Cycloaddition. XIII. The Thermal and Photosensitized Cycloaddition of Trifluoroethylene to Butadiene. Competitive Concerted and Biradical Mechanisms

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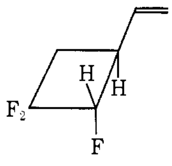
Abstract: Unlike tetrafluoroethylene, trifluoroethylene yields 13% of the 1,4 adduct, 4,4,5-trifluorocyclohexene (**5**, Table I) on thermal addition to butadiene at 215°, the remainder of the cross-cycloadducts being a mixture of four vinylcyclobutanes differing in orientation and configuration (**1**–**4**). The preferred orientation, by 2:1, is that with the CFH group adjacent to the vinyl. The products of photosensitization show diminished regioselectivity among the vinylcyclobutanes. The proportion of trifluorocyclohexene in the product varies with the triplet excitation energy of the sensitizer, from less than 1% for phenanthrene and acetophenone to 22% for fluorenone. It is concluded that not more than one-sixth of the cyclohexene in the thermal cycloadduct can have arisen *via* the biradical mechanism, most of this product representing direct competition of the concerted (2 + 4) Diels–Alder mechanism with the stepwise biradical path.

It is a peculiarity of tetrafluoroethylene and of 1,1-dichloro-2,2-difluoroethylene (1122) that their thermal cycloadditions to conjugated dienes do not follow the concerted Diels–Alder path to cyclohexenes, but instead yield cyclobutanes by way of biradicals.[1] The formation of small amounts of 1,4-addition products by 1122 with butadiene[2] and especially with 2-substituted butadienes[3] and certain cis-fixed dienes[4] has shown that this mode of addition is favored by increased s-cis conformation in the diene, but no single experiment has been able to establish whether fluorinated olefins perform 1,4 addition by a concerted mechanism or by a partial 1,6 ring closure of a cisoid biradical. It does appear,[1] from what rate measurements there are, that substitution of fluorine into ethylene greatly increases the rate of cyclobutane formation with relatively much less effect upon the rate of 1,4 addition.

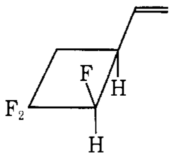
It is obvious that there must be a class of borderline reagents in which neither the concerted nor the biradical stepwise mode of cycloaddition will occur to the complete exclusion of the other. We have observed such behavior in vinylidene fluoride, trifluoroethylene, and allene.[5] We here report the behavior of trifluoroethylene in cycloaddition to butadiene.

Results

Structures of Cycloadducts. The thermal cycloaddition of trifluoroethylene and 1,3-butadiene at 215° gave a product showing four fractions on analysis by glpc on a 6-ft column of diisodecyl phthalate. No systematic change in the relative peak heights was observed in four samples in which the ratio of diene to trifluoroethylene was varied from 1:3 to 3:2. By catalytic hydrogenation the third fraction (after separation on a $^3/_8$ in. × 20 ft column of diisodecyl phthalate, 20% on Chromosorb P, at 120°) was converted into a mixture readily separable into two fractions by the same column. (This procedure is the "Method A" of Table I.) There were thus five cycloadducts, **1**–**5**, corresponding in some order to the five possible (2 + 2) and (2 + 4) adduct structures A–E. Of the five products



A



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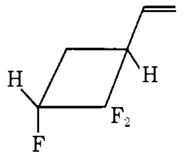

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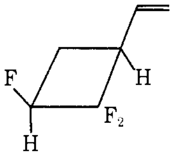

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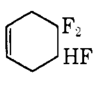
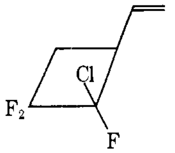


E

the one with the highest retention time, **5**, was the only one with an nmr spectrum showing only two ethylenic protons, and **5** was accordingly the cyclohexene E. Potassium *tert*-butoxide in *tert*-butyl alcohol converts **5** into fluorobenzene, identical by ir and by retention time on two glpc columns with authentic material.

Isomers **1** and **3** were shown to be 1-vinyl-2,3,3-trifluorocyclobutanes (A, B) as follows. The addition of trifluorovinyl chloride to butadiene yields the two cyclobutanes **6** and **7**,[6,7] in accord with the strong orienting effect produced by the radical-stabilizing property of chlorine compared to fluorine, also seen in the reactions of 1122.[1] Treatment of the mixture of **6** and **7** with



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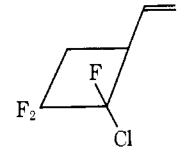

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(1) P. D. Bartlett, *Science*, **159**, 833 (1968), and references cited there.

(2) J. S. Swenton and P. D. Bartlett, *J. Amer. Chem. Soc.*, **90**, 2056 (1968).

(3) P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *ibid.*, 90, 2049 (1968).

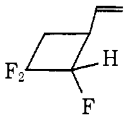
(4) P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, 90, 6067 (1968).

(5) L. E. Walker and P. D. Bartlett, *ibid.*, **95**, 150 (1973).

(6) P. L. Barrick, U. S. Patent 2,462,345; *Chem. Abstr.*, **43**, 4293g (1949).

(7) J. D. Park, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **25**, 990 (1960).

Table I. Thermal and Photosensitized Cycloaddition of Trifluoroethylene and Butadiene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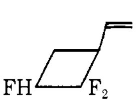
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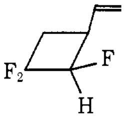
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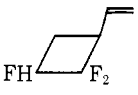
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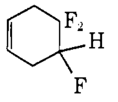
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Conditions	Product, % of Cross Adducts				
	1	2	3	4	5
Thermal, 215°					
Method A	29.3	14.9	30.4	12.8	12.7
Method B	27.3	14.8	30.7	13.0	13.8
Photosensitizer (E_T, kcal)					
Acetophenone (73.6)	28.5	22.5	29.5	19.0	~0.5
Phenanthrene (62)	26.5	23.0	29.5	20.5	~0.5
1-Acetonaphthone (56.4)	27.0	19.5	25.5	18.0	10.0
Biacetyl (54.9)	25.0	18.0	25.0	18.5	11.0
Fluorenone (53.3)	26.0	12.5	20.5	18.5	22.5

lithium aluminum hydride in refluxing tetrahydrofuran dechlorinated it to a mixture with the same retention times in glpc as **1** and the (3 + 4) mixture. Hydrogenation of the dechlorination product gave a mixture of the hydrogenation products of **1** and **3**; **1** and **3** accordingly are 1-vinyl-2,3,3-trifluorocyclobutanes.

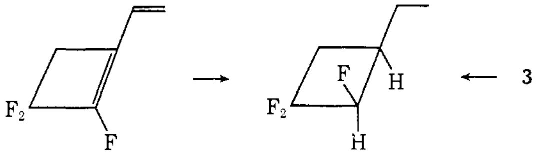
This assignment is supported by the mass spectra, summarized in Table II. Cleavage of the cyclobutane ring to monofluorobutadiene, *m/e* 72, is characteristic of A and B, while the corresponding cleavage of C and D gives difluorobutadiene, *m/e* 90. The last line of Table II shows that the intensity ratio of peak 72 to peak 90 is 37 times as great for isomer **1** as for isomer **2**, while the mixture of **3** and **4** has a value, 2.6, close to its composition, **3**:**4** = 2.4:1, confirming that **3** has the same orientation as **1**, with the single fluorine atom adjacent to the vinyl group.

Table II. Mass Spectra of the Trifluoroethylene–Butadiene Adducts at 70 eV

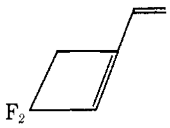
Mass *m/e*	Peak intensities relative to the base peak[a] Isomer number			
	1	2	3 + 4	5
136	1.2	0.9	3.4	36
116	1.1	0.4	0.1	3.5
115	1.0	0.2	0.1	7.6
106				3.9
103	1.0	0.2	0.1	4.0
97	3.1	0.8	0.3	4.6
96	1.2	0.4	0.1	3.9
95	2.7	1.1	0.3	6.6
90	7.6	36	16	42
77	5.9	1.6	5.1	10.5
73	2.6			4.8
72	56	7.4	41	100
64	3.4	5.4	6.9	6.9
59	7.3	0.6	5.5	9.0
57	5.3		4.1	5.4
55	5.8	4.8	5.2	
54	100	100	100	47
53	8.1	2.2	7.1	4.3
52	5.8		3.4	
51	10.5		8.0	7.0
50	4.0		3.0	3.6
Ratio 72/90	7.4	0.2	2.6	2.4

[a] Peaks which contribute less than 3% of a base peak are not entered unless a larger peak of the same mass is observed for one of the other compounds. Peaks with *m/e* less than 50 are not included. The stronger peaks in this category include 28, 29, 39, and 46 for all the compounds.

Basic dehydrohalogenation of the mixture of **6** and **7** proceeded in two stages, the isomer with the longer retention time in glpc reacting in 1 hr at or below 25°, while the other isomer was also dehydrohalogenated in 15 min at reflux. The single product, **8**, shows twin triplets at δ 2.74 and 2.53, $J \sim 2$ Hz in addition to normal signals for a vinyl group. The triplets are normal for CH_2 adjacent to CF_2 in a four-membered ring, the splitting of 12 Hz being due to the olefinic fluorine atom across the ring.[8] Catalytic hydrogenation of **8** again yields a single product, **9**, which would be expected to have the fluorine atom and the ethyl group cis to each other. **9** proves to be the hydrogenation product of **3**,


8 9

so that **1** is **A** and **3** is **B**. The mixture of **1** and **3**, obtained by dechlorination of the mixture of **6** and **7**, could be converted to 1-vinyl-3,3-difluorocyclobutene (**10**) in 20% yield by potassium *tert*-butoxide in refluxing *tert*-butyl alcohol in 2 hr. Some starting material was recovered; possibly only the isomer **3**, of favorable configuration, was dehydrofluorinated under these conditions. The 60-mHz nmr spectrum of **10** differed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from that of **8** in having a single triplet, $J \sim 2$, for the ring methylene and a 1-H singlet at δ 5.9, between the protons of the vinyl signal.

Photosensitized Cycloadditions. In addition to the thermal reaction carried out at 215°, photosensitized cycloadditions were done at room temperature with trifluoroethylene and butadiene, taken in a mole ratio of 5:1, and 6–8 mol % of photosensitizer based on butadiene. Conversions of the butadiene were from 40 to 99%; the products consisted mostly of butadiene

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(8) C. M. Sharts and J. D. Roberts, *J. Amer. Chem. Soc.*, 79, 1008 (1957).

Table III. Comparison of Trifluoroethylene Cycloaddition with Photosensitized Dimerization of Butadiene

Conditions	E_T[a]	(1 + 3)/ (2 + 4)	1/3	2/4	5	% vinylcyclohexene in dimer	
						This work	Ref 9
Thermal, 215°		2.16	0.96	1.16	12.7		
		2.09	0.89	1.14	13.8		
Photosensitized[b]							
Acetophenone	73.6	1.41	0.97	1.20	~0.6	3	3
Phenanthrene	62	1.29	0.89	1.11	~0.4	4	
1-Acetonaphthone	56.4	1.41	1.05	1.08	9.9	23	20
Biacetyl	54.9	1.36	1.00	0.97	11.9	29	35
Fluorenone	53.3	1.49	1.29	0.68	22.4	44	43

[a] G. S. Hammond, M. S. Herkstroeter, and A. A. Lamola, *J. Amer. Chem. Soc.*, **86**, 4537 (1964). [b] At room temperature.

dimers, with 1–5% of cross-cycloadducts. A standard analytical procedure was adopted using a glpc column of 10% 1,2,3-tris(2-cyanoethoxy)propane on 60–80 mesh Chromosorb P. This separated all products except for **3** and **4**, which formed a combined fraction. Chromatography of a parallel sample (after heating to isomerize the divinylcyclobutane) on a column of tricresyl phosphate, 10% on Chromosorb P, separated **3** and **4** from each other and from the rest. This method (method B) was also applied to the analysis of the thermal cycloadduct mixture. Table I compares the two methods for the thermal cycloadduct, and also records the proportions of cross cycloadducts in the cycloaddition with five photosensitizers having triplet excitation energies from 53.3 to 73.6 kcal/mol.

Table III compares the regioselectivities in the thermal and photosensitized reactions. The excited butadiene triplet which initiates the addition is appreciably less selective at 25° than is the ground-state diene at 215°; the latter attacks the CF_2 end of the olefin with a preference of 2.1 over the CHF end, whereas the excited state shows a preference of only 1.4, independent of the sensitizer used.

Discussion

The chief difference between the thermal and photosensitized reactions concerns the amount of trifluorocyclohexene in the product. For the two sensitizers of highest triplet energy, 62 and 73.6 kcal/mol, the cross adducts are more than 99% vinylcyclobutanes. For three sensitizers of energies from 56.4 to 53.3, the trifluorocyclohexene comprises from 9.9 to 22.4% of the cross adducts, being highest for the sensitizer of lowest energy. These results are parallel to those previously observed by Liu, Turro, and Hammond[9] in the photosensitized dimerization of butadiene. The sharply increasing amount of trifluorocyclohexene with the sensitizers of lower energy, shown in Table III for comparison, was interpreted as a consequence of a lower energy requirement for the transfer of triplet excitation to butadiene in the s-cis rather than the s-trans conformation. The term "s-cis" or "cisoid" for a distinguishable conformation of butadiene refers to molecules in a form far enough removed from the s-trans, of minimum energy, to permit direct formation of excited states or biradicals with cis allylic character. There appears to be no ground-state energy minimum corresponding to a fully cisoid conformation of butadiene,[4,10] but C_2 and C_3 are more π bonded in the excited state than in the ground state. As a result, among sensitizers capable of activating butadiene at all, those of lowest energy are considered to give the greatest proportion of cis triplets capable of forming biradicals which can close to six-membered rings. It is consistent with this interpretation that a similar effect should be observed in all photosensitized cycloadditions to butadiene, and it is also appropriate that photosensitized cycloadditions to cyclopentadiene, which can be only s-cis, should yield product compositions independent of the sensitizer.[11]

The clearest experimental distinction between concerted and stepwise cycloaddition is based upon retention or loss of configuration during cycloaddition, where either or both of the reactants have determinable geometrical configuration. The present results offer another experimental distinction, available where configuration is not involved but where a product, in this case trifluorocyclohexene, can be formed by either a concerted or an unconcerted mechanism. The problem is to what extent this 1,4-addition product in the thermal cycloaddition can be attributed to ring closure of a cisoid biradical. We propose that the triplet biradicals involved in photosensitized cycloaddition are good models of thermal biradicals with respect to product distribution, since the product formation occurs only on conversion from the triplet to the singlet state, and there are no constraints on the triplet that should make its internal rotations or eventual product distribution different from that of singlet biradicals such as occur in thermal cycloadditions.[12] According to the equation of Aston, Szasz, Woolley, and Brickwedde,[13] butadiene at 215° contains 15.4% of the cisoid conformation; in the case of 1122 thermal cycloaddition over a range of temperature yields only one molecule of dichlorodifluorocyclohexene for every 6.9 molecules of cisoid butadiene, which would lead us to expect a 2.2% yield of 1,4 adduct[2] in the present case by the biradical mechanism. The average yield of 0.5% (Table I) with the two high-energy photosensitizers at 25° corresponds to an expectancy of 2.2% for the yield of trifluorocyclohexene by the biradical mechanism at 215° on the independent assumption that cisoid and transoid triplet biradicals are formed statistically by a high-energy sensitizer and afford the same product distribution as singlet biradicals formed thermally. Each of these treatments tells us that of the 13% of trifluorocyclo-

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(9) R. S, H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, 87, 3406 (1965).

(10) (a) A. A. Bothner-By and D. Jung, *ibid.*, 90, 2342 (1968); (b) A. A. Bothner-By and D. F. Koster, *ibid.*, 90, 2351 (1968).

(11) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968).

(12) B. D. Kramer and P. D. Bartlett, *J. Amer. Chem. Soc.*, **94**, 3934 (1972).

(13) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

hexene actually found in the thermal cycloadduct, only about 2% can be from the biradical mechanism and the rest must be due to a surfacing of the concerted-reaction capability inherent in every diene–alkene reacting pair, but thoroughly latent in tetrafluoroethylene. Hence the total observed reaction between butadiene and trifluoroethylene is 11% concerted and 89% stepwise in mechanism.

Experimental Section

Cycloaddition Reactions. General Handling Procedure. Both thermal and photosensitized reactions were run in ampoules of heavy walled (at least 2 mm) Pyrex tubing. The ampoules, with predrawn necks, were annealed overnight in an annealing furnace before use and the final seal was also annealed carefully. The ampoules must not be more than a quarter full if they are to be heated. Failure to take any of these precautions may result in violent explosion of the ampoule. Both sealing and opening were done with the ampoules immersed sufficiently deeply in liquid nitrogen to freeze the contents.

Thermal Cycloaddition of 1,3-Butadiene and Trifluoroethylene. A 1-g sample of 1,3-butadiene (Union Carbide instrument grade, distilled before use) and 3 g of trifluoroethylene (Peninsular Chem Research Co., distilled bulb-to-bulb before use, bp −52°) were condensed into an ampoule surrounded by a Dry Ice–acetone bath. The ampoule was degassed by two freeze–pump–thaw cycles and then sealed as described. The ampoule was heated in a tube oven for 24 hr at 215 ± 5°. After cooling to room temperature, the contents were frozen by immersing the bottom of the tube in liquid nitrogen and the tube was opened. The excess trifluoroethylene was evaporated and the remaining contents distilled at 100–120°. Preparative glpc separation of the cross-adducts from each other as well as from 4-vinylcyclohexene and 1,5-cyclooctadiene was accomplished by two passes on a tricresyl phosphate column (30 ft × 0.25 in., 20% liquid phase on 60–80 mesh Chromosorb P, column temperature 90°, 30-μl injections, helium carrier gas flow rate 75 ml/min).

Analysis and Characterization of Cycloadducts. The isomers were analyzed as shown in Table IV. Analyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Table IV

	C	H	F	F (by difference)
Calcd for $C_6H_7F_3$	52.94	5.19	41.88	
Found				
1	52.74	5.25	41.67	42.01
2	52.70	5.27		42.53
3 and **4**	53.03	5.35	42.00	41.62
5	52.80	5.25		41.95

Table II summarizes the mass spectra of the cycloadducts.

Thermal Cycloaddition of Butadiene and Chlorotrifluoroethylene. In a heavy-walled Pyrex tube cooled to −80° with a Dry Ice–acetone bath were placed about 50 mg of hydroquinone, 9 g of butadiene, and 17 g of chlorotrifluoroethylene. The tube was sealed off so as to have a total inside volume of about 100 ml. This and a second tube containing the same amount of diene and hydroquinone and 13 g of chlorotrifluoroethylene were heated at 115° for 7 hr and the contents combined for work-up. The product amounted to 32.8 g, bp 115°–116° (lit.[6] 115°[6]; 109° (631 mm)).[7]

Photosensitized Cycloaddition of 1,3-Butadiene and Trifluoroethylene. Materials. Acetophenone (Fritsche Inc.), biacetyl (Eastman white label), and 1-acetonaphthone (Eastman Blue Label) were treated with maleic anhydride in triglyme at 230° for 10 min to remove anthracene and then recrystallized from 95% ethanol. 9-Fluorenone (Matheson Coleman and Bell) was recrystallized from 95% ethanol.

Irradiation Procedure. The reaction ampoules were charged with 0.35 g of 1,3-butadiene, 5 to 15 mol % (based on butadiene) of sensitizer, and a fivefold molar excess of trifluoroethylene (2.7 g). For those reactions run at 0 or 25°, 1.0 and 0.5 ml, respectively, of ethyl ether was also added to solubilize the sensitizer. (Product distributions do not change if the ether is left out but the yields are much lower for identical irradiation times.) The ampoules were degassed once by a freeze–pump–thaw cycle and sealed under vacuum. They were then strapped to a Pyrex immersion well in the appropriately thermostated water or water–methanol bath and irradiated with a 450-W Hanovia medium-pressure mercury lamp. Irradiation times were varied between 20 and 100 hr.

Product Analysis. After irradiation the ampoules were cooled in liquid nitrogen and opened; 50 mg of *n*-octane was added as an internal standard and the untreated trifluoroethylene (and any butadiene) distilled off. The contents of each tube were washed out and distilled. The pot residue was weighed to determine polymer amount. For acetophenone and phenanthrene, both of which were recoverable quantitatively from the reaction, no polymer appeared to be formed; 7% involatile product was formed when 1-acetonaphthone was used and 20% when 9-fluorenone was the sensitizer. Biacetyl was completely destroyed during the irradiation and appreciable side products other than cross-adducts and dimers of butadiene were formed.

The distilled reaction mixture was divided into two parts, one of which was placed in a small tube, degassed, sealed, and heated to 120° for 30 min to isomerize all the *cis*-1,2-divinylcyclobutane to 1,5-cyclooctadiene. Both samples were then analyzed on a column of 10% 1,2,3-tris(2-cyanoethoxy)propane, 30 ft × 1/8 in., 60–80 mesh Chromosorb P. (No difference in cross-adduct distribution was found in the two samples.) This column separated all the butadiene dimers from each other and from the cross-adducts, but separated only **1**, **2**, and **5** from a combined **3** and **4** peak. A column of 10% tricresyl phosphate, 30 ft × 1/8 in., 60–80 mesh Chromosorb P was used (for the heat-treated sample) to determine the ratio of **3** to **4** (the latter peaks would be covered by the *cis*-1,2-divinylcyclobutane if it had not been removed by heating).

A flame ionization response factor of 1.5 for cross adducts relative to octane was determined on adducts separated from the thermal reaction. Only **1** was collected in sufficient amounts from the photosensitized reaction for identification by matching ir spectra with adduct collected from the thermal reaction. The remaining photoadducts were identified by injecting samples both with and without added individual adducts obtained from the thermal reaction. Peak areas were determined on most runs with a disc integrator, although some were determined as well with a Hewlett-Packard 3370A digital integrator.

Preparation of 1-Vinyl-2,3,3-trifluorocyclobutene. A solution of alcoholic potassium hydroxide was prepared by adding 0.68 g (0.01 mol) of 85% potassium hydroxide to 15 ml of absolute ethanol. To this solution was added with stirring 1.7 g (0.01 mol) of 1-vinyl-2-chloro-2,3,3-trifluorocyclobutane (**6** + **7**). The resultant mixture was heated for 15 min on an oil bath. At the end of this time a large amount of precipitated potassium chloride was present. To the mixture was added 50 ml of water and 30 ml of ether. The aqueous layer was washed twice with 15 ml of ether. The combined ether solution was washed three times with 15-ml portions of water, dried over magnesium sulfate, filtered, and concentrated. The residue (2.5 g), a colorless solution, contained about 65% ether, and 10% ethanol. A new peak having a lower retention time than the starting material and representing about 24% of the mixture was observed on either MNPN or DIDP. The new compound was isolated pure by preparative vpc (MNPN column). The 60-mHz nmr spectrum showed t, δ 2.54, J = 3 Hz (1 H); t, δ 2.74, J = 3 Hz (1 H); m, δ 5.14–5.61 (2 H); dd, δ 6.55, J = 17, 11 Hz (1 H). Ultraviolet spectrum in 95% ethanol showed λ_{max} 225 nm (log ϵ 4.45).

When the same procedure as above was employed except that the reaction temperature was maintained at or below 25° for 1 hr, vpc analysis showed that one isomer of the **6** + **7** mixture (the one with higher retention time on DIDP or MNPN) was converted to **8** leaving the other isomer. Presumably then it is **6**, with the H and Cl trans, that has the longer retention time.

Hydrogenation of 1-Vinyl-2,3,3-trifluorocyclobutene (8). The hydrogenation was carried out on 2.27 g (0.017 mol) of **8** with 50 mg of platinum oxide in 20 ml of glacial acetic acid in a 450-ml Parr apparatus under 41 psi of hydrogen. A total drop in hydrogen pressure of 34 psi occurred over a 17-min period. The mixture was filtered and shaken with 50 ml of water and 80 ml of pentane. The pentane solution was washed four times with 25-ml portions of water, dried, filtered, and concentrated to 5 ml with a 2-ft vacuum-jacketed Helipak column. This solution was separated by preparative glpc, yielding 283 mg (13%) of starting material and 630 mg (27%) of **9** identified by its nmr spectrum. *Anal.* Calcd for

$C_6H_9F_3$: C, 52.17; H, 6.56; F, 41.26. Found: C, 52.22; H, 6.57; F, 41.47. The nmr spectrum showed t, δ 0.92, J = 7.5 Hz (3 H); m, δ 1.2–1.95 (2 H); m, δ 1.95–2.75 (3 H); dq, J = 52, 7.5 Hz (1 H).

Dechlorination of 1-Vinyl-2-chloro-2,3,3-trifluorocyclobutane (6 + 7). Tetrahydrofuran (50 ml) was added to 4.60 g (0.12 mol) of lithium aluminum hydride in a 250-ml flask. This mixture was cooled in an ice bath and stirred while 13.47 g (10 ml, 0.079 mol) of 1-vinyl-2-chloro-2,3,3-trifluorocyclobutane was added in 1-ml portions over a 5-min period. The mixture was then heated under reflux for 6.5 hr with stirring, stirred overnight, and then heated for a further 4 hr. The mixture was cooled in ice and 50 ml of cold 25% sulfuric acid was slowly added, followed by 50 ml of water and 150 ml of pentane. The pentane fraction, after 12 washings with 100-ml portions of water, was dried over calcium chloride and magnesium sulfate, filtered, and concentrated to about 10 ml through a 2-ft vacuum-jacketed Helipak column with a bath temperature of 50°. The separation of the product, a mixture of **1** and **3**, from solvent and starting material was accomplished by preparative glpc on the DIDP column with 1-ml injections. This column also yielded separate samples of pure **1** and **3**. The total yield of dechlorination product was about 40% without optimization. A similar reaction carried out in ether solution gave a yield not exceeding 20%.

Hydrogenation of the Butadiene–Trifluoroethylene Adducts. The hydrogenation of 0.324 g of distilled butadiene–trifluoroethylene reaction mixture (which contained about equal amounts of adducts and butadiene dimers) in 25 ml of glacial acetic acid using 40 mg of platinum oxide was carried out at 1 atm and 25°. Seventy-five minutes were required for the uptake of 96 ml (about the expected amount) of hydrogen. Work-up as above gave 1.25 g of a colorless pentane solution.

The hydrogenation of 0.68 g of an nmr sample of the vpc fraction containing **3** and **4**, about 40% in carbon tetrachloride, was carried out by adding the solution and 20 mg of platinum oxide to 25 ml of acetic acid and hydrogenating at 10 psi pressure in a Parr apparatus. After 40 min the pressure had fallen to 6 psi and did not drop any further. The usual work-up afforded 1.32 g of a pentane solution. The nmr of this solution showed that the unsaturated group had been completely hydrogenated. Vpc analysis showed two peaks at retention times greater than for solvent and in the ratio of 2.2 to 1. These peaks have the same retention times as two peaks in the trace from the hydrogenation of the whole mixture from butadiene and trifluoroethylene (all comparisons on a 20-ft DIDP column).

Conversion of Trifluorocyclohexene (5) into Fluorobenzene. Pure **5** (100 mg, 0.007 mol) was added to a solution of 470 mg of potassium *tert*-butoxide in 5 ml of *tert*-butyl alcohol. The mixture was heated to reflux for 1.5 hr, cooled and shaken with 4 ml of water and 5 ml of pentane. Carbon tetrachloride (1.0 ml) was added to the nonaqueous phase, which was dried and separated by distillation and vapor phase chromatography to yield a carbon tetrachloride solution of fluorobenzene for an ir spectrum. This spectrum was identical with that of authentic fluorobenzene.

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Cycloaddition. XIV. The Thermal Cycloaddition of Trifluoroethylene to Some Conjugated Dienes, and of Vinylidene Fluoride to Butadiene

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Abstract: Structures have been assigned to the thermal cycloadducts of vinylidene fluoride to butadiene and, except for cis–trans isomerism, to those of trifluoroethylene to isoprene, 2,3-dimethylbutadiene, and *cis*- and *trans*-1,3-pentadiene. Substantial amounts of (2 + 4) cycloadducts are obtained along with the (2 + 2) products. In the latter, the preferred orientation is that with the less fluorinated carbon atom adjacent to the unsaturated group in the cyclobutane. Trifluorovinyl chloride yields 1-alkenyl-2-chloro-2,3,3-trifluorocyclobutanes with the same dienes, this single orientation making it possible to establish the structures of the trifluoroethylene adducts by dechlorinating the alkenylchlorotrifluorocyclobutanes. Approximate rate constants have been assigned to the trifluoroethylene cycloadditions through their competition with the well-known dimerizations of the dienes.

In the thermal cycloaddition of fluorinated alkenes to conjugated dienes interest centers about the competition between concerted (Diels–Alder) and stepwise (biradical) mechanisms. The former lead exclusively to cyclohexenes, while the latter are capable of producing both cyclohexenes and cyclobutanes.[1] Therefore the determination of product compositions is the starting point for ascertaining the mechanism of the reaction. Earlier observations with 1,1-dichloro-2,2-difluoroethylene[2–8] have appeared to establish it as a typical biradical reagent affording cyclohexenes from dienes only by way of s-cis biradicals. In the case of butadiene, such s-cis biradicals close to cyclohexenes and vinylcyclobutanes in the ratio of 1:5,[4] while substitution of bulky groups in the 2 position of butadiene leads to an increase both of the fraction of biradicals

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