the procedure of Capon and Chapman.[13] Steam distillation of the strongly acid reaction medium yielded 2-chloro-4-*t*-butylaniline (**27**) directly, bp 136–137°, $n^{20}D$ 1.5495, the refractive index being determined on a product of preparative vpc on a column of 15% SE 52 and 5% Bentone-34. The conversion of **27** into 3-chloro-4-fluoro-*t*-butylbenzene (**15b**) was carried out by the procedure based upon those reviewed by Roe[14] wherein diazonium fluoroborate was precipitated, air dried, and pyrolyzed under conditions of the vpc separation of **15a** and **15b**. The product prepared in this manner was shown to be identical with the minor component of the aromatization mixture. It had bp 81–82° (10 mm) and a refractive index of $n^{20}D$ 1.4968 after vpc on a QF-1 column.

For preparation of the other isomer **22** was nitrated to **23** by the procedure of Carpenter, *et al.*[12] **23** was hydrolyzed directly to **25** with 50% potassium hydroxide, the nitroamine being isolated as red-brown crystals, mp 103–104.5° (lit.[12] 102.5–105.5°). The amine **25** was converted to 3-nitro-4-chloro-*t*-butylbenzene (**26**) by diazotization in concentrated sulfuric acid[15] and reaction with cuprous chloride as described by Hartman and Brethphen.[16] Compound **26** was accompanied by substantial amounts of *m*-nitro-*t*-butylbenzene, the main fraction of the steam distilled and redistilled product consisting of 89% of **26** and 11% of *m*-nitro-*t*-butylbenzene as determined on a column of 20% Apiezon L on Chromosorb P. The yield of **26** in this step was thus 28%.

The nitro compound **26** was reduced to the amine **28** with 100 mesh iron metal at reflux in a mixture of ethanol and water containing calcium chloride. After distillation (bp 131–134° (14 mm)) and preparative vpc on a column with 15% SE 52 and 5% Bentone-34 on Chromosorb W 2-chloro-5-*t*-butylaniline (**28**) was isolated, $n^{20}D$ 1.5490.

3-Fluoro-4-chloro-*t*-butylbenzene (**15a**) was obtained from **28** by exactly the same procedure for introducing fluorine as was used in the preparation of **15b**. It was obtained by distillation (bp 81–82° (10 mm)) and preparative vpc on a QF-1 column as a colorless liquid, $n^{20}D$ 1.4975, showing greater than 99.8% purity by analytical vpc. The over-all yield of **15a** from acetanilide was 11%. This compound was shown to have the retention time of the major component of the aromatized mixture under the conditions of the analytical vapor chromatography.

The composition of the 1,4 cycloadducts to isoprene was similarly established by aromatization and by synthesis of 3-chloro-4-fluorotoluene. This compound was prepared by diazotizing 2-chloro-*p*-toluidine (Aldrich Chemical Co.) in the presence of fluoroboric acid (Baker Chemical Co.) and pyrolysis of the resulting diazonium salt. A 25% yield of 3-chloro-4-fluorotoluene, bp 152–154°, was obtained. The material showed the expected 1:1 ratio of aromatic (τ 2.85 to 3.30) to aliphatic (τ 8.80 singlet) protons with no extraneous signals. When the synthetic material was added to the mixture of toluenes obtained from the aromatization of the isoprene–1122 1,4 adducts and this mixture was analyzed by vpc, the minor component was enhanced by a factor of 6 with no other change in the appearance of the spectrum.

The elementary analyses of 20 cycloadducts and derived compounds are shown in Table VII.

Acknowledgment. We thank the National Science Foundation, National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the B. F. Goodrich Co. for support of different parts of this work. We also thank the National Academy of Sciences–National Research Council for a postdoctoral fellowship to J. S. S. and the National Science Foundation for a postdoctoral fellowship to A. S. W. and for a predoctoral fellowship to B. D. K.

---

[13] B. Capon and N. B. Chapman, *J. Chem. Soc.*, 600 (1957).

[14] A. Roe, *Org. Reactions*, **5**, 193 (1949).

[15] H. H. Hodgson and J. A. Walker, *J. Chem. Soc.*, 1620 (1933).

[16] W. W. Hartman and M. R. Brethphen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 162.

Cycloaddition. VI. Competitive 1,2 and 1,4 Cycloaddition of 1,1-Dichloro-2,2-difluoroethylene to Butadiene

John S. Swenton and Paul D. Bartlett

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received September 18, 1967*

Abstract: A reinvestigation of the cycloaddition of 1,1-dichloro-2,2-difluoroethylene (1122) to butadiene has revealed the presence of a small amount of a second component in the product. This component is shown to be 1,1-dichloro-2,2-difluoro-Δ^4-cyclohexene on the basis of spectroscopic evidence and its dehydrohalogenation by strong base to *o*-chlorofluorobenzene. A study of the temperature dependence of 1,2 and 1,4 addition of 1122 to butadiene shows that the fraction of 1,4 adduct changes with temperature in the same way as the fraction of butadiene having the cisoid conformation. The 1,4 adduct varies in amount from 0.9% at 60° to 2.3% at 176°. Within experimental error the difference in activation energy between 1,2 and 1,4 addition of 1122 to butadiene is only the energy difference between cisoid and transoid butadienes.

The preceding paper in this series[1] confirmed a prediction of the biradical mechanism for cyclobutane-forming cycloaddition of fluorinated olefins to open-chained dienes. Since the 1,2 cycloaddition is associated with a prevalent transoid conformation of the diene, substituents tending to favor the cisoid conformation should increase the amount of 1,4 cycloaddition by the biradical mechanism. The observation[1] that even a methyl group in the 2 position causes isoprene to yield 1.6% of 1,4 addition with 1,1-dichloro-2,2-difluoroethylene (1122) at 80° prompted a reinvestigation of the well-known case of butadiene itself, for which only 1,2 cycloaddition of fluorinated olefins has previously been reported.[2,3]

Results

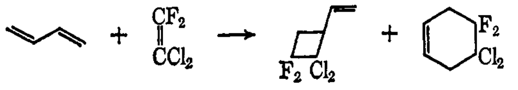
The reaction of butadiene with 1122 has now been found to form, as a minor product, the 1,4 adduct,

---

[1] Part V: P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Am. Chem. Soc.*, **90**, 2049 (1968).

[2] Part I: P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964).

[3] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).



1 2

1,1-dichloro-2,2-difluoro-Δ^4-cyclohexene (2). This product, amounting to less than 1% of the cycloadduct at 60°, was isolated by preparative vapor phase chromatography and distinguished from the 1,2 cycloadduct by its nuclear magnetic resonance spectrum and by its conversion with potassium *t*-butoxide into *o*-chlorofluorobenzene.

The nmr spectrum shows the presence of ethylenic and allylic hydrogens in the ratio of 2.00:4.20, in a pattern closely similar to that seen in the 1,4 cycloadducts to the 2-alkylbutadienes of part V.[4] The ethylenic absorption occurs at τ 4.38. The two ring hydrogens adjacent to chlorine absorb at τ 6.87, and the two adjacent to fluorine in a triplet (J = 13 cps) centered at τ 7.18 with its downfield portions submerged under the τ 6.87 peak. A high-resolution mass spectrum performed through the courtesy of Dr. John M. Wright shows a parent peak at 185.9814, equal to the calculated value for $C_6H_6Cl_2F_2$. The observed ratio of m, $m + 2$, and $m + 4$ was 55.9:37.4:6.6 (calcd 56.8:37.1:6.9). The principal peaks and their intensities were 186 (21), 151 (42), 115 (100), 95 (19), 54 (20), the prevalent fragmentations being loss of Cl, loss of Cl and HCl, loss of Cl, HCl, and HF, and loss of the elements of 1122.

Treatment of 2 with potassium *t*-butoxide and *t*-butyl alcohol led in 76% yield to *o*-chlorofluorobenzene, identified by vpc retention time and superimposable infrared spectra in carbon tetrachloride and carbon disulfide.

Temperature Dependence of 1,2 *vs.* 1,4 Addition for Butadiene and 1122. The 1,4-adduct formation from these cyclic dienes in 1122 could proceed by either of two pathways: (1) a concerted process of the Diels–Alder type involving orbital overlap related to that involved in the formation of π complexes, and (2) a two-step biradical mechanism involving initial addition to the cisoid form of the diene.[1] In both cases the product composition should vary with the cisoid–transoid conformational distribution of the diene. In case 2 there seems to be a good chance that this distribution alone will govern the temperature dependence of the product ratio, while in case 1 it is only by chance that this could be the case, since the rate-determining steps in the competing modes of cycloaddition would then be different. It may be noted that, in terms of the current orbital-overlap interpretation of concerted cycloaddition reactions,[5] any merging of one-step and two-step mechanisms into one another is limited to the type of cycloaddition ($2 + 4n$ π electrons) where the concerted mechanism is "allowed." When, as here, there is competition between a 4-electron and a 6-electron cycloaddition, these are either by entirely different mechanisms, or both are stepwise.

Aston, *et al.*,[6] concluded from a thermodynamic analysis that transoid butadiene was favored over cisoid by 2.3 kcal/mol. Use of eq 1, which fits the results of these investigators, indicates that the amount of cisoid butadiene at equilibrium should approximately double between 60 and 160°, a range accessible for cycloaddition studies.

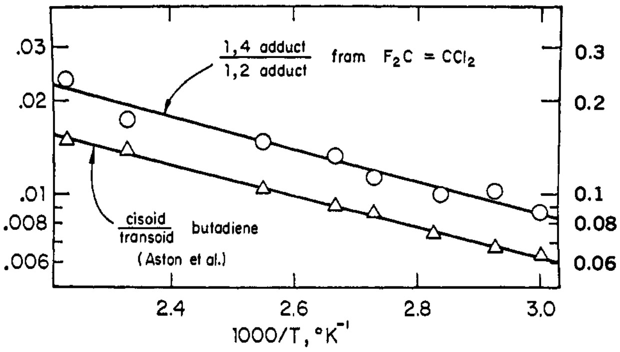


Figure 1. Temperature dependence of product (left-hand scale) and diene conformation (right-hand scale) for cycloaddition of 1,1-dichloro-2,2-difluoroethylenes to butadiene.

$$K = (\text{cisoid})/(\text{transoid}) = 1.84e^{-1180/T} \qquad (1)$$

Table I and Figure 1 show the amounts of 1,4 cycloadduct found from 60 to 176°, and for comparison, the amount of cisoid butadiene in the thermal conformational equilibrium calculated from eq 1. The fourth column in Table I shows that the 1,4 cycloadduct represents an essentially constant fraction of the cisoid butadiene over this temperature range.

Table I. Temperature Dependence of 1,4 Addition of 1,1-Dichloro-2,2-difluoroethylene (1122) to Butadiene

Temp, °C	Found, % 1,4 adduct	Calcd, % cisoid (eq 1)	% cisoid/ % 1,4 adduct
60.0	0.86	5.83	6.9
68.0	1.00	6.19	6.2
78.5	0.98	6.89	6.9
94.0	1.11	7.83	7.0
101.7	1.32	8.25	6.3
120.0	1.49	9.34	6.2
156.0	1.72	11.74	6.7
176.0	2.32	12.96	5.6

Discussion

If the temperature study had shown a large difference in the response of the 1,4 addition and that of the conformational equilibrium to temperature, it might have constituted evidence for independent mechanisms of the two modes of cycloaddition. The actual result means that such evidence is lacking. In another case (2-neopentylbutadiene, part V)[1] we have found that 1,4 cycloaddition of 1122 and of maleic anhydride do not respond similarly to the introduction of a neopentyl group at the 2 position of butadiene. Pending further evidence, which is now being developed in this laboratory, we regard the 1,4 cycloaddition of 1122 as proceeding by a branch of the biradical mechanism, and we may analyze it as in Scheme I.

If we regard the conformational equilibrium as mobile and each subsequent step as irreversible, we arrive at the following equation for the relative rates of formation of 1,2 and 1,4 adducts as a function of the

---

[4] See ref 1, Table III.

[5] R. Hoffmann and R. B Woodward, *ibid.*, 87, 2046 (1965).

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

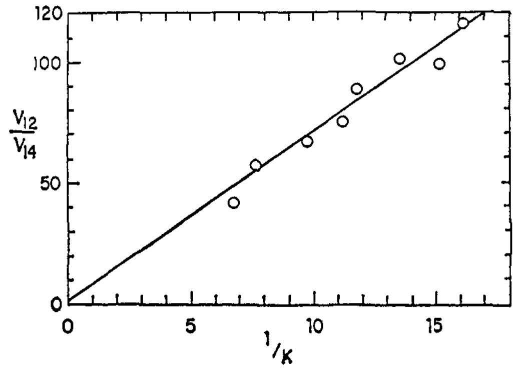


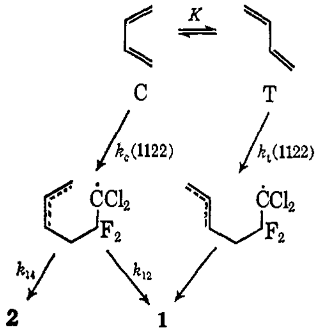
Figure 2. Plot of mode of cycloaddition *vs.* conformational equilibrium according to eq 2.

rate constants and of the equilibrium constant $K = (C)/(T)$. Equation 2 shows that the ratio of product

$$\frac{V_{12}}{V_{14}} = \frac{k_{12}}{k_{14}} + \frac{k_t}{k_c K}\left(1 + \frac{k_{12}}{k_{14}}\right) = a + \frac{b}{K} \qquad (2)$$

isomers depends not only upon the conformational equilibrium constant K but upon the two rate constant ratios k_{12}/k_{14} and k_t/k_c. We can test this relationship with our figures over a range of temperature only if these two rate ratios remain almost constant as the temperature changes. This might well be so; k_{12} and k_{14} are for radical couplings and should have similar and very low activation energies, while k_t and k_c refer to such similar processes that their temperature coefficients might be identical. Figure 2 does not prove the correctness of these assumptions, but the assumptions are at least consistent with the line obtained and with a value of $b = 6.9 \pm 0.3$. Because of the long distance from the points to the intercept the value of a is very uncertain (3 ± 3), and we cannot resolve b reliably into the contributions from the two rate ratios.

Scheme I



Experimental Section

The nmr spectra were recorded at 60 Mc in carbon tetrachloride with tetramethylsilane as internal standard. Because of the small amount of material available, a special microtube from NMR Specialties of 25-μl capacity was used for these measurements. Infrared spectra were recorded on a Perkin-Elmer Infracord. Vapor phase chromatography was accomplished on an F & M Model 609 apparatus using flame ionization detection or an F & M Model 300 with thermal conductivity detection.

Preparation and Isolation of Butadiene–1122 1,4 Adduct. A mixture of 19.5 g (0.36 mol) of butadiene and 40.0 g (0.30 mol) of 1122 was heated for 10 hr at 145° in a thick-walled sealed tube. After evaporation of the unreacted butadiene and 1122 at room temperature there was obtained 45 g of dark liquid. Distillation of the material at atmospheric pressure gave the following fractions: fraction I, 129–144°, 4.7 g, mostly butadiene dimers; fraction II, 145°, 11.9 g, 1,2 adduct; fraction III, 145°, 12.2 g, 1,2 and 1,4 adduct; removal of volatile components with 2-mm vacuum for 2 hr yielded fraction IV, 12.4 g, 1,2 and 1,4 adduct.

The distillation not only afforded separation of the butadiene dimers from cycloadducts, but also served to enrich the last two fractions with respect to 1,4 adduct.

Final separation was achieved by preparative vapor phase chromatography on a 20 ft × $^3/_8$ in. γ-methyl-γ-nitropimelonitrile (MNPN) column (column 110°, collector 170°, detector 210°, injector 40°, and nitrogen flow 100 cc/min). The 1,2 adduct was nicely separated from the 1,4 adduct (retention times 22.5 and 60.0 min, respectively).

The ir spectrum of 1,4 adduct (CCl_4) showed: 3.22 (w), 3.37 (w), 6.02 (w), 6.15 (w), 7.02 (s), 7.39 (s), 7.41 (s), 7.53 (s), 7.84 (s), 8.20 (s), 8.51 (s), 8.75 (s), 9.15 (s), 9.30 (s), 10.06 (s), 10.27 (s), 10.36 (s), 10.60 (s), and 11.19 (s) μ.

Aromatization of 1,1-Dichloro-2,2-difluoro-Δ^4-cyclohexene. The adduct, 0.1934 g (1.04 mm), was dissolved in 2 ml of *t*-butyl alcohol and added to a solution of 0.327 g of potassium *t*-butoxide in 8 ml of *t*-butyl alcohol. After refluxing for 10 hr under nitrogen the yellow solution and separated solid were transferred (ether) to a separatory funnel, washed three times with water, and dried over sodium sulfate. Removal of the ether gave 2.1 g of colorless liquid which showed three peaks on vpc (20 ft × $^1/_8$ in. MNPN at 100°) with retention times: 2.4 min (ether), 4.8 min (*t*-butyl alcohol), and 19.2 min. The peak at 19.2 min was enhanced by addition of *o*-chlorofluorobenzene. The aromatization product collected from the vpc showed an ir spectrum (CCl_4 and CS_2) identical with that of *o*-chlorofluorobenzene obtained from Columbia Organic Chemicals. The yield of product based on vpc isolation was 76%.

Reaction of Butadiene with 1122 at Various Temperatures. In a typical procedure a stock solution was prepared from 18.25 g (0.14 mol) of 1122 and 2.96 g (0.055 mol) of butadiene. The material was added to 2-ml ampoules each containing 3 mg of di-*n*-butylammonium picrate, and the tubes were sealed. The tubes were heated for the indicated amount of time in either an oil bath (60–101° runs) or a tube oven (120–176°). The temperature in the first system was maintained within ±0.01° while temperature control in the tube oven was probably not better than ±2. The tubes were heated for the indicated time and analyzed on a 10 ft × 0.25 in. diisododecyl phthalate column at 115° using flame ionization detection. The sequence of peaks was: 1,2 adduct (28 min), unknown compound (47 min), and 1,4 adduct (59 min). The relative areas were not corrected for the flame sensitivity of the two adducts because of shortage of 1,4 adduct. The unknown compound amounted to about 10% of the 1,4 adduct using flame ionization detection; however, with thermal conductivity the peak was hardly discernible.

Acknowledgment. We thank the National Academy of Sciences–National Research Council for a postdoctoral fellowship to J. S. S. in 1965–1966, and the National Science Foundation, National Institutes of Health, and donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.