tris-β-cyanoethoxypropane column. The compositions of the products are summarized in Table I, and their nmr spectra in Table II.

To determine the isomeric composition of the recovered hexadienes a 19 ft × $^1/_4$ in. diisodecyl phthalate column was used.

Anal. Calcd for $C_8H_{10}F_4$ [**4**-*tt*(F)]: C, 52.75; H, 5.53; F, 41.72. Found: C, 53.15; H, 5.52; F, 41.74.

Acknowledgment. Parts of this work were supported by the B. F. Goodrich Company, and others by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

Cycloaddition. XI. Evidence for Reversible Biradical Formation in the Addition of 1,1-Dichloro-2,2-difluoroethylene to the Stereoisomers of 1,4-Dichloro-1,3-butadiene

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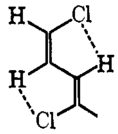
Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. *Received September 3, 1968*

Abstract: 1,1-Dichloro-2,2-difluoroethylene (1122) adds thermally to 1,4-dichloro-1,3-butadiene at 150° about as fast as it does to 2,4-hexadiene at 80°. Addition to the pure geometrical isomers yields cyclobutanes showing complete loss of configuration in the ring and predominant retention in the side chain. There is, however, from 3 to 7% of geometrical isomerization of the diene coupled to the cycloaddition mechanism and resulting formation of 1–5% of cycloadducts with altered configuration in the side chain. The results may be semiquantitatively explained by reversible formation of the intermediate biradical, with rates of cleavage relative to ring closure of 0.23–0.34. Proton and fluorine nmr spectra provide detailed confirmation of the structures and configurations of the three isomeric dienes and four isomeric chlorovinylcyclobutanes.

As with 2,4-hexadiene,[1,2] the three stereoisomers of 1,4-dichloro-1,3-butadiene have been separated in a pure state.[3–7] For comparison with the previously studied case, we have added 1,1-dichloro-2,2-difluoroethylene ("1122") thermally to the *cis,cis* (mp −4.8 to −3.0°), *cis,trans* (mp −32 to −30°), and *trans,trans* (mp 38.0–39.6°) isomers of this dichlorodiene.

Results

The Isomeric 1,4-Dichlorobutadienes. The crude 1,4-dichloro-1,3-butadiene resulting[3] from the zinc dechlorination of 1,3,4,4-tetrachloro-1-butene[4] was found to contain the *cis,cis cis,trans*, and *trans,trans* isomers in the ratio of 30:50:20. These proportions are not far from the isomer composition of mixtures of 1,4-dichloro-1,3-butadienes after equilibration by iodine in benzene at 100° (50.9:40:9.1) and 150° (43.4:44.5:12). Viehe and Franchimont[5] explain the preponderance of the *cis,cis vs.* the *trans,trans* form by "nonbonded interaction" of the type indicated in formula **1**-*cc*, which should contribute to a lowering of the energy of the *cis,cis* compound in its transoid conformation.



1-*cc*

cis,cis-1,4-Dichloro-1,3-butadiene, which has a much shorter retention time with most columns, was obtained in a pure state (mp −4.8 to −3.0°) by preparative vpc. From the remaining mixture, the *trans,trans* compound was isolated by crystallization at −79° and recrystallizing from pentane, mp 38.0–39.6°. From the mother liquors pure *cis,trans* isomer (mp −32 to −30°) was obtained by preparative vpc. The melting points given by Criegee[3,6] are 37–38° (*trans,trans*), −20° (*cis,trans*), and −5° (*cis,cis*). A recent examination[7] of the ir spectrum of the *trans,trans* compound agrees with Criegee's assignments. Viehe and Franchimont[5] also examined the ir spectrum and reached the same conclusions.

The nmr spectra of the three isomers (Figures 1–3), which have not been analyzed because of their complexity, also seem to be in agreement with the assigned geometry. Thus, one would expect symmetrical patterns for the *trans,trans* and *cis,cis* compounds, and a more complex and asymmetrical spectrum for the *cis,trans* isomer which has no center of symmetry.

Cycloaddition of 1122 to the 1,4-Dichlorobutadienes. 1,1-Dichloro-2,2-difluoroethylene (1122) is much less reactive toward 1,4-dichlorobutadiene than toward 2,4-hexadiene, a temperature 70° higher being required in the former case to achieve similar conversions. However, at 150° after 24–78 hr the corresponding four adducts were formed in high yield, the structure and stereochemistry of the products being shown conclusively by nmr.

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(1) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

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

(3) R. Criegee, W. Hörauf, and W. D. Schellenberg, *Ber.*, **86**, 126 (1953).

(4) W. Bauer, *Chimia* (Zurich), **5**, 147 (1951).

(5) H.-G. Viehe and E. Franchimont, *Ber.*, **97**, 602 (1964).

(6) R. Criegee, private communication.

(7) E. Braye, *Bull. Soc. Chim. Belges*, **72**, 699 (1963).

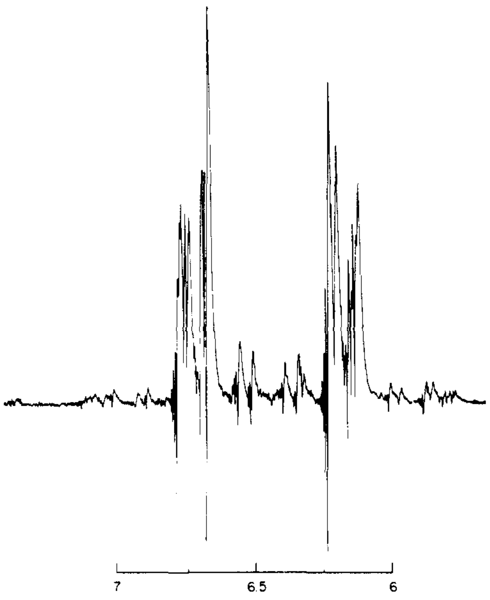


Figure 1. Proton nmr spectrum of *cis,cis*-1,4-dichloro-1,3-butadiene; 60% solution in carbon tetrachloride.

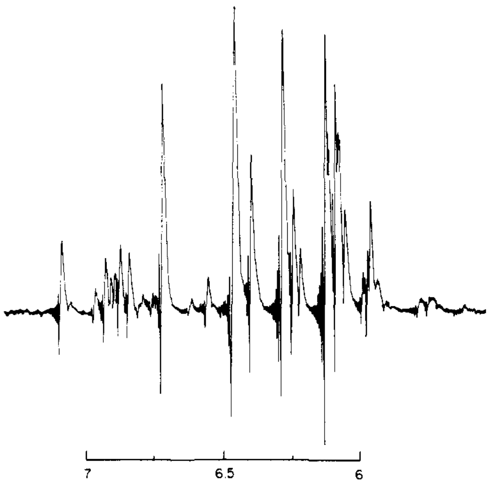


Figure 2. Proton nmr spectrum of *cis,trans*-1,4-dichloro-1,3-butadiene; 60% solution in carbon tetrachloride.

Nmr Spectra. Some characteristic features of the 60-Mc nmr spectra of the cycloadducts are summarized in Table I, and the spectra are shown in Figures 4–7. Since the four protons have sufficiently different chemical shifts the signals could be assigned unambiguously in spite of strong mutual couplings. Among the adduct isomers, assigned letters A–D in the order of their elution in vpc, the largest differences are those between the coupling constants of the ethylenic protons in the *cis* (7 cps) and *trans* (13 cps) side chains. The H geminal to chlorine on the ring is at lower field than that geminal to chlorovinyl, and for a given side-chain configuration each ring proton absorbs at lower field when the ring configuration is *cis* than when it is *trans*.

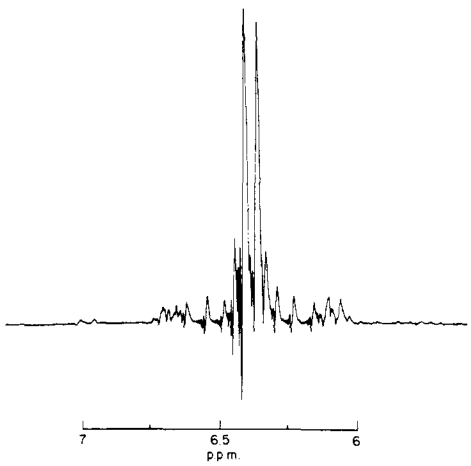
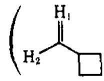
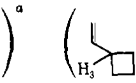
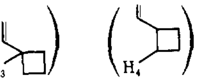
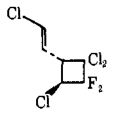
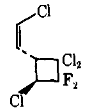
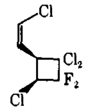
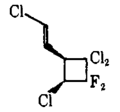


Figure 3. Proton nmr spectrum of *trans,trans*-1,4-dichloro-1,3-butadiene; 60% solution in carbon tetrachloride.

Fluorine nmr spectra at 40 Mc were determined through the courtesy of Dr. Robert C. Hopkins, for adducts B, C, and D. These are basically AB spectra. In isomers C and D, the downfield pair of lines are split into triplets and the upfield pair into double doublets; in B the downfield lines appear as doublets, while the upfield groups are further split by a small coupling making two groups of eight lines each. The separations are summarized in Table II. The observed differences in chemical shift for F(1) and F(2) are of the expected magnitude.[8] Phillips found in 1,1,2,2-tetrafluorocyclobutane that a chlorine substituent caused a chemical-shift difference between the geminal fluorines next to it of 400 cps (30-Mc spectrum). We assume the magnitude of the effect of a β-chlorovinyl across the ring to be between that of an α-chlorovinyl and a vinyl

Table I. Characteristic Features of the Proton Nmr Spectra of the 1,4-Dichloro-1,3-butadiene–1,1-Dichloro-2,2-difluoroethylene Adducts (40% Solutions in Carbon Tetrachloride)

Isomer	 $J_{H_1H_2}$, cps	 δ_{H_3}, ppm	 δ_{H_4}, ppm
 A	13.2	3.26	4.36
 B	7.2	3.93	4.38
 C	7.3	4.28	4.93
 D	13.1	3.67	4.86

[a] Absolute values.

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[8] W. D. Phillips, *J. Chem. Phys.*, 25, 949 (1956).

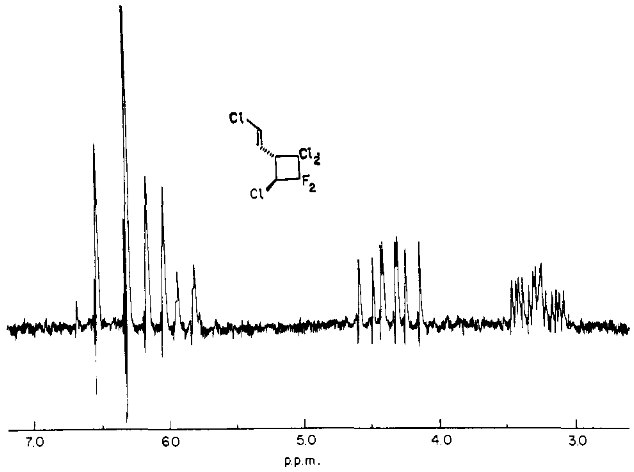

Figure 4. Proton nmr spectrum of adduct A from 1,4-dichloro-1,3-butadiene and 1,1-dichloro-2,2-difluoroethylene; 40% solution in carbon tetrachloride.

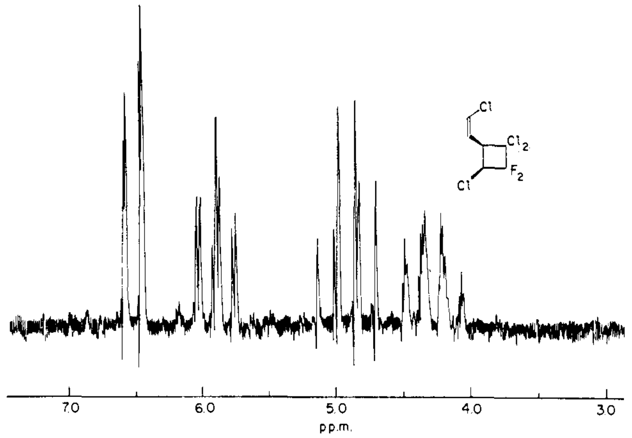

Figure 6. Proton nmr spectrum of adduct C from 1,4-dichloro-1,3-butadiene and 1,1-dichloro-2,2-difluoroethylene; 40% solution in carbon tetrachloride.

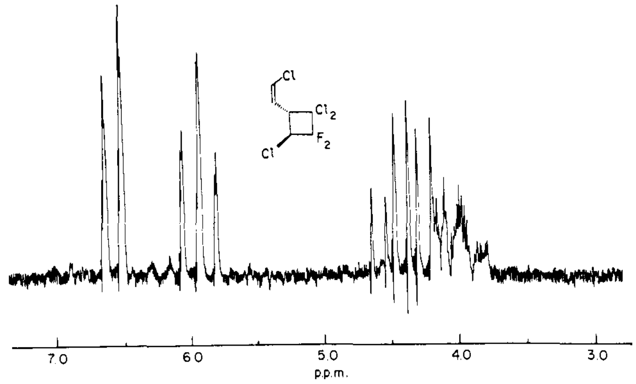

Figure 5. Proton nmr spectrum of adduct B from 1,4-dichloro-1,3-butadiene and 1,1-dichloro-2,2-difluoroethylene; 40% solution in carbon tetrachloride.

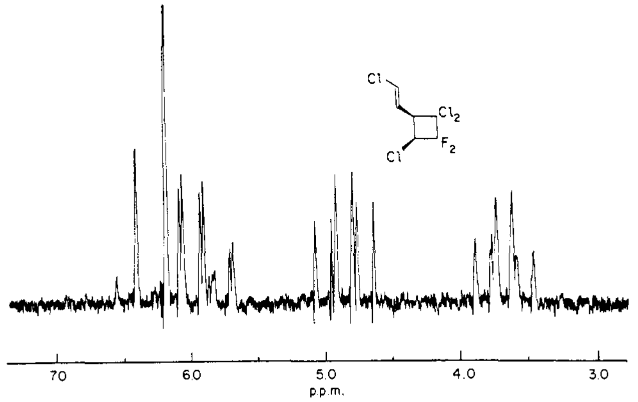

Figure 7. Proton nmr spectrum of adduct D from 1,4-dichloro-1,3-butadiene and 1,1-dichloro-2,2-difluoroethylene; 40% solution in carbon tetrachloride.

which he observed to be 255 and 232 cps, respectively. Correcting these values for a 40-Mc spectrum we obtain for the differentiating effect of adjacent chlorine and opposite β-chlorovinyl 534 and 325 cps. The *combined* effect of the two groups, in the absence of mutual interactions, should then be 859 and 209 cps, depending on their relative orientations. Since ring puckering[9] must be enhanced by *trans*-α substituents but diminished by *cis*-α substituents, there is a limit to the accuracy to be expected from this type of estimate. It would seem that the $\Delta\delta$ values of Table II are in reasonable accord with the available analogies.

Table II. Evaluation of F–F Interactions in the Nmr of 1,4-Dichloro-1,3-butadiene–1,1-Dichloro-2,2-difluoroethylene Adducts

	B[c]	C[c]	D[c]
J_{FF}[a], cps	179.2	182.7	187.5
Distance between midpoints of doublets, cps	666	491.5	498
$\Delta\delta$,[b] cps	641.4	456.3	461.4

[a] Absolute values. [b] Calculated by means of the equation $\Delta\delta = \sqrt{D^2 - J_{FF}^2}$. [c] See Table I for isomer designations.

The F–H coupling constants from the fluorine nmr are in good agreement with those derived from the proton nmr spectra. Table III lists the coupling constants from four proton and three fluorine nmr spectra. For completeness the assignments of the H–F coupling constants are also indicated for isomer A, for which no fluorine nmr spectrum was determined, and three other couplings are indicated in parentheses where the degree of resolution of the proton spectra did not permit their evaluation in one of the appropriate absorbing regions. In 22 cases the couplings have been observed in the signals for both nuclei concerned.

There appears to be no unambiguous way at present of assigning the H–F coupling constants according to the configurations of the fluorine atoms in the ring, although it would be a self-consistent assignment to call F_1 *cis* to the two ring protons in C and D (coupled only to H_4) and *cis* to H_4 in A and B.

Product Composition. Table IV shows the results of vpc analyses of the cycloaddition products. As might be expected from the results of part X,[2] these cycloadditions at 150° also show isomerization of the diene coupled with the addition mechanism. Again a control experiment shows only slight (1.1%) isomerization of *cis,cis*-dichlorobutadiene in 24 hr under the conditions of the cycloadditions. The only cycloadducts were compounds A–D; as expected from the biradical

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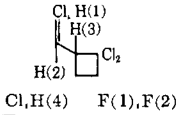
(9) On nonplanarity of cyclobutane derivatives see (a) H. P. Lemaire and R. L. Livingston, *J. Am. Chem. Soc.*, **74**, 5732 (1952); (b) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).

Table III. Coupling Constants[a] of the Adducts of 1,4-Dichloro-1,3-butadiene and 1,1-Dichloro-2,2-difluoroethylene

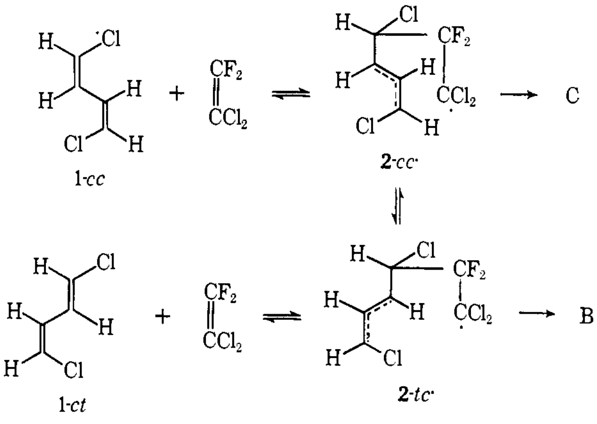
	H(1)	H(2)	H(3)	H(4)	F(1)	F(2)
A^b	13.1—	13.3		10.7–	(10.7)	
			9.8—	9.8		
		7.5—	7.5	6.1—	—	6.1
			3—	—	(3)	
			1.8—	—	—	(1.8)
		0.8—	—	—	(0.8)	
B^b				10.2—	10.3	
			(∼9.9)-	∼9.9		
		7.8—	7.8			
	7.2—	7.2		6.0—	—	5.7
	0.75		(3.5)—	—	3.5	
	0.75	0.7—	—	—	0.8	
C^b				9.0—	9.3	
			(9.0)—	9.0		
		8.8—	∼8			
	7.3—	7.3		7.3—	—	7.2
	0.9		7.2—	—	—	7.2
		1.5—	—	—	1.3	
D^b	13.0—	13.1		9.5—	9.7	
			9—	8.9		
		9.3—	9	7.1—	—	7.2
			7—	—	—	7.2
		1.5—	—	—	1.5	

[a] Absolute values in cycles per second. Values in parentheses have not been observed. [b] See Table I for isomer designations.

configuration along with 3.62% of isomerized diene recovered.

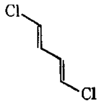
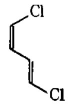
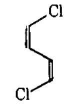
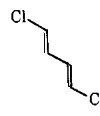
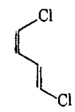
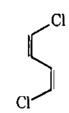
Discussion

These results may be explained by the mechanism discussed in the preceding paper of this series:[2] reversible addition of 1122 to the diene to form a biradica



capable of rotation about all of its single bonds; ring closure in any phase of rotation about the single bond that was originally double, to yield the two normal products; or cleavage after rotation to yield isomerized diene.

Table IV. Products of the Reaction of the Three Isomeric 1,4-Dichloro-1,3-butadienes with 1,1-Dichloro-2,2-difluoroethylene at 150°[a]

	Reaction time, hr	Recovered dienes, %			Total	Cycloadducts, %				
						A^c	B^c	C^c	D^c	A + B + C + D
	24	33.2	0.2	3.81	37.2	0.5 (0.8)^b	33.8 (53.6)^b	21.1 (33.5)^b	0.6 (1)^b	55 (88)^b
	78	0.46	5.08	3.16	8.7	59.7 (65.5)^b	2.21 (2.43)^b	2.58 (2.83)^b	21.0 (23.1)^b	85.5 (93.8)^b
	24	4.53	2.87	49.3	56.7	13.2 (30.5)^b	17.7 (40.7)^b	7.24 (16.7^b)	4.67 (10.7)^b	42.8 (98.6)^b
 [d]	24	98.9	0.025	1.1	100^e	...	...	...	...	...

[a] Numbers are based on vpc areas. [b] Yield based on reacted diene, %. [c] See Table I for isomer designations. [d] Control experiment with $CHCl_3$ instead of $CCl_2{=}CF_2$. [e] *I.e.*, no other peaks were observed with comparable retention times; however, no test for higher boiling reaction products was made.

mechanism, the *cis,cis*-diene gave B and C, the *trans,trans* gave A and D, and the *cis,trans* gave all four isomeric products. In addition, however, the product from *cis,cis*-dichlorobutadiene contained 1.1% of products with altered side chain, along with 3.83% of isomerized starting material, and the *trans,trans*-dichlorobutadiene (which had reacted 78 hr instead of 24) yielded 4.79% of adducts with altered side-chain configuration along with 3.62% of isomerized diene recovered.

In the addition of 1122 to 2,4-hexadiene,[1] the ratio of adducts with *trans* to those with *cis* ring configuration was 3.16 in addition to the *cis,cis* isomer, 3.17 and 5.03, respectively, in addition to the *cis* and *trans* double bonds of the *cis,trans* isomer, and 5.13 in addition to the *trans,trans* isomer of the diene. From these figures it was possible to conclude that rotation in the biradical was ten times as fast as ring closure.[10]

In the present instance the temperature is much higher and reversibility has become important. Rotation has come much closer to equilibrium in the dichlorobutadiene intermediates than in those from 2,4-hexadiene: the ratios corresponding to those above are here 1.60, 2.83, 2.45, and 2.84. It is thus not possible in the present instance to determine a ratio of rate constants for biradical rotation and ring closure. It is possible, however, to estimate the relative frequency with which a biradical formed from *cis,cis* or from *trans,trans* starting material undergoes cleavage in competition with ring closure.

In Scheme I the symbol **2**-*c* is used to denote the rotationally equilibrating biradical **2**-*cc* ⇄ **2**-*tc* with *cis* side chain, formed from *cis,cis*-dichlorobutadiene and 1122. Similarly, **2**-*t* is the rotationally equilibrating biradical with *trans* side chain. Since at this temperature internal rotation comes essentially to equilibrium, it is unnecessary to distinguish between the rotational conformations. At the end of a cycloaddition run with *cis,cis*-diene as starting material, the amount of **2**-*c* which has undergone cleavage is related to the amounts of cycloadducts and dienes by eq 1.

Scheme I

$$\begin{tikzcd}
 & \mathbf{1}\text{-}cc + 1122 \arrow[d, shift right, "k_1"'] & \\
\mathbf{3}\text{-}cc\ (=\mathrm{C}) & \mathbf{2}\text{-}c \arrow[l, "k_{\mathrm{C}}"'] \arrow[r, "k_{\mathrm{B}}"] \arrow[u, shift right, "k_{-1}"'] \arrow[d, shift right, "k_{-2}"'] & \mathbf{3}\text{-}tc\ (=\mathrm{B}) \\
 & \mathbf{1}\text{-}ct + 1122 \arrow[u, shift right, "k_2"'] \arrow[d, shift right, "k_3"'] & \\
\mathbf{3}\text{-}ct\ (=\mathrm{D}) & \mathbf{2}\text{-}t \arrow[l, "k_{\mathrm{D}}"'] \arrow[r, "k_{\mathrm{A}}"] \arrow[u, shift right, "k_{-3}"'] \arrow[d, shift right, "k_{-4}"'] & \mathbf{3}\text{-}tt\ (=\mathrm{A}) \\
 & \mathbf{1}\text{-}tt + 1122 \arrow[u, shift right, "k_4"'] &
\end{tikzcd}$$

[**2**-*c* cleaved] =

$$\frac{k_{-1}+k_{-2}}{k_{-2}}\left\{\mathbf{1}\text{-}ct + \frac{k_2+k_3}{k_3}(\mathbf{3}\text{-}ct + \mathbf{3}\text{-}tt + \mathbf{1}\text{-}tt)\right\} \quad (1)$$

Similarly

[**2**-*t* cleaved] =

$$\frac{k_{-3}+k_{-4}}{k_{-3}}\left\{\mathbf{1}\text{-}ct + \frac{k_2+k_3}{k_2}(\mathbf{3}\text{-}cc + \mathbf{3}\text{-}tc + \mathbf{1}\text{-}cc)\right\} \quad (2)$$

In this treatment any *repeated* passage of material through the same reversible cycle is ignored, since the ring closure reactions are irreversible and represent the major modes of reaction of the biradicals. If the photoisomerization of 1,4-dichlorobutadiene, which comes to a known equilibrium, is presumed to be analogous to the central spine of Scheme I, with iodine atoms taking the place of 1122 but with the relative rate constants being similar, we can derive the ratios $k_{-1}k_2/k_1k_{-2} = 0.97$ and $k_{-3}k_4/k_3k_{-4} = 3.7$ from the data of ref 5 cited above. By putting the initial and final concentrations and times of the runs of Table IV into a second-order rate equation we estimate that k_1, $(k_2 + k_3)$, and k_4 are about 1.46, 1.13, and 1.31 l./(mol Msec), respectively. From the product analysis in the case of the *cis,trans*-diene we find that k_2/k_3 is 1.40. This allows evaluation of all the constants needed for eq 1 and 2. Thus

$$\frac{k_{-1}+k_{-2}}{k_{-2}} = 1 + \frac{k_{-1}}{k_{-2}} = 1 + 0.97\frac{1.46}{1.13(1.40/2.40)} = 3.15$$

$$\frac{k_2+k_3}{k_3} = 1 + 1.40 = 2.40$$

$$\frac{k_2+k_3}{k_2} = 1 + \frac{k_3}{k_2} = 1.71$$

$$\frac{k_{-3}+k_{-4}}{k_{-3}} = 1 + \frac{k_{-4}}{k_{-3}} = 1 + \left(\frac{k_3k_{-4}}{k_{-3}k_4}\right)\left(\frac{k_4}{k_3}\right) = 1.76$$

The diene isomerization observed in the 24-hr control experiment with *cis,cis*-diene represents an upper limit to the needed correction, since less diene is present during most of the cycloaddition than during the control. Arbitrarily we subtract the 1.1% observed in the control from the experimental (**1**-*ct*) in the cases of both *cis,cis* and *trans,trans* starting material. The units chosen are per cents of starting material, since we are evaluating competitive rate ratios, and it is necessary only that the same units be used throughout.

Then

$$[\mathbf{2}\text{-}c\text{ cleaved}] = 3.15\{(3.81 - 1.1) + 2.40(1.1 + 0.2)\} = 3.15(5.83) = 18.4$$

$$[\mathbf{2}\text{-}t\text{ cleaved}] = 1.76\{(3.16 - 1.1) + 1.71(4.79 + 0.46)\} = 19.4$$

$$\left(\frac{\text{cleavage}}{\text{closure}}\right)_{cis} = \frac{18.4}{55} = 0.335$$

$$\left(\frac{\text{cleavage}}{\text{closure}}\right)_{trans} = \frac{91.4}{85.5} = 0.227$$

The difference between these figures for the two biradicals, though small, is probably real, although any flaw in the analogy with the iodine isomerization might have an effect as great as this.

1,4-Dichlorobutadiene is in contrast to 2,4-hexadiene in that at each double bond the *cis* configuration is stable relative to the *trans*. A similar contrast appears in the relative reactivities of the two double bonds in the *cis,trans* isomer. Whereas *cis,trans*-2,4-hexadiene shows a preference of 1.37 to 1 for addition to the *cis* double bond, the corresponding isomer of 1,4-dichlorobutadiene favors addition to the *trans* double bond by 1.40 to 1. This is consistent with ground-state stabilization playing a role of about the expected magnitude in determining the relative rates of attack.

Experimental Section

Preparation of the Three Isomeric 1,4-Dichloro-1,3-butadienes.[3,4] **1,3,4,4-Tetrachloro-1-butene.** 1,2-Dichloroethylene (860 g, *cis* and *trans*, Matheson Colemen and Bell, bp 56–62°) was refluxed for 14 days with 9 g of dibenzoyl peroxide. After the removal of unreacted starting material, distiilation gave the following fractions: (1) bp 40–84.2° (18.5 mm), 24.3 g; (2) bp 84.2–94.0° (18.5 mm), 241 g (28% conversion); (3) bp 94.0–94.3° (18.5 mm), 15.8 g.

Dechlorination. A solution of 140 g of 1,3,4,4-tetrachloro-1-butene (fraction 2, 0.73 mol) in 140 cc of methanol was added dropwise in the course of 105 min to a stirred suspension of 315 g of zinc dust (4.82 g-atoms) in 420 cc of methanol. Toward the end of the

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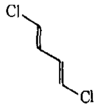
(10) In eq 2 on page 625 of ref 1, for $(x/y)_{trans}$ read $(y/x)_{trans}$.

addition the mixture was refluxing very gently. After 24-hr stirring at room temperature the filtrate was acidified with 500 cc of dilute hydrochloric acid and extracted with methylene chloride. Drying and evaporation of the solvent gave an oil, which on distillation gave the fractions shown in Table V.

Table V[a]

			%		
Fraction no.	Bp, °C (mm)	Wt, g			
1	...	1.6	31.4	38.2	14.5
2	29.5–37 (15–25)	8.3	38.3	43.8	16.0
3	31.4–35.0 (16.5)	56.6	30.8	49.6	19.6
4	35–60 (16.5)	7.3	13.3	60.4	26.4
5	>60 (16.5)	0.7	0.5	3	0.5
Total yield, 73.4 g (82% of theory)			22.0 g	36.8 g	14.6 g

[a] Percentages are based on vpc peak areas (10-ft β,β'-oxydipropionitrile, column, 75°; retention times, 23, 35, and 38 min).

Separation. Preparative vpc (tris-β-cyanoethoxypropane, 90°; injector temperature 130°; detector temperature 250°; 160 cc of He/min; 650-μl autoinjections) gave pure *cis,cis*-diene (retention time 60 min, mp −4.8 to −3.0°). The *cis,trans* (95 min) and *trans,trans* compounds (102 min) were collected as a mixture from which on cooling to −79° most of the *trans,trans* product crystallized. Additional crude *trans,trans*-diene was obtained from fraction 4. It was purified by low-temperature crystallization from pentane and distillation (80–100° (bath, 55 mm), mp 38.0–39.6°). After an attempt to remove the remaining *trans,trans* compound by reaction with maleic anhydride (2-hr refluxing in dioxane) had failed pure *cis,trans* product was obtained by preparative vpc (δ-nitro-δ-methylpimelonitrile, 100°; injector temperature 146°; detector temperature 178°; 160 cc of He/min; 70-μl injections; retention time: *cis,trans*, 35 min). The melting point of the pure material was −32 to −30°.

Cycloadditions. ***cis,cis*-1,4-Dichloro-1,3-butadiene.** *cis,cis*-Diene (4.7 g, 100% pure, 39 mmol), 35 cc of 1,1-dichloro-2,2-difluoroethylene (400 mmol), and a little di-*n*-butylammonium picrate were heated for 24 hr to 150°. The faintly yellow solution was worked up in the usual way leading to the following fractions: (1) from trap, 11.8 g; (2) bp 55–77° (9.0 mm), 0.5 g; (3) bp 77.2–79.0° (9.0 mm), 4.3 g; (4) 160° (bath, 9.0 mm), 1.1 g (0.2 g of brown resin remained).

The composition of the distillate is given in Table IV. Vpc analyses were made on a 10 ft × 0.25 in. β,β'-oxydipropionitrile column (70°; injector temperature 190°; detector temperature 260°; 60 cc of He/min, F & M 300) for the unreacted dienes, and on a 10 ft × 0 25 in. silicone rubber column (100°; injector temperature 270°; detector temperature 250°; flow rate position 7, F & M 609) for the adducts (retention times: A, 48 min; B, 51 min; C, 49 min; D, 70 min)

Preparative separation of the products from all dichlorobutadiene additions was performed on a silicone SE-30 column (132°; injector temperature 202°; detector temperature 240°; 160 cc of He/min). The retention times were: A, 48 min; B, 50 min; C, 55 min; D, 63 min. Depending on the isomer composition of the mixture, a diethylene glycol adipate (cross-linked) column was also used (412°; injector temperature 208°; detector temperature 208°; 160 cc of He/min). Here the sequence of elution was: B, 52 min; A, 58 min; C, 64 min; and D, 103 min. This column proved useful for the separation of pure B and larger amounts of D.

***trans,trans*-1,4-Dichloro-1,3-butadiene.** The *trans,trans* compound (1.3 g, 100% pure, 10.6 mmol), 9 cc of 1,1-dichloro-2,2-difluoroethylene (100 mmol), and a little di-*n*-butylammonium picrate were heated at 150° for 78 hr. Two fractions—8.3 g from the trap, and 2.82 g of a colorless oil (bp 90–150° (bath, 9 mm))—were obtained. The weight of the brown residue was 0.3 g. For isomer composition see Table IV.

***cis,trans*-1,4-Dichloro-1,3-butadiene.** The *cis,trans* isomer (0.30 g) (purity higher than 99.5%, contained traces of *trans,trans*-diene, 2.44 mmol), 2.9 cc of 1,1-dichloro-2,2-difluoroethylene (25 mmol), and a little di-*n*-butylammonium picrate were heated for 24 hr to 150°. Distillation of the brownish reaction mixture gave 1.00 g (Dry Ice–acetone trap) + 0.268 g (bp 85–140° (bath, 11.5 mm)) of products; *cf.* Table IV.

Control Experiment. *cis,cis*-1,4-Dichloro-1,3-butadiene (0.75 g, 100% pure, 6.1 mmol) was heated with 6 cc of chloroform (Fisher Certified Reagent) and a trace of di-*n*-butylammonium picrate to 150° for 24 hr. The brown solution from which brown particles had separated was analyzed for isomeric dienes by vpc (see Table IV).

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