potassium *t*-butoxide in *t*-butyl alcohol–pyridine. After hydrolysis and careful work-up to ensure isolation of all hydrocarbon product, nmr analysis showed signals only of starting compounds and no evidence for the *trans* stereoisomers.

Acknowledgment. We are grateful to the National Science Foundation and the U. S. Army Research Office (Durham) for financial support of this research.

Cycloaddition. X. Reversibility in the Biradical Mechanism of Cycloaddition. Tetrafluoroethylene and 1,1-Dichloro-2,2-difluoroethylene with 2,4-Hexadiene

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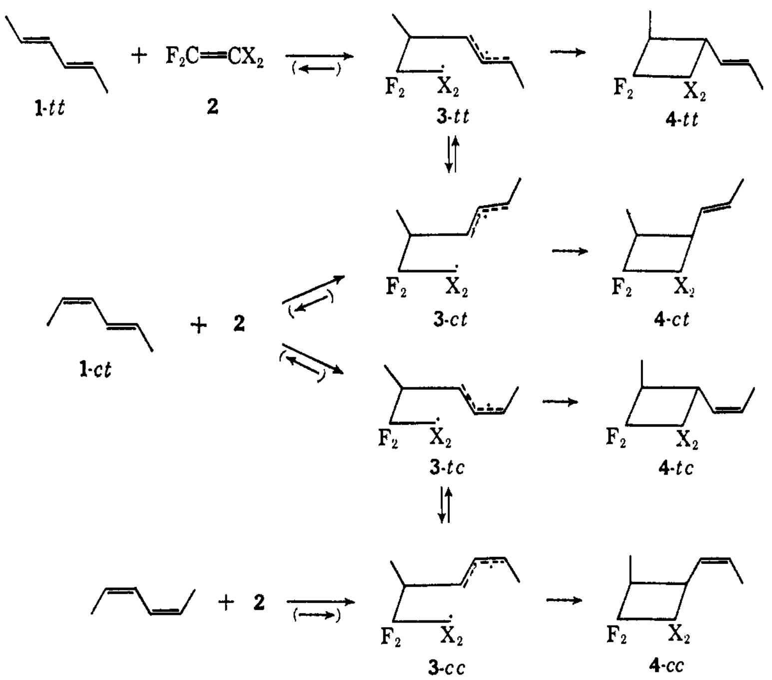
Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. *Received September 3, 1968*

Abstract: The four stereoisomeric cyclobutanes from thermal cycloaddition of 1,1-dichloro-2,2-difluoroethylene ("1122") to the stereoisomeric 2,4-hexadienes[1] at 80° have been isolated by preparative vapor phase chromatography and their configurations as previously assigned have been confirmed by nuclear magnetic resonance. Tetrafluoroethylene at 120° adds to *trans,trans*-2,4-hexadiene to yield only the two stereoisomeric *trans*-propenylcyclobutanes in a *trans*/*cis* ratio in the ring of 4.2, and with no isomerization of the recovered diene. At this same temperature the addition of 1122 to *trans,trans*-2,4-hexadiene is attended by isomerization of the diene and formation of minor amounts of *cis*-propenylcyclobutanes along with major amounts of the *trans*-propenylcyclobutanes. The isomerization is interpreted as due to reversal of the initial biradical formation, which may occur after rotation in the biradical. The similar amounts of loss of configuration with tetrafluoroethylene and 1122 lead to the suggestion that the rate of ring closure is controlled, not by the rate constant of radical–radical combination, but by the rate of rotations about the three single bonds of the biradical to bring it into a conformation suitable for ring closure from an original distribution of non-*cis* conformations.

The thermal addition of 1,1-dichloro-2,2-difluoroethylene ("1122") to the geometrical isomers of 2,4-hexadiene yields mixtures of cyclobutanes of identical orientation but differing in configuration at the ring.[1] The proportions of the products correspond to incomplete rotational equilibration of an intermediate biradical **3** (Chart I); from the relative amounts of **4**-*tt* and **4**-*ct* from **1**-*tt* and **1**-*ct* when $X = Cl$, it was possible to conclude that **3**-*ct* is converted by internal rotation into **3**-*tt* with a rate constant ten times that with which it closes to **4**-*ct*. The same figure could be arrived at by using the **4**-*tc*/**4**-*cc* ratios from **1**-*ct* compared to **1**-*cc*.

Chart I



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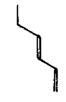
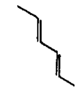
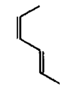
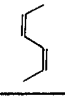
[1] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

Table I. Cycloadditions of *trans,trans*-2,4-Hexadiene, 120°, 24 hr

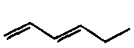
	Recovered dienes, %				Cycloadducts, %[a]					
					4-*tt*	4-*tc*	4-*cc*	4-*ct*	Unknown	Total
$CF_2{=}CF_2$	..	18.2	..	..	50.4 (61.6)	...	12.1 (14.8)	...	*b* ...	62.5 (76.4)
$CCl_2{=}CF_2$	0.06	1.4	0.73	0.07	35.6 (36.5)	2.50 (2.55)	12.2 (0.40)	0.39	...	50.7 (52.0)

[a] Upper figure, per cent conversion; lower figure, in parentheses, yield based on unrecovered diene. [b] Five small unknown peaks were present, <1%.

Both of these competing rate constants might be sensitive to structural changes. An increase in the steric requirement of X or of the groups in the diene might slow the interconversion of **3**-*tt* and **3**-*ct* appreciably, and it appeared possible that the rate constant for ring closure to **4** might be increased or decreased by lowering or raising the resonance energy of the biradical **3**. In the hope of gaining more insight into these processes we undertook to compare 1122 with tetrafluoroethylene. In the course of the work we developed several practical methods for separating the isomeric 2,4-hexadienes and prepared sufficient quantities of the adducts **4**, X = Cl, to determine their nmr spectra and confirm the previous configurational assignments. This paper also describes the comparison of **2** (X = F and Cl) in cycloaddition to **1**-*tt*.

Results

The diene was prepared in quantity (a) by the dehydration of 2-hexen-4-ol with toluenesulfonic acid, and (b) by the pyrolysis of 2,5-diacetoxyhexane at 510–525°. The product of direct dehydration was a mixture of four isomers: **1**-*tt*, 35.0%; **1**-*ct*, 38.7%; **1**-*cc*, 1.6%; and **5**, 24%. Potassium *t*-butoxide in dimethyl sulfoxide equilibrated the diene mixture to the new proportions: **1**-*tt*, 56%; **1**-*ct*, 36%; **1**-*cc*, 3.4%; **5**, 4.6%. Small amounts of the pure isomers were prepared as before by vapor phase chromatography using both a Beckman Megachrom and an Aerograph Autoprep. For the preparation of larger amounts of **1**-*cc* the previously described procedure[1] is useful in which the amount of *cis,cis* isomer is increased by photosensitized isomerization, **1**-*tt* and **5** are removed by reaction with maleic anhydride, and **1**-*ct* with tetracyanoethylene. It was found that the reaction of the isomer mixture with sulfur dioxide in an autoclave at 25° for 22 hr gave a yellowish crystalline sulfone in 42% yield, mp 43.7–44.7°. Heating to 130–140° gave a 67% return of **1**-*tt* containing no impurities detectable by vapor phase chromatography.



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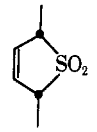


6

Since 1,3-hexadiene undoubtedly reacts with sulfur dioxide, either this diene must have undergone some isomerization under the conditions of the reaction, or its sulfone must have been efficiently removed during the crystallization of **6**, or perhaps have been more stable against thermal SO_2 elimination than the sulfone of **1**-*tt*.

Tetrafluoroethylene (**2**, X = F) was prepared by the zinc dust reduction of 1,2-dibromo-1,1,2,2-tetrafluoroethane, collected and stored at liquid nitrogen temperature and purified by two distillations. Many explosions were experienced during its cycloadditions until special ampoules were used of heavier glass than had been used in other cycloadditions.

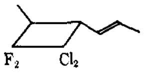
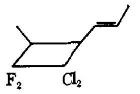
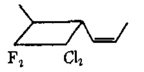
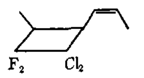
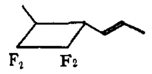
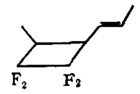
Cycloaddition of 1122 to the 2,4-hexadiene isomers was carried out in the same way and with the same results as in ref 1, except that samples large enough for nmr investigation were isolated by preparative vapor phase chromatography. The reaction of tetrafluoroethylene with *trans,trans*-2,4-hexadiene is so much slower than that of 1122 that a temperature 40° higher must be used to obtain comparable rates. For comparison the addition of 1122 to *trans,trans*-2,4-hexadiene was also carried out at 120°, the temperature at which tetrafluoroethylene gave satisfactory yields in 24 hr. The composition of the product and of the recovered diene in each case is shown in Table I.

The nmr spectra of the four isolated cycloadducts of 1122 to the isomeric 2,4-hexadienes afford independent evidence of their configurations and confirm the previous assignments.[1] Each isomer has two methyl doublets, J = 5–7 cps, corresponding to the ring methyl group (δ 1.13, 1.07, 1.17, and 1.04 in isomers A, B, C, and D, respectively) and the methyl group in the propenyl side chain (δ 1.75, 1.76, 1.72, and 1.67, respectively). In isomers C and D each member of the latter doublet is further split by about 1 cps, as is appropriate for interaction with the *trans*-situated ethylenic proton in a *cis*-propenyl side chain. In agreement with this assignment the complex multiplets in the unsaturation region for isomers C and D include upfield components split into approximately 1-cps quartets. These multiplets are relatively broad and well resolved; the corresponding signals for isomers A and B are sharply peaked near the center, suggesting a basic AB system with $J/\Delta\delta$ larger than in the other isomers.

Of the four isomeric adducts the two which are assigned *trans* configuration in the ring have the saturated methyl signal at lower field (A 1.13, C 1.17) and the ring proton multiplet at higher field (A 2.7, C 2.9) than the others (B 1.07 and 3.15, D 1.04 and 3.5, respectively), as would normally be the case for the geometries assigned.

The chemical shifts for the four adducts of 1122 to the 2,4-hexadienes and for the two adducts of tetrafluoroethylene to *trans,trans*-2,4-hexadiene are summarized in Table II.

Table II. 60-Mc Nmr Spectra of Cycloadducts[a]

Compound		Olefinic H	Side-chain Me	Ring Me	Ring H
	A 4-*tt*(Cl)	~5.5 m	1.75 d	1.13 d	~2.7 m
	B 4-*ct*(Cl)	~5.5 m	1.76 d	1.07 d	~3.15 m
	C 4-*tc*(Cl)	~5.6 m	1.72 dd	1.17 d	~2.9 m
	D 4-*cc*(Cl)	~5.6 m	1.67 dd	1.04 d	~3.5 m
	4-*tt*(F)	~5.5 m	1.71 d	1.16 d	~2.5 m
	4-*ct*(F)	~5.5 m	1.73 d	1.04 d	~2.9 m

[a] m = multiplet, d = doublet, dd = doublet doublet.

Discussion

The product of the reaction of tetrafluoroethylene with *trans,trans*-2,4-hexadiene corresponds qualitatively to that observed at the lower temperature with 1122. Both of the adduct isomers show simple doublets in the nmr for the side-chain methyl group, without the extra splitting which occurs from the α hydrogen in a *cis*-propenyl group. These are therefore the expected two isomers, **4**-*tt*(F) and **4**-*ct*(F), and they are present in the ratio 4.2:1. The corresponding ratio for 1122 is 5 at 80° and 2.9 at 120°. Tetrafluoroethylene is indeed causing less loss of configuration during cycloaddition than 1122 does, but the difference seems hardly commensurate with the estimated 8-kcal difference in the resonance energies of the $-CF_2\cdot$ and $-CCl_2\cdot$ radicals. According to the estimates made earlier[1] of the rate constants for intramolecular rotation and for ring closure of the biradicals from 1122, these rate constants are nearly large enough so that if the radical combination were between different molecules its rate would be diffusion controlled, The equivalent situation for a reaction of a biradical is to be "rotation controlled"; ring closure can occur no faster than a dimensionally appropriate conformation can be produced by internal rotations.

In the closure of a four-membered ring there are three intramolecular rotations of the biradical which must all be in the right phase for reaction to occur. In an unconcerted mechanism there is no reason to suppose that the 1,4 biradical is formed in any particular conformation with respect to the 2,3 bond; the extended chain form of the biradical may even be preferred. There is then a built-in delay in the ring closure of even the most reactive biradicals, before a conformation occurs which is simultaneously favorable at the 1,2, 2,3, and 3,4 bonds. It may be the waiting for this favorable conjunction of rotational phases which allows the *cis–trans* isomerization during cycloaddition, rather than any slowness in the radical–radical combination.[2] In a forthcoming paper of this series we shall present evidence that in certain stepwise cycloadditions by way of a *dipolar ion*, a coulombic orienting force in the first step eliminates or greatly diminishes this period in which the system searches for a favorable orientation for ring closure.

In the results with 1122 at 120° we see some phenomena which were entirely absent at 80°. Of the recovered hexadiene, 35% is isomerized at one or both of the double bonds, and 2.7% is structurally isomerized to the 1,3 isomer. At the same time, the 47.8% of the normal adducts, **4**-*tt*(Cl) and **4**-*ct*(Cl), which constituted the whole product at 80°, are here accompanied by 2.89% of the two abnormal products, **4**-*tc*(Cl) and **4**-*cc*(Cl). These evidently arise by addition to isomerized diene.

Both the experiments on tetrafluoroethylene addition and also a control experiment on *trans,trans*-hexadiene alone showed that the isomerization does not occur in the absence of 1122. It is therefore reasonable to suppose that the isomerization becomes an inherent part of the mechanism of cycloaddition as the temperature is raised. A probable mechanism for this isomerization can be represented by simply inserting reversible arrows in Chart I at the formation of each of the biradicals **3** from the starting materials **1** and **2**. There is then a three-step path for the conversion of **1**-*tt* to **1**-*ct* and another for **1**-*ct* → **1**-*cc*. This mechanism will account for *trans–cis* isomerization occurring only during the cycloaddition process, for the occurrence of small amounts of the abnormal cycloadducts, and for the increasing amount of isomerization with rising temperature, since high temperature always favors radical cleavage in competition with radical combination. That such reversibility should appear at a lower temperature in 1122 cycloaddition than in that of tetrafluoroethylene is reasonable in view of greater ground-state destabilization of the latter olefin. Cleavage of the biradical must be more exothermic when the resulting olefin is 1122 than when it is tetrafluoroethylene. There is also an analogy between this phenomenon and the "ceiling temperature" in free-radical polymerization, which is lower for olefins with stabilizing groups on the double bond than for those without.[3]

We have not established as yet whether the formation of 1,3-hexadiene also occurs by way of the biradical or is due to adventitious acid in the 1122 preparations.

Experimental Section

Tetrafluoroethylene. In a 1 l., three-necked, round-bottomed flask fitted with a 250-ml, pressure-equalizing dropping funnel, a Trubore stirrer, and a 10-cm reflux condenser were placed 700 ml of N,N-dimethylformamide and 450 g (6.89 g-atoms) of zinc dust. 1,2-Dibromo-1,1,2,2-tetrafluoroethane (500 g, 1.92 mol) was added dropwise with stirring. The temperature was maintained at 80–90° with an oil bath. Tetrafluoroethylene was rapidly liberated and

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[2] The likelihood of biradical formation in conformations unfavorable for ring closure in cycloaddition has been pointed out by J. A. Berson and E. J. Walsh, Jr. [*J. Am. Chem. Soc.*, **90**, 4732 (1968)], in comparison with a less rotationally equilibrating oxy-Cope rearrangement.

[3] F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948).

Table III

Sample of 2,4-hexadiene	Ret time, min	Composition, %: Low-boiling material	*trans*-1-Ethyl-1,3-butadiene	2,4-Hexadiene: *trans,trans*	*cis,trans*	*cis,cis*
trans,trans	20	0.2	2.2	97.2	0.4	. . .
cis,trans	29	. . .	. . .	0.3	99.4	~0.1
cis,cis	44					~90%
Mixed dienes	. . .	4.6		56	36	3.4

collected in a liquid nitrogen trap. The tetrafluoroethylene was distilled twice from a Dry Ice-acetone cooled trap to a liquid nitrogen trap. The yield was 137.7 g (72%).

1,1-Dichloro-2,2-difluoroethylene (1122) was purchased from Peninsular ChemResearch, Gainesville, Fla., redistilled, and stored as described in ref 1.

The 2,4-Hexadienes. Mixtures of hexadienes, including *trans*-1,3-hexadiene and the three 2,4-hexadienes, were prepared in two alternative ways: (1) by preparation and dehydration of 2-hexen-4-ol, and (2) by pyrolysis of the diacetate of 2,5-hexanediol obtained commercially.

2-Hexen-4-ol. To 87 g of magnesium turnings (3.63 g-atoms) and 600 cc of anhydrous ether was added 395 g of ethyl bromide (3.63 mol; bp 38–39°, distilled from phosphorus pentoxide) in 800 cc of anhydrous ether. After the addition, which took 70 min, the brown Grignard solution was stirred for another 40 min and cooled with an ice–salt mixture, and to it 230 g of freshly distilled crotonaldehyde (3.28 mol; bp 99–102°) was added dropwise at −15 to −8° with vigorous stirring. The light brown mixture was then kept for 30 hr and worked up with 400 g of concentrated sulfuric acid and 2 kg of ice at room temperature. After washing and drying of the organic layer and evaporation of the solvent the following fractions were obtained: 30.4 g (96% pure by vpc), bp 40–44° (12 mm); 34 g (97% pure), bp 44° (11–12 mm); 183 g (97% pure), bp 44–46° (11 mm); 15 g (94% pure), bp 46–50° (11 mm); corresponding to a total yield of 254 g of pure 2-hexen-4-ol (78% yield).

Dehydration. 2-Hexen-4-ol (262 g, 97% pure, 2.54 mol) was heated with 2 g of *p*-toluenesulfonic acid, and the volatile reaction products were distilled through a 20 × 2 cm Vigreux column. After separation from water and drying over calcium chloride, the crude olefins were redistilled (15 × 1 cm Vigreux column) to give the following two fractions (percentages of *trans*-1,3-hexadiene and *trans,trans*-, *cis,trans*-, andc *is,cis*-2,4-hexadienes, respectively, in parentheses, vpc analysis on a 10-ft β,β′-oxydipropionitrile column, 32°): 142 g, bp 79–85.2° (25, 36, 38, 1.5%); 11.0 g, bp ~85° (9.7, 39, 49, 2.5%) corresponding to a total yield of 152 g (73%) of diene mixture, isomer distribution 24:35.0:38.7:1.6).

2,5-Diacetoxyhexane. 2,5-Hexanediol (Eastman practical, 2 kg, 17.2 mmol), 10 lb of acetic anhydride (~44 mol), and 2 lb of pyridine were refluxed for 4.5 hr. Under reduced pressure (aspirator) about 4 l. of low-boiling material was distilled. Subsequently, the following fractions were obtained: (1) bp 71–106° (18 mm), ~800 g; (2) bp 116.8–117.4° (18 mm), ~200 g; (3) bp 117.4–118.7° (18 mm), 2378 g; (4) bp 118.7–~122° (18 mm), 247 g. Fractions 2–4 (2925 g, 82% of theory) consisted essentially of the diacetate.

Pyrolysis to Diene Mixture. 2,5-Diacetoxyhexane (2625 g, 13 mol) was added dropwise into a vertically mounted pyrolysis tube (55 cm long and 27-mm diameter; constricted to 12-mm diameter for a length of 25 cm, packed with 2-cm Pyrex tubes. The column was encased for 33 cm in a combustion furnace, and the temperature of the central section of the heated portion was maintained at 510–525°. During pyrolysis the system was slowly flushed (~50 cc/min) with prepurified nitrogen gas dried through two calcium chloride towers. The yellow pyrolysate was collected in a 2-l., three-necked, round-bottomed flask immersed in an ice–salt mixture. A Dry Ice–acetone condenser which led into a Dry Ice–acetone trap was connected to the ice–salt trap to ensure condensation of the volatile hexadienes.

The pyrolysate was then distilled through a vacuum-jacketed column 60 cm long, 1.2-cm diameter, packed with tantalum wire. Fractions were taken from 60 to 111°. The distillation fractions were washed with cold water and cold saturated bicarbonate solutions until no more CO_2 evolution was evident, and then again with water. The olefins were then dried over molecular sieves, yield ~60%.

Isomerization of the Hexadienes. In a 5-l., three-necked, round-bottomed flask equipped with stirrer, condenser, drying tube, and stopper were placed 2.5 l. of dimethyl sulfoxide and 35 g of potassium *t*-butoxide. The mixture was vigorously stirred. To this was added 273 g of a mixture of hexadienes. The mixture immediately turned black. It was stirred and heated on the steam bath for 3 hr. After storing at 0° overnight, the flask was fitted with a vacuum distillation head, and the dienes were distilled at 1-mm pressure. The receiver was cooled in an acetone–Dry Ice bath. The distillate was washed three times with water to remove any DMSO or *t*-BuOH, yield 237 g (87%).

Separation of the Hexadiene Mixture. Injections of 500-μl samples on the Autoprep Carbowax 20M column (83°; detector temperature 124°; flow rate 220 cc of He/min) gave a clean separation between *trans*-1,3-hexadiene (retention time 10 min) and the three isomeric 2,4-hexadienes (retention times 13, 14, and 15 min) for *trans,trans*, *cis,trans*, and *cis,cis* compound, respectively.

Reaction of the Isomeric 2,4-Hexadienes with Sulfur Dioxide. A freshly distilled 2,4-hexadiene mixture (34.0 g, 0.415 mol), a little pyrogallol, and di-*n*-butylammonium picrate, and 80 cc of peroxide-free ether were sealed in a glass-lined steel bomb at −78°. The mixture was allowed to warm to 25° and, having been kept at this temperature for 22 hr, it was cooled again, opened, and freed from excess sulfur dioxide by evaporation at slowly rising temperature. The yellow liquid was separated from 1.5 g of gummy material. At −78°, faintly yellow crystals separated. A second crop was obtained from the mother liquors after the addition of about 15% of pentane. The sulfone (25.2 g; 42%) melted at 43.7–44.7° (Backer, Strating, and Kool[4] give 43–43.5°; for the product of the same reaction at 100° with a smaller excess of sulfur dioxide, they report a yield of 1.5%).

Decomposition of Sulfone. On heating to 130–140°, 20.9 g of the above sulfone (0.143 mol) gave a yellow liquid which, after repeated shaking with 10% aqueous sodium carbonate solution and after washing with water and drying, was distilled in a nitrogen atmosphere: 7.9 g of *trans,trans*-2,4-hexadiene (67%), bp 80.4°. No impurity was detectable by vpc.

Preparation of pure samples of all four hexadienes was accomplished by preparative vapor phase chromatography. Samples (5.5 cc) of the hexadiene mixture were injected into a Beckman Megachrom preparative gas chromatograph. Four parallel sequences of two stainless steel columns (8 ft × $^5/_8$ in.) were employed, the first packed with 20% β,β′-oxydipropionitrile on 40–60 Chromosorb P, and the second with 35% saturated silver nitrate in diethylene glycol. With a column temperature of 37°, injector and detector at 100°, and a helium pressure of 17 psi (inlet) and 1.1 psi (outlet), the purity of the collected hexadienes (recovery ~60%, liquid nitrogen as coolant) is shown in Table III.

The *trans,trans*-2,4-hexadiene as obtained from the Megachrom was purified further with a 20 ft × $^3/_8$ in. β,β′-oxydipropionitrile column (Autoprep, column 62°; injector temperature ~50°; detector temperature 220°; flow rate 100 cc of He/min; 250-μl autoinjections). The collected *trans,trans*-2,4-hexadiene contained less than 0.5% impurities.

Cycloadditions. The general procedure was the same as that previously described.[1] Small amounts of hydroquinone, di-*n*-butylammonium picrate, or "Terpene B" (a terpene fraction boiling at 176–196°) were used to inhibit diene polymerization.

The cycloadditions with tetrafluoroethylene were carried out in special thick-walled, sealed tubes,[5] which were charged and opened at liquid nitrogen temperature.

After evaporation of the excess fluorinated reagent the products were separated by preparative vapor phase chromatography on a

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[4] H. J. Backer, J. Strating, and C. M. H. Kool, *Rec. Trav. Chim.*, **58**, 778 (1939).

[5] Provided through the courtesy of Dr. D. C. England of the Du Pont Co.

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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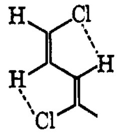
Abstract: 1,1-Dichloro-2,2-difluoroethylene (1122) adds thermally to 1,4-dichloro-1,3-butadiene at 150° about as fast as it does to 2,4-hexadiene at 80°. Addition to the pure geometrical isomers yields cyclobutanes showing complete loss of configuration in the ring and predominant retention in the side 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.

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.



1-*cc*

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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