1}, but no unsaturated CH or C═C stretch. The mass spectrum had parent (*m/e* 278, RA = 55), *p*-F (*m/e* 259, RA = 47), *p*-CF_3 (*m/e* 209, RA = 82), and CF_3 (*m/e* 69, RA = 87) ions.

2,3,3,4-Tetrafluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (8). Furan (0.29 g, 4.25 mmol) and perfluorocyclopropene (4.25 mmol) were sealed in an nmr tube and allowed to stand several days at room temperature (heating gave resinification). The product was **8** in about 30% yield (by ^{1}H nmr integration). The infrared spectrum had absorptions at 3090 (unsat. CH) and 1200 (CF) cm^{-1}. The mass spectrum had a parent (*m/e* 180, RA = 17) ion.

2,4-Bis(trifluoromethyl)-3,3-difluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (9). Furan (0.29 g, 4.25 mmol) and cyclopropene **2** (4.25 mmol) were sealed in an nmr tube and allowed to warm to room temperature. Reaction was instantaneous and gave a quantitative yield of **9**. The infrared spectrum had absorptions at 3120, 3028 (unsat. CH), 1603 (HC═CH), and 1200 (CF) cm^{-1}. The mass spectrum had a *p*-2H (*m/e* 278, RA = 1), but no parent ion. However, it was consistent with the assigned structure: *p*-CF_3 (*m/e* 211, RA = 7), *p*-CF_3,F (*m/e* 192, RA = 15), CF_3 (*m/e* 69, RA = 43).

3,5-Bis(trifluoromethyl)-4,4-difluorotetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (10). Cyclopropene **2** (18.5 g, 0.087 mol) was introduced slowly above the surface of quadricyclane (7.82 g, 0.085 mol) cooled to −45° in a 25-ml, three-necked, round-bottomed flask equipped with a gas inlet tube, Dry Ice condenser, and magnetic stirrer. After the addition was complete, the solution was allowed to warm to room temperature and then distilled to give tetracycle **10** (bp 61° (14 mm), 19.7 g, 76% yield). The infrared spectrum had absorptions at 3075 (unsat. CH), 2995, 2910 (sat. CH), 1643 (HC═CH), 1480 (CH_2), and 1200 (CF) cm^{-1}. The mass spectrum had parent (*m/e* 304, RA = 1.5), C_5H_6 (*m/e* 66, RA = 100), and CF_3 (*m/e* 69, RA = 11) ions.

3,4,5,5-Tetrafluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (11). Quadricyclane (0.24 g, 2.6 mmol) and perfluorocyclopropene (2.6 mmol) were sealed in an nmr tube and allowed to stand 24 hr at room temperature. No reaction occurred. The tube was heated at 100° for 21 hr. The ^{1}H nmr spectrum showed a little norbornadiene, unreacted quadricyclane, and **11**. The mass spectrum had parent (*m/e* 204, RA = 7) and C_5H_6 (*m/e* 66, RA = 100) ions.

4,5,5,6-Tetrafluoropentacyclo[5.3.0.0^{2,10}.0^{3,8}.0^{4,6}]decane (12) and 4,4,5,6-Tetrafluorotetracyclo[5.3.0.0^{2,10}.0^{3,8}]dec-5-ene (13). Norbornadiene (0.36 g, 3.95 mmol) and perfluorocyclopropene (3.9 mmol) were sealed in an nmr tube and heated at 90° for 22 hr. Vpc indicated the presence of two new products. The major product was tetracycle **13**. The infrared spectrum had absorptions at 3050 (cyclopropyl CH), 2950, 2875 (sat. CH), 1750 (FC═CF), 1472 (CH_2), and 1200 (CF) cm^{-1}. The mass spectrum had parent (*m/e* 204, RA = 64), *p*-F (*m/e* 185, RA = 22), and C_6H_6 (*m/e* 78, RA = 100) ions. The minor product, pentacycle **12**, was identified only on the basis of its ^{19}F nmr spectrum.

4,6-Bis(trifluoromethyl)-5,5-difluoropentacyclo[5.3.0.0^{2,10}.0^{3,8}.0^{4,6}]decane (14). Norbornadiene (0.36 g, 3.95 mmol) and cyclopropene **2** (3.95 mmol) were sealed in an nmr tube and allowed to stand at room temperature. After several hours pentacycle **14** was formed quantitatively. The infrared spectrum had absorptions at 3050 (cyclopropyl CH), 2950, 2875 (sat. CH), and 1200 (CF) cm^{-1}. The mass spectrum had *p*-H (*m/e* 303, RA = 18), *p*-H,F (*m/e* 284, RA = 7), *p*-H,CF_3 (*m/e* 234, RA = 29), CF_3 (*m/e* 69, RA = 68), and C_5H_6 (*m/e* 66, RA = 100) ions.

Acknowledgment. The author acknowledges the assistance of Mrs. N. P. Hillyard and Mr. C. B. Matthews in obtaining and interpreting the mass spectra.