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

**Acknowledgment.** We thank the National Science Foundation and the National Institutes of Health for grants in support of this work. B. M. J. was assisted by a National Science Foundation Predoctoral Fellowship from 1966 to 1970. L. E. W. held a Postdoctoral Fellowship from the National Institutes of Health in 1966–1967.

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

**Leigh E. Walker and Paul D. Bartlett***

*Contribution from the Converse Memorial Laboratory, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.* *Received April 20, 1972*

**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

---

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

(2) P. D. Bartlett, G. E. H. Wallbillich, and L. K. Montgomery, *J. Org. Chem.*, **32**, 1290 (1967).

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

(4) J. S. Swenton and P. D. Bartlett, *ibid.*, **90**, 2056 (1968).

(5) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *ibid.*, **91**, 405 (1969).

(6) P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

(7) P. D. Bartlett, International Congress of Pure and Applied Chemistry, 23rd, Vol. 4, Butterworths, London, 1971, p 281.

(8) J. Mallet, Thesis, Harvard University, 1972.

having the s-cis conformation and of the fraction of these that close to six-membered rings.[3] Other recognized factors in this competition of mechanisms are the extent of destabilization of the alkene,[9] its possession of radical-stabilizing substituents, polar complementarity between the alkene and the diene, and, in geometrically constrained systems,[10] the $C_1$–$C_4$ distance in the diene. Photosensitized cycloaddition has been useful as a biradical model in establishing some of these conclusions.[7,11,12]

In this paper we report the thermal cycloaddition of vinylidene fluoride and trifluoroethylene to butadiene and several of its methyl-substitution products. The temperatures of these cycloadditions are high, indicating that vinylidene fluoride and trifluoroethylene are not in the class of very active producers of biradicals. Also the fraction of cyclohexenes in the products becomes so high (up to 74%) as to indicate prevalence of the concerted Diels–Alder mechanism, not because this mechanism is exceptionally favorable, but because the competing formation of biradicals is quite slow. In several cases the relative amounts of diene dimers and cross adducts formed, combined with known rate constants for dimerization, allow semiquantitative estimates of the rate constants for the cycloadditions. Observations on the regioselectivity of the cycloadditions throw a little more light on the nature of the singlet biradical formation process.

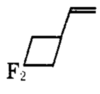
## Results

**Vinylidene Fluoride.** The heating of butadiene with vinylidene fluoride in heavy-walled Pyrex tubes at temperatures up to 200° gave only dimers of butadiene. Vapor chromatograms of products formed at temperatures from 225 to 260° showed small amounts of three peaks at retention times shorter than that of vinylcyclohexene, indicated in Table I as A, B, and C. Component C was isolated by vapor chromatography in the amount of 12 mg from 1.8 ml of the distilled product mixture and was shown to be 4,4-difluorocyclohexene by its nmr spectrum (unresolved 2-H multiplet at τ 4.4, several peaks at τ 4.2–8.5, 6 H). Too little of A and B was available for isolation and structure determination; the structures shown were assigned by glpc comparison with a sample of 1-vinyl-3,3-difluorocyclobutane made by lithium aluminum hydride dechlorination of the known[14] single (2 + 2) cycloadduct of 1,1-dichloro-2,2-difluoroethylene to butadiene. The enhancement of the peak for isomer A in the mixture is also consistent with the orientation of trifluoroethylene in its (2 + 2) cycloaddition,[13] where CHF appears as the slightly preferred radical-forming site.

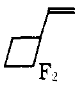
**Table I.** Reaction of Vinylidene Fluoride with Butadiene

| Temp, °C | Time, hr | Crude yield,[a] g | % cross adducts | Adduct composition, % A | B | C |
|---|---|---|---|---|---|---|
| 225 | 65 | 0.63 | 1.9 | 16 | 11 | 74 |
| 250 | 42 | 0.43 | 5.6 | 21 | 14 | 65 |
| 250 | 48 | 2.1[b] | 4.7 | 24 | 14 | 62 |
| 260 | 48 | 2.1[b] | 4.5 | 22 | 16 | 62 |

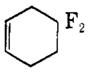
[a] With 70–100-ml tubes, vinylidene fluoride/butadiene molar ratio 2.5–3.0. Total material per tube 8–11 g. [b] Contents of three tubes combined.



A

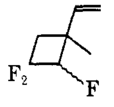


B

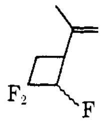


C

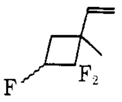
**Trifluoroethylene and Isoprene.** The thermal and photosensitized cycloaddition of trifluoroethylene to butadiene is described in an accompanying paper.[13] Isoprene and trifluoroethylene at 212° yield a product mixture containing ten cross-cycloadducts in addition to the expected dimers of isoprene. Six of these products are separated by a diisodecyl phthalate (DIDP) column and the other four are paired in fractions (2 and 8) whose nmr spectra indicate two components each. The 1,2 adducts, the 3,4 adducts, and the 1,4 adducts are distinguishable by the number (3, 2, and 1, respectively) of ethylenic protons that they display in the nmr. The 2,3,3-trifluoro-1-alkenylcyclobutanes (**1** and **2**) can be distinguished from their 2,2,3 isomers (**3** and **4**) by comparison[13] with the dechlorination products of the corresponding trifluorovinyl chloride adducts **7** and **8** which have only adjacent chlorine and alkenyl groups. The structures of **5** and **6** were determined by the alkaline dehydrofluorination of the isomers to *m*- and *p*-fluorotoluenes, which could be distinguished and analyzed by their infrared spectra. The structural assignments, without assignment of cis or trans configuration, are shown in Table II, two isomers corresponding to each orientation of the 1,2 and 3,4 adducts, **1–4**.



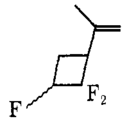
**1**
(cis + trans)



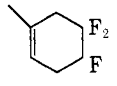
**2**
(cis + trans)



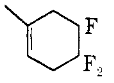
**3**
(cis + trans)



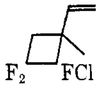
**4**
(cis + trans)



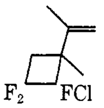
**5**



**6**



**7** $\xrightarrow{LiAlH_4}$ 1 (isomers 1 and 3)



**8** $\xrightarrow{LiAlH_4}$ 2 (isomers 4 and 7)

**Trifluoroethylene and 2,3-Dimethylbutadiene.** Of the five fractions in the cross cycloadduct of trifluoroethylene and 2,3-dimethylbutadiene at 215°, the fifth

---

(9) P. D. Bartlett and R. Wheland, *J. Amer. Chem. Soc.*, **94**, 1996 (1972).

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

(11) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965).

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

(13) P. D. Bartlett, B. M. Jacobson, and L. E. Walker, *J. Amer. Chem. Soc.*, **95**, 146 (1973).

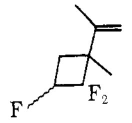
Table II. Cycloadducts of Trifluoroethylene to Isoprene at 212°

| Isomer | % of adduct mixture Run 1 | Run 2 | Structure |
|---|---|---|---|
| 1 | 24.0 | 22.0 | **1** |
| 2 | 7.5 | 7.3 | **3** |
| 3 | 21.4 | 20.3 | **1** |
| 4 | 8.0 | 8.0 | **2** |
| 5 | 9.3 | 8.7 | **3** |
| 6 | 2.7 | 2.5 | **4** |
| 7 | 7.5 | 8.0 | **2** |
| 8 | 3.3 | 4.7 | **4** |
| 9 | 10.2 | 11.7 | **5** |
| 10 | 5.4 | 6.9 | **6** |

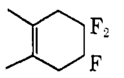
is readily recognized as a 1,4 adduct (**12**) by its single methyl peak in the nmr and the absence of ethylenic absorption, both features being in contrast to the other four adduct isomers. Of these four, the first and third were identical with products of $LiAlH_4$ dechlorination of the cycloadduct mixture (**9**) of trifluorovinyl chloride to dimethylbutadiene which, as in the cases of butadiene and isoprene, have a single orientation but a mixture of configurations. Table III shows the composition of the cycloadduct and the assignment of structures to the components.

**9**
(cis + trans)

**10**
(cis + trans)



**11**
(cis + trans)

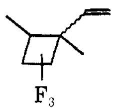


**12**

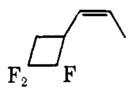
Table III. Cycloadducts of Trifluoroethylene to 2,3-Dimethylbutadiene at 212°

| Isomer | % of adduct mixture | Structure | % by structure |
|---|---|---|---|
| 1 | 27.6 | **10** | 53.1 |
| 2 | 7.3 | **11** | 17.3 |
| 3 | 25.5 | **10** | |
| 4 | 10.0 | **11** | |
| 5 | 29.7 | **12** | 29.7 |
| | Ratio of orientations | | |
| **10**/**11** | 3.1 | | |

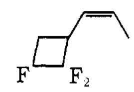
**Trifluoroethylene and the 1,3-Pentadienes.** The 20 possible isomers are covered by structures **13–19**. The first three vpc fractions, totaling 4.5% of the cis and 4% of trans cycloadduct, are assigned structure **13** both because the 3,4 adducts would be expected to be eluted first and because the nmr spectrum of the total cycloadduct shows about this proportion of methyl not on a double bond. These three peaks are also present in the cycloadducts from both *cis*- and *trans*-pentadienes, which is not true of the isomers (**14–17**) with configuration in the side chain.[14] These fractions were not isolated nor further resolved into the larger number of isomers that may well have been present.



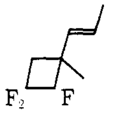
**13**
(8 isomers)



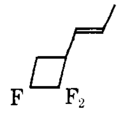
**14**
(2 isomers)



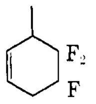
**15**
(2 isomers)



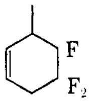
**16**
(2 isomers)



**17**
(2 isomers)



**18**
(2 isomers)



**19**
(2 isomers)

In the cycloadduct mixture from *cis*-1,3-pentadiene the fractions corresponding to peaks 4, 5, 6, and 7 were isolated by preparative vpc. Fractions 4 and 6 correspond by nmr and retention time to the two isomers prepared by dechlorinating the *cis*-piperylene–trifluorovinyl chloride cycloadduct, and accordingly these adducts have orientation **14**. It follows that the other two, 1,2-cycloadducts from the cis diene, must correspond to orientation **15** (peaks 5 and 7). By the same process of comparison with dechlorination products of the chlorotrifluoroethylene cycloadducts, the *trans*-propenylcyclobutanes from *trans*-1,3-pentadiene are assigned as in Table IV.

Table IV. Cycloadducts of Trifluoroethylene to *cis*- and *trans*-1,3-Pentadiene

| *cis*-1,3-Pentadiene | | | *trans*-1,3-Pentadiene | | |
|---|---|---|---|---|---|
| Fraction[a] | % | Structure | Fraction | % | Structure |
| 1 + 2 | 4[b,d] | **13** | 1 + 2 | 3.5[b,d] | **13** |
| 3 | 0.5[d] | **13** | 3 | 0.5[d] | **13** |
| 4 | 33 | **14** | 4 | 27 | **16** |
| 5 | 16.5 | **15** | 5 | 12.5 | **17** |
| 6 + 7 | 46[c] | **14** + **15** | 5b | 4 | *e* |
| | | | 6 | 28 | **16** |
| | | | 7 | 11.5 | **17** |
| | | | 8 | 9.3 | **18, 19** |
| | | | 9 | 2.8 | |

[a] On DIDP. [b] Two peaks. [c] Two peaks only slightly separated; (**14**)/(**15**) = ~2.5. [d] These peaks alone had identical retention times in the chromatograms from the cis and trans isomers. [e] A peak separated by MNPN and TCEP columns, but not identical with **14**, **15**, **16**, or **17**.

## Discussion

It should be possible to use the information obtained from the vpc product analyses to determine approximate rate constants for the cycloadditions, since each reaction involves a competition between a cross addition and a diene dimerization whose rate constant has been reported in the literature. The relationships involved are those of eq 1 and 2, where $x$ is the concentration of cycloaddition reagent, $y$ is that of the diene, $u = y/x$, and $m = k_a/(k_d - k_a)$.

$$\frac{dy}{dx} = \frac{k_d y}{k_a x} + 1 \tag{1}$$

$$\ln \frac{x_0}{x} = m \ln \frac{u_0 + m}{u + m} \tag{2}$$

---

[14] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, 616 (1964).

**Table V.** Approximate Rate Constants for Cycloadditions of Trifluoroethylene at 212°

| Diene | $10^4k_d$ | Ref | $x_0$ | $x$ | $u_0$ | $u$ | $m$ | $10^4k_a$ |
|---|---|---|---|---|---|---|---|---|
| Butadiene | 1.9 | *a* | 10.1 | 8.6 | 0.505 | 0.186 | 0.34 | 0.5 |
| | | | 5.8 | 3.8 | 1.33 | 0.710 | 2.2 | 1.3 |
| | | | 5.4 | 3.6 | 1.5 | 0.5 | 0.66 | 0.8 |
| Isoprene | 4.6 | *b* | 4.9 | 3.9 | 0.61 | 0.103 | 0.27 | 1.0 |
| 2,3-Dimethylbutadiene | 0.65 | *c* | 5.5 | 4.0 | 0.674 | 0.375 | −8.6 | 0.7 |

[a] G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725 (1939). [b] C. Walling and J. Peisach, *J. Amer. Chem. Soc.*, **80**, 5819 (1958). [c] J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

In principle, the compositions with respect to starting materials and products in a cycloaddition conducted for a known time at constant temperature should suffice for the determination of $m$ and therefore of $k_a$ from a known value of $k_d$. The practical limitations include the occurrence of variable amounts of diene polymerization, not recorded in the glpc results, the possibility of some reaction taking place in the liquid phase whereas the calculations assume uniform distribution of reactants in the vapor, and the fact that both $k_a$ and $k_d$ depend (and to different extents) on pressure, although under our conditions such dependence is relatively small. Three runs with butadiene with different reactant ratios and concentrations yielded values of $k_a$ with a mean deviation of 36%, indicating that the rate constants obtained in this way have only semiquantitative significance. Table V shows the figures used and the constants obtained for butadiene, isoprene, and 2,3-dimethylbutadiene. In addition, $k_a$ for vinylidene chloride and butadiene at 250° was estimated as $1.2 \times 10^{-5}$ l./(mol sec) by the equation applicable when the alkene is present in such excess as to be at essentially constant concentration.[15] The values of $k_d$ in Table V are calculated in each case from the activation parameters in the literature based on measurements whose conditions, temperature, and pressure ranges included or most closely approached those of this work. Table VI combines the results of rate and product distribution and assigns partial rate constants for the (2 + 2) and (2 + 4) additions of the reagents to the several dienes.

**Table VI.** Rate Constants for 1,2- and 1,4-Cycloaddition

| Reactants | Temp, °C | $10^4k_a$ | $10^4k_{(2+2)}$ | $10^4k_{(2+4)}$ | % 1,4 |
|---|---|---|---|---|---|
| Trifluoroethylene and | | | | | |
| Butadiene | 212 | 0.84 | 0.72 | 0.12 | 14 |
| Isoprene | 212 | 1.0 | 0.83 | 0.17 | 17 |
| 2,3-Dimethylbutadiene | 212 | 0.74 | 0.52 | 0.22 | 30 |
| Vinylidene fluoride and butadiene | 250 | 0.12 | 0.04 | 0.08 | 67 |

Trifluoroethylene reacts with dienes much more slowly than either tetrafluoroethylene or 1,1-dichloro-2,2-difluoroethylene, the factor in the latter case being of the order of $10^5$. The slower the overall cross cycloaddition, the larger fraction of the product is of the Diels–Alder type. This result agrees with the conclusion previously reached[1,13] that the ability to cycloadd *via* biradicals is more sensitive to structural variations than the ability to undergo concerted (2 + 4) cycloaddition. As the ability to form a favorable biradical becomes less, the concerted mechanism overtakes the stepwise one and a larger fraction of the reaction proceeds in the Diels–Alder manner.

In general the rates and orientations seen in the (2 + 2) cycloadditions in the present work are in good accord with previous experience with the biradical mechanism. Trifluoroethylene, though an unfavorable biradical-forming reagent compared to 1122, shows the same effects of methyl substitution in the diene on that part of its reaction which proceeds in the (2 + 2) manner as does 1122; isoprene shows mild acceleration in reaction at the substituted double bond, mild retardation in reaction at the unsubstituted double bond, and increased (2 + 4) cycloaddition, just as with 1122 at the much lower temperature of 80°. These results add nothing to the strong evidence[13] that about 11% of the reaction between trifluoroethylene and butadiene is concerted, but if this is so it is also normal that isoprene shows an increase in its concerted rate over butadiene, just as it does in reacting with maleic anhydride.[16]

The expected increase in skew conformation in 2,3-dimethylbutadiene might be expected to favor neither stepwise nor concerted addition, since all coplanar forms of the diene and of allylic radicals derived from it are mildly hindered by the methyl groups. In fact, while the (2 + 2) addition is less in rate and in proportion than with butadiene, the rate of the (2 + 4) cycloaddition has approximately doubled, again reflecting the effect of the same structure change on the rate of reaction with maleic anhydride.[16]

Again in these cycloadditions the regioselectivity indicates that $-CHF$ is a somewhat favored site for an odd electron in a biradical compared to $-CF_2$. The preference is only slightly greater in isoprene than in butadiene and is not very different in 3,4 from what it is in 1,2 cycloaddition (Table VII). Oddly, toward

**Table VII.** Regioselectivity in Trifluoroethylene–Isoprene Cycloaddition

| Structure | % of adduct mixture Run 1 | % of adduct mixture Run 2 |
|---|---|---|
| **1** | 45.4 | 42.3 |
| **2** | 15.5 | 16.0 |
| **3** | 16.8 | 16.0 |
| **4** | 6.0 | 7.2 |
| **5** + **6** | 15.6 | 18.6 |
| Ratio of orientations | | |
| **1**/**3** | 2.7 | 2.6 |
| **2**/**4** | 2.6 | 2.2 |
| (**1** + **3**)/(**2** + **4**) | 2.9 | 2.5 |

---

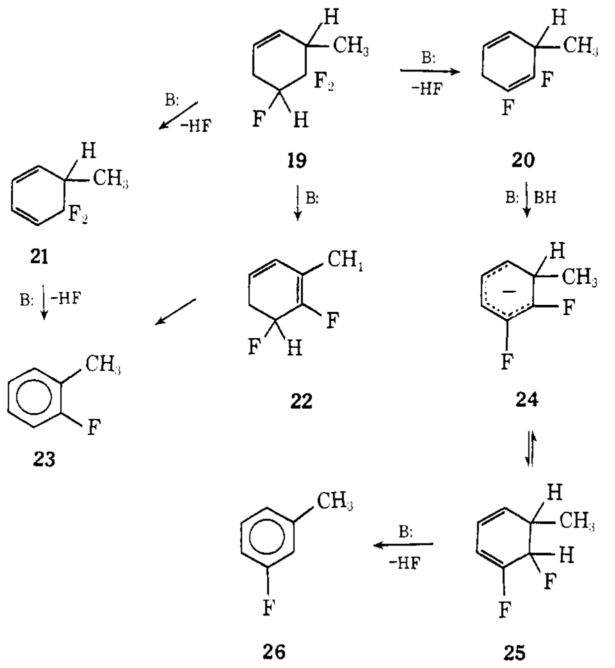
[15] P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 628 (1964).

[16] D. Craig, J. J. Shipman, and R. B. Fowler, *ibid.*, **83**, 2884 (1961).

butadiene the regioselectivity between $-CF_2$ and $-CH_2$ is slightly less than between $-CF_2$ and $-CHF$ (Table I and ref 13). It does not seem likely that the difference in temperature between 212 and 250° can account for this difference. Probably the order of free radical accommodation is $-CH_2 > -CHF > -CF_2$, but the formation of the first C–C bond in the two-step mechanism is enough more favorable at $-CH_2$ to prevent the regioselectivities from forming a smooth series where one of the test compounds has the $-CH_2$ group and the other does not.

There is an unresolved question with respect to the orientations in the products **18** and **19** from *trans*-piperylene and trifluoroethylene. Vapor chromatography (Table IV) suggests that these isomers are present in the ratio of 3.3 to 1. However, the apparently complete dehydrofluorination of these combined fractions yields *m*- and *o*-fluorotoluenes in the ratio of 19:1. If the chromatographic fractions represent pure **18** and **19** as assigned, these results mean that the dehydrofluorination of these trifluorocyclohexenes is not by a purely E2 mechanism, but involves reversible anion formation with, therefore, the possibility of allylic rearrangement (Scheme I). The most acidic hydrogen in **19** may well be the one geminal to the single fluorine atom, despite its nonallylic character. The related carbanion can form no diene but **20**, which is unconjugated and destabilized by the fluorines on the double bond. Removal of its most acidic hydrogen would lead through **24** to the more favored diene **25**, which would now result in *m*-fluorotoluene (**26**) rather than the expected ortho isomer. Either of the possible E2 processes, *via* **21** or **22**, would lead from **19** to *o*-fluorotoluene (**23**).

**Scheme I**



If this surmise is correct, the reversibility of anion formation depends critically upon the structure, for the isoprene adducts **5** and **6** are aromatized to a fluorotoluene mixture in agreement with the glpc analysis and with expectancy based on the E2 mechanism. The only difference between the two cases is that **5** has a secondary allylic proton pair rather than a tertiary allylic proton, vicinal to the geminal $CF_2$ group. This $CH_2$ may in that case be more acidic than the nonallylic $-CHF$ proton, avoiding the formation of an intermediate that requires rearrangement in order to aromatize.

It is of interest that the attack of *free radicals* on trifluoroethylene occurs preferentially at the less fluorinated carbon atom, in contrast to the biradical formation in cycloaddition. Table VIII summarizes several such selectivities reported in the literature. A significant difference between free radical attack and biradical formation is that the former is exothermic and the latter endothermic, so that the transition state for free radical attack has experienced less electron reorganization from the starting materials than that for cycloaddition. Thus the Hammond postulate suggests that the initial electron availability at the bonding site, relative to the electron accommodation at the free radical site, is more important in free radical attack than in biradical formation.

**Table VIII.** Regioselectivity in Free-Radical Attack on Trifluoroethylene

| Radical | $RCF_2CHF\cdot/RCHFCF_2\cdot$ formed | Ref |
|---|---|---|
| $F_3CS\cdot$ | 0.04 | *d*, *c* |
| $HS\cdot$ | 0.18 | *e* |
| $H_2P\cdot$ | 0.18 | *b* |
| $CH_3S\cdot$ | 0.28 | *d*, *c* |
| $CF_3\cdot$ | 0.35 | *a* |
| $Br\cdot$ | 0.82 | *a* |
| Biradical formation by dienes | 2–3 | This work |
| Cationic attack (HCl, ICl, $CH_3OH$) | ~0 | *a*, *b*, *f* |

[a] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957). [b] R. Fields, H. Goldwhite, R. N. Haszeldine, and J. Kirman, *J. Chem. Soc. C*, 2075 (1966). [c] R. N. Haszeldine, *et al.*, unpublished, cited in footnote *b*. [d] J. F. Harris, Jr., and F. W. Stacey, *J. Amer. Chem. Soc.*, **83**, 840 (1961). [e] J. F. Harris, Jr., and F. W. Stacey, *ibid.*, **85**, 749 (1963). [f] J. D. Park, W. R. Lycan, and J. R. Lacher, *ibid.*, **73**, 711 (1951).

## Experimental Section

The procedures for the sealed tube reactions were those described elsewhere[13] for the case of trifluoroethylene and butadiene. Trifluoroethylene (Peninsular Chem. Research, Inc.), vinylidene fluoride, butadiene, and chlorotrifluoroethylene (all from the Matheson Company) were used directly from the cylinders as received. Isoprene was a recently distilled commercial sample. Part of the 2,3-dimethylbutadiene was prepared by the method in ref 17 and part was purchased from the Aldrich Chemical Co.

**Reaction of Butadiene with Vinylidene Fluoride.** The runs described in Table I were carried out by condensing the indicated amounts of vinylidene fluoride and butadiene into Pyrex tubes of 1-in. outside diameter, each containing about 50 mg of hydroquinone. Tubes that were sealed containing more than about one-seventh of their total volume of liquid at −95° exploded when heated above 100°. At the end of the heating period the tubes were opened and the crude product mixture was distilled, the material boiling up to 130° being collected. Analytical glpc gave the compositions indicated in Table I. Adduct C was obtained (12 mg) by injecting three 0.6-ml portions of the mixture on a DIDP column at 120°and collecting the appropriate fraction.

---

(17) "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 312.

Table IX. Addition of Chlorotrifluoroethylene to Dienes

| Diene | Reaction temp, °C | Heating time, hr | Diene wt, g | Olefin wt, g | Distilled product, g | Bp, °C |
|---|---|---|---|---|---|---|
| Butadiene | 110 | 8.5 | 5 | 12 | 8.8 | 112–119<br>(Mostly 115–116) |
| Butadiene | 110 | 10 | 5, 7[a] | 7, 14[a] | 22.6 | 115–116 |
| Butadiene | 115 | 7 | 9, 9[a] | 17, 13[a] | 32.8 | 115–116 |
| Chloroprene | 120 | 14.5 | 5 | 9.5 | 7.9[b] | 145–150 |
| Isoprene | 110 | 8 | 4 | 7 | 6.5[b] | 128–136 |
| 2,3-Dimethylbutadiene | 120 | 14.5 | 1.5 | 8.5 | 2.6 | 139–152 |
| *cis*-1,3-Pentadiene | 115 | 28.5 | 2.1 | 5 | 5.2 | 139–142 |
| *trans*-1,3-Pentadiene | 115 | 28.5 | 2.5 | 5 | 4.3 | 140–143 |

[a] Two tubes run together, product combined for distillation. [b] The ratio of (**1,2**)/(**3,4**) products for chloroprene is 3.3, for isoprene 3.8.

**Preparation of 3,3-Difluoro-1-vinylcyclobutane.** To a solution prepared from 2.93 g (0.077 mol) of $LiAlH_4$ in 10 ml of THF was added 2.28 g (1.6 ml, 0.012 mol) of 1-vinyl-2,2-dichloro-3,3-difluorocyclobutane. The mixture was refluxed for 32 hr. Dilute sulfuric acid was added slowly to the mixture. The organic layer was taken up in pentane, washed with water, and distilled through a spinning band column leaving 0.94 g of crude product. The pure product (100 mg) was obtained *via* preparative glpc with a 22 × 0.25 in. γ-nitro-γ-methylpimelionitrile column.

**Structures of the Isoprene–Trifluoroethylene Adducts.** The crude product mixture from the addition of 4 ml of isoprene to 5 g of trifluoroethylene in a sealed tube at 218° for 16.2 hr was analyzed on the 12-ft DIDP column without interference from the isoprene dimers or other impurities. The second adduct fraction when collected on the Autoprep and then rechromatographed with an MNPN column shows two peaks in the ratio 2:5. The nmr spectrum of the mixture shows two ring methyl signals at 8.6 and 8.7 τ in the ratio 53:17. The relative amounts of isomers **2** and **3** shown in Table II were obtained by averaging these two ratios. The separation of components 9 and 10 on the 22-ft MNPN column (75°, flow 50 ml per min) was good at first but declined with age and use of the column. The total cycloadduct was subjected to elemental analysis. *Anal.* Calcd for $C_7H_9F_3$: C, 55.99; H, 6.04; F, 37.96. Found: C, 56.01; H, 6.24; F, 38.10.

**Dechlorination of Chlorotrifluoroethylene–Isoprene Adducts.** A 2-g sample of lithium aluminum hydride and 2.8 g (0.015 mol) of the chlorotrifluoroethylene–isoprene adducts were added to 50 ml of ether. The mixture was stirred overnight, cooled in ice, and treated slowly with 40 ml of 25% sulfuric acid and 50 ml of water. The ether solution was washed with water (50 ml), dried over calcium chloride, filtered, concentrated, and distilled to give 2.1 g of a mixture which assayed for 80% starting material and 20% product. The product isomers were collected by preparative glpc for comparison with the isoprene adduct mixture with respect to chromatography on both MNPN and DIDP columns.

It was subsequently found that the yield of such a dechlorination reaction is at least doubled under similar conditions by the use of tetrahydrofuran instead of ether as the solvent.

**Conversion of Methyltrifluorocyclohexenes to Fluorotoluenes.** The aromatization was accomplished by treating 70 mg (0.47 mmol) of the pure 1,4-adduct mixture (5 and 6) with the solution of 188 mg (1.7 mmol) of potassium *tert*-butoxide in 2 ml of *tert*-butyl alcohol. The mixture was refluxed for 2.5 hr, cooled, and treated with 1 ml of water and 5 ml of pentane. Carbon tetrachloride (0.5 ml) was added to the pentane and the resulting solution was washed three times with 5-ml portions of water, dried over calcium chloride, filtered, and concentrated to about 1 ml. The carbon tetrachloride and fluorotoluene fractions were collected and subjected to analysis by ir and glpc. Although the two fluorotoluenes are not separated from each other, vapor chromatography was carried out on both MNPN and DIDP columns to establish identity of the retention times with those of the known compound. For infrared comparison known solutions of *m*- and *p*-fluorotoluenes were prepared by adding 0 to 60 μl of *m*-fluorotoluene and 0–60 μl of *p*-fluorotoluene (total of each sample 60 μl) to 1.0 ml of carbon tetrachloride and these solutions were scanned on the same instrument. Linear curves were then obtained for absorption *vs.* concentration of *m*-fluorotoluene at 7.7, 7.8, 8.6, 10.7, 11.5, and 14.6 μ and for *p*-fluorotoluene at 5.2, 8.0, 8.5, 9.0, 9.7, and 11.7 μ. From these curves the composition of the aromatization mixture and hence of the 1,4-adduct mixture was determined.

**Structures of the 2,3-Dimethylbutadiene–Trifluoroethylene Adducts.** Tetrahydrofuran (35 ml) and 3.5 g (0.17 mol) of the 2,3-dimethylbutadiene–chlorotrifluoroethylene adduct were added to 3.3 g (0.089 mol) of lithium aluminum hydride. The mixture was stirred, refluxed for 7 hr, and cooled, and 40 ml of 25% sulfuric acid was slowly added followed by 50 ml of water and 50 ml of pentane. The pentane extract was washed ten times with 25 ml of water, dried over calcium chloride, filtered, and concentrated to 10 ml of solution using a 2-ft vacuum-jacketed column packed with glass beads. Short-path distillation of the concentrate gave, after an 8-ml fraction containing mostly pentane and tetrahydrofuran, a 2.09-g fraction, bp 120–135° (bath 140–160°) and leaving 165 mg of a light yellow free-flowing residue. The main fraction was shown by vapor chromatography to contain 17% tetrahydrofuran, 58% of the one isomer of **10**, 15% of the other isomer of **10**, and 10% of the starting material (**9**). The residue contained the isomers of **10** and starting material in the ratio of 42:17:41, respectively. The yield of **10** is about 50% and the ratio of the two isomers is about 4:1. Pure samples of the isomers were obtained using the DIDP preparative column at 130° with a helium flow of 150 ml per min. These compounds have the same retention times as the adducts **1** and **3** in Table III on both MNPN and DIDP columns.

Analysis of the 2,3-dimethylbutadiene–trifluoroethylene adducts gave the following. Calcd for $C_8H_{11}F_3$: C, 58.52; H, 6.76; F, 34.72. Found for the sum of fractions 1–4: C, 58.68; H, 7.00; F, 34.34. Found for fraction 5: C, 58.69; H, 6.79; F, 34.83.

**Cycloaddition of Trifluoroethylene to *cis*-1,3-Pentadiene.** In a 24-cm long 0.75-in. o.d. heavy-walled Pyrex tube were placed 50 mg of hydroquinone, 3.5 ml of *cis*-1,3-pentadiene, and 5 g of trifluoroethylene. The tube was sealed and heated in a tube oven at 215 ± 4° for 16 hr. The tube was cooled, opened, and warmed to room temperature. The 3.8 g of crude product was distilled to give 2.4 g of an adduct fraction boiling from 98 to 128° (bath temperature from 125–180°). In a separate experiment from 4.5 ml of *cis*-pentadiene and 7 g of trifluoroethylene heated at 220 ± 3° for 22.3 hr, 6 g of black solution was obtained which yielded on work-up 3.8 g of colorless liquid, bp 110–140° (bath temperature 150–170°), and 1.17 g of black residue. Analysis of the adduct mixture gave the following. Calcd for $C_7H_9F_3$: C, 55.99; H, 6.04; F, 37.96. Found: C, 56.09; H, 6.18; F, 38.13.

Vapor chromatography on DIDP preparative column at 120° with 0.2-ml injections yielded three easily separated major isomers (fractions 4–6, Table IV) comprising 95.5% of the cycloadduct.

**Preparation *via* the Chlorotrifluoroethylene Adducts.** Chlorotrifluoroethylene (5 g) and *cis*-pentadiene (2.6 ml) were heated with a little hydroquinone in a heavy-walled Pyrex tube at 115° for 28.5 hr. The contents of the tube was distilled giving 5.15 g of liquid, bp 139–142°.

This adduct (2.63 g, 1.4 mmol) was dechlorinated with lithium aluminum hydride in tetrahydrofuran as described for the other dechlorinations. The product was extracted with pentane and the washed pentane extract concentrated to 4 ml. From this solution sufficient quantities of the two isomers of **14** were isolated by means of an MNPN preparative column to obtain nmr spectra which confirmed their identity with fractions 4 and 6 of Table IV.

**Cycloaddition of Trifluoroethylene to *trans*-1,3-Pentadiene.** This cycloaddition, carried out in the same manner as the others at 216° for 15.5 hr, yielded 3.33 g of crude product which on short-path distillation gave 2.52 g of colorless liquid boiling at 128–143° and leaving 0.8 g of residue. A second preparation with 4.3 ml of *trans*-pentadiene and 7 g of trifluoroethylene at 220° for 22.3 hr gave 3.62 g of volatile product, bp 120–140°. The DIDP Autoprep column at 120° with a helium flow of 120–125 ml/min separated the 1,2 and 3,4 adducts from the 1,4 adducts and all the adducts from the dimers.

The adduct (4.3 g) was prepared from chlorotrifluoroethylene (5 g) and *trans*-pentadiene (3 ml). Dechlorination in the same manner as for the cis case consumed all the starting material. The product isomers were obtained pure for nmr spectra by preparative glpc.

**Structure of the *trans*-1,3-Pentadiene–Trifluoroethylene 1,4 Cycloadducts.** Fractions 8 and 9 of Table IV were obtained free of the other components by preparative vapor chromatography. The mixture of these two components (75 mg) was added to a solution containing 131 mg of potassium *tert*-butoxide in 1.6 ml of *tert*-butyl alcohol. The solution was refluxed for 1.5 hr, diluted with water, and extracted with pentane. The pentane extract was washed four times with 5-ml portions of water, dried over calcium chloride, decanted, and concentrated with a 10-cm bead-packed column. The fluorotoluene peak was collected by preparative glpc and examined as a carbon tetrachloride solution by glpc and infrared analysis. The infrared spectrum was compared with those obtained from a series of solutions prepared in an analogous manner to those used in the study of the aromatization products from the isoprene cycloadducts. This analysis showed that the *o*-fluorotoluene contributes less than 10% to the fluorotoluene mixture. Glpc analysis (22 ft MNPN) indicates a ratio of *o*- to *m*-fluorotoluene of 1:19.

**Addition of Chlorotrifluoroethylene to Dienes.** Hydroquinone (∼50 mg) was placed in a heavy-walled Pyrex tube cooled to −80° with a Dry Ice–acetone bath and the amounts of diene and chlorotrifluoroethylene indicated in Table IX were added.

**Acknowledgment.** We gratefully acknowledge support of this research by grants from the National Science Foundation and the National Institutes of Health. L. E. W. thanks the National Institutes of Health for a postdoctoral fellowship.

# Stereochemistry of the Noncatalytic Addition of Molecular Deuterium to Cyclopentadiene[1]

**F. A. L. Anet* and Francois Leyendecker[2]**

*Contribution No. 2972 from the Department of Chemistry, University of California, Los Angeles, California 90024.* *Received April 11, 1972*

**Abstract:** The noncatalytic reaction of deuterium gas with cyclopentadiene at 300° is found by nmr spectroscopy to give both *cis*-3,5-dideuteriocyclopentene and undeuterated cyclopentene. With deuterons and olefinic protons decoupled, the proton spectrum of *cis*-3,5-dideuteriocyclopentene is analyzed as an $A_2BC$ system where the A protons are on $C_3$ and $C_5$ and the BC protons are on $C_4$. The following parameters are obtained: $\delta_A = 2.282$ ppm, $\delta_B = 1.797$ ppm, $\delta_C = 1.808$ ppm, $J_{AB}(\text{trans}) = 5.63$ Hz, $J_{AC}(\text{cis}) = 9.46$, $J_{BC}(\text{gem}) = -12.74$ Hz. The difference ($0.012 \pm 0.002$ ppm) between $\delta_B$ and $\delta_C$ represents a real stereochemical isotope-effect chemical shift. The formation of undeuterated cyclopentene is ascribed to a concerted Woodward–Hoffmann allowed suprafacial transfer of two hydrogen atoms from *cis*-3,5-dideuteriocyclopentene to cyclopentadiene. The stereochemistry of the deuterated cyclopentene is in agreement with a concerted suprafacial 1,4 addition of molecular deuterium to cyclopentadiene.

The thermal, noncatalytic eliminations of molecular hydrogen from 1,4-cyclohexadiene[3] and cyclopentene[4] to give benzene and cyclopentadiene, respectively, appear to be concerted reactions obeying the Woodward–Hoffmann rules.[5] Baldwin[4c] has shown that both 1,2 and 1,4 eliminations of hydrogen from cyclopentene take place at 550°, and that 1,4 elimination is favored over 1,2 elimination by a factor of 6. It has also been observed that molecular hydrogen can add to cyclopentadiene in an uncatalyzed reaction to give cyclopentene.[4d] Only in the cyclohexadiene case,[3d,e] however, has the stereochemistry of the addition or elimination of molecular hydrogen been determined. In the present work, we have studied the uncatalyzed addition of molecular deuterium to cyclopentadiene as a means of determining the stereochemistry of the reaction.

## Results and Discussion

The reaction of cyclopentadiene with a large excess of deuterium gas at a pressure of about 40 atm (measured at room temperature) was carried out in a stainless-steel vessel containing phenothiazine at 300° for 4.5 hr. Experiments with hydrogen gas showed that the presence of phenothiazine effectively inhibited hydrogenation reactions catalyzed by the walls of the vessel, and completely prevented the formation of cyclopentane. At 300°, the hydrogenation was effectively irreversible.

The cyclopentene fraction was isolated by vpc from the volatile reaction product of the cyclopentadiene–deuterium reaction, and its 100-MHz proton spectrum was obtained under (i) normal conditions, (ii) with the deuterons decoupled, and (iii) with both the deuterons and the olefinic protons decoupled (Figure 1). Only the spectrum taken under condition iii will be discussed in detail.

The most likely structure for the "deuterated cyclopentene" is *cis*-3,5-dideuteriocyclopentene (I).

---

(1) This work was supported by USPHS Grant No. GM12769.

(2) Holder of an Otan fellowship.

(3) (a) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966); (b) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967); (c) S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, **89**, 5351 (1967); (d) H. M. Frey, A. Krantz, and I. D. R. Stevens, *J. Chem. Soc. A*, 1734 (1969); (e) I. Fleming and E. Wildsmith, *Chem. Commun.*, 223 (1970).

(4) (a) D. W. Vanas and W. D. Walters, *J. Amer. Chem. Soc.*, **70**, 4035 (1948); (b) H. Tanji, M. Uchiyama, A. Amano, and H. Tokuhisa, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **70**, 307 (1967); (c) J. E. Baldwin, *Tetrahedron Lett.*, 2953 (1966); (d) C. J. Grant and R. Walsh, *Chem. Commun.*, 667 (1969).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 141.