Cycloaddition. IV. Addition Products of 1,1-Dichloro-2,2-difluoroethylene to a Further Series of Dienes

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Adducts of 1,1-dichloro-2,2-difluoroethylene (1122) to dienes, previously reported, have been further characterized and degraded. Adducts to *cis*-1-chlorobutadiene, 2,3-dichlorobutadiene, 2-methoxybutadiene, *trans*-1,3-hexadiene, *cis*- and *trans*-3-methyl-1,3-pentadienes, norbornene, and norbornadiene have been prepared and characterized. One product is strongly predominant or exclusively formed in each case, the selectivity in the 3-methyl-1,3-pentadienes being greater than predicted from the effects separately observed in isoprene and the piperylenes, although the measured rate of addition to 2,3-dimethylbutadiene was very close to that predicted. The *exo* addition of 1122 to norbornene and norbornadiene is to the 2,3 positions, while the *endo* addition leads to a tetracyclic product with the halogenated bridge from C-2 to C-6 (**28**). Addition of sulfur dioxide to several of the dienes resembles the Diels–Alder reaction in proceeding 1,4 and selecting the *trans* isomers. Subsequent thermal decomposition of the sulfones yields the *trans* dienes. 4-Methyl-1,3-pentadiene yields a rearranged cyclic sulfone, whose thermal decomposition gives 2-methyl-1,3-pentadiene. The latter appears to polymerize too readily to add to 1122. The exclusive 1,2 addition to 2-methoxy-1,3-butadiene is considered an example of polar factors in the formation of a biradical intermediate.

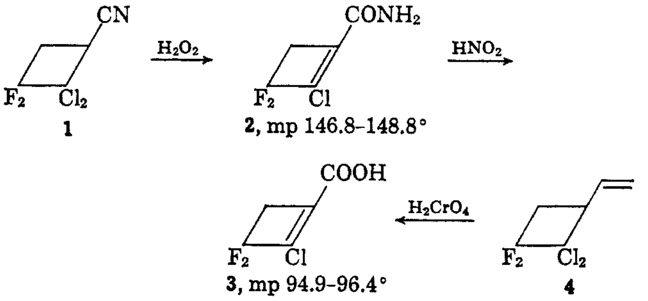
In previous papers of this series[1] 1,1-dichloro-2,2-difluoroethylene (1122) was added to butadiene, isoprene, *cis*- and *trans*-piperylenes, chloroprene, cyclopentadiene, and the three geometrical isomers of 2,4-hexadiene. The adducts to all the open-chain dienes were exclusively cyclobutanes, no cyclohexenes being found. The orientations of the products, the effects of methyl and chlorine substitution and of configuration upon the rates of cycloaddition, and especially the characteristic configurational changes during addition to the 2,4-hexadienes, were interpreted as compelling evidence for a biradical intermediate in these cycloadditions. In part I the structures of the adducts to butadiene, isoprene, and chloroprene were shown by oxidative degradation, while others were deduced from their characteristic nuclear magnetic resonance (nmr) spectra.

In the present paper a number of implications of the previous work have been followed out; some identifications and analyses have been completed; 13 more cycloadducts of 1122 have been prepared and characterized. Again the reactivities and orientations are consistent with a biradical mechanism, but there are now evidences of polar factors operating, much as in other free-radical reactions. It is found that the 1,4 addition of sulfur dioxide to dienes has a selectivity similar to that of the Diels–Alder reaction, and this reaction is useful in the preparation of certain geometrical and structural isomers of dienes.

Identifications.—In part I[1a] the adduct **4** of 1122 to butadiene was converted to the unsaturated acid **3** by oxidation with chromic acid. The acid **3** has now been prepared independently from the acrylonitrile–1122 cycloadduct **1** (Scheme I) (mixture melting point).

The adduct **5** (Scheme II), from 1122 and 2,3-dimethylbutadiene, was likewise degraded to the acid **7**, which was identical spectroscopically to the hydrolysis product of the 1122–methyl methacrylate cycloaddition product. In two competitive rate determinations the rate constants of 2,3-dimethylbutadiene and isoprene in cycloaddition with 1122 were found to be in the ratio 0.66:1.

SCHEME I



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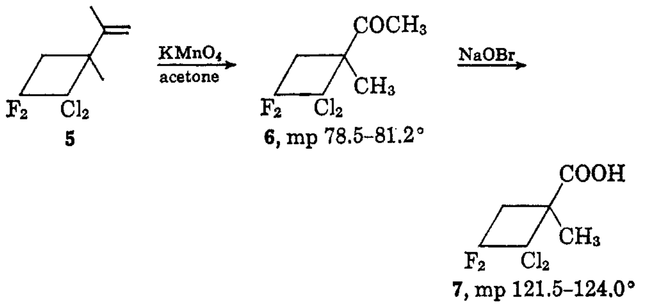
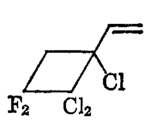


Both the 1,2 adduct **8** and the 3,4 adduct **9** of chloroprene and 1122 have been purified and analyzed. Likewise, the purification and analyses of **10** and **11**, prepared earlier from cyclohexadiene, have been completed. These products are formed as 93 and 6%, respectively, of the liquid product from cyclohexadiene and 1122 held at 80° for 48 hr. A more rapidly eluted



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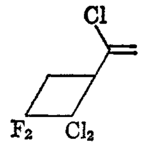

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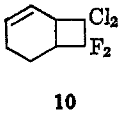

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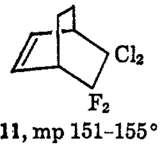

11, mp 151-155°

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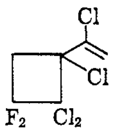
[1] (a) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964); (b) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); (c) P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

product comprising 1% of the product was not identified.

New Cycloadditions.—2,3-Dichlorobutadiene gave, in addition to a small amount of gummy polymer, a single camphorlike product, mp 53–59° (**12**). *cis*-1-Chlorobutadiene yielded a homogeneous adduct [vapor phase chromatography (vpc) on diisodecyl phthalate and *tris*-β-cyanoethoxypropane columns] shown to be **13** by its nmr spectrum. The rates of these cycloadditions were of the same order of magnitude as those of the chloroprene or butadiene additions.



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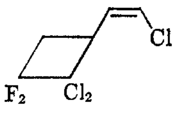

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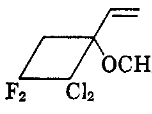

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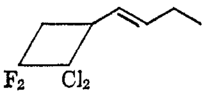
2-Methoxybutadiene appeared an interesting case because oxygen, as a first-row element, could not have the ability of chlorine to delocalize an odd electron, but could contribute to a local cationic structure in the transition state for biradical formation. The cycloadduct **14** was the only identified product from this addition, although 2% of a second component (retention time 16.8 min compared to 37.2 for **14**) was present.

***trans*-1,3-Hexadiene,** like *trans*-piperylene, yielded a single adduct representing attack on the unsubstituted double bond (**15**).



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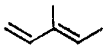
Accompanying the preparation of 2-ethylbutadiene (see part V) was 68% of a mixture of *cis*- and *trans*-3-methyl-1,3-pentadienes (**16** and **17**, respectively).



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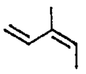

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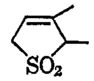

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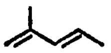
The isomers (23 and 77%, respectively) were separated by vpc on a Silicone QF 1 column. Reaction of the mixture with sulfur dioxide at room temperature for 24 hr gave the sulfone **18** in 16% yield; on decomposition this sulfone afforded **16** and **17** in the ratio of 97:3. When the original mixture of **16** and **17** was added to a fourfold excess of maleic anhydride, warming occurred; after standing overnight the unreacted diene was found to be 99.6% pure **17** in 78% recovery.

Two dienes, *trans*-2-methyl-1,3-pentadiene (**19**) and 4-methyl-1,3-pentadiene (**20**), were found to yield the same sulfone (**21**) on reaction with sulfur dioxide at room temperature for 15 hr in the presence of pyrogallol.



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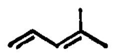

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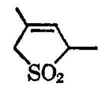

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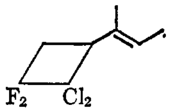
Decomposition of **21** led to pure **19** in 62% yield. On the attempt to prepare a cycloadduct of 1122 from this diene, only a black tar resulted from distillation of the product. It seems possible that the cooperative effects of the two methyl groups so activate the diene that its polymerization takes precedence over cross-cycloaddition.

The two 3-methyl-1,3-pentadienes **16** and **17** led to cycloadducts **22** and **23**, respectively, in normal fashion. Tables I and II show the vapor chromatographic results in the two cases. The most striking feature of the reaction of the two stereoisomers **16** and **17** is the difference in yields, the *trans* compound affording about twice as much of the cycloadduct. (Only with the *trans*-diene did a dark brown coloration and insoluble oily by-products appear during the course of the reaction.) Confirmatory results were obtained with a *mixture* of **16** and **17**. The formation of about 1% of the "wrong" isomer (with respect to the geometry of the side chain) should probably be attributed to *cis–trans* isomerization of the diene prior to the addition, rather than to a concerted isomerization during the cycloaddition reaction itself. Several instances will be reported in parts VII and VIII of the easy isomerization of conjugated dienes under the conditions of cycloaddition. Although the structures of A and B have not been established, the assignments A = **24** and B = **25** would be in agreement with the experimental results (starting with *cis* and *trans* diene, the amounts A *vs.* B formed are in the ratio 1:3.2 and 1:7, respectively).



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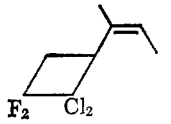

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Table I

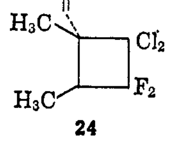
Products of the Reaction of *trans*-3-Methyl-1,3-pentadiene **17** with 1,1-Dichloro-2,2-difluoroethylene

Compound	Retention time, min	Peak area, %	G	Yield, % of theory
Low boiling	6–18	1.9	...	...
A	33	0.4	...	...
B	42	2.8	...	...
C = **22**	53.5	1.4	0.11	1.4
D = **23**	66.5	93.6	7.4	94

Table II

Products of the Reaction of *cis*-3-Methyl-1,3-pentadiene **16** with 1,1-Dichloro-2,2-difluoroethylene

Compound	Retention time, min	Peak area, %	G	Yield, % of theory
Low boiling	5–20	5.2	...	...
A	33	0.6	...	...
B	41	1.9	...	...
C = **22**	58.5	91.2	0.313	46.2
D = **23**	62	1.1	0.004	0.56



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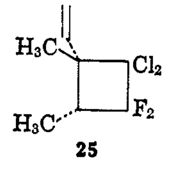

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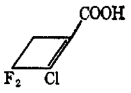
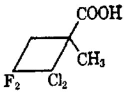
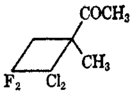
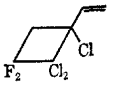
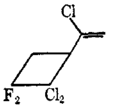
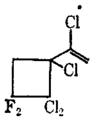
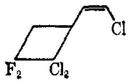
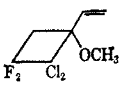
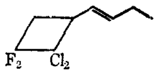
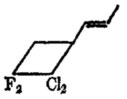
The reaction of *cyclohexene* with 1122 was carried out at 220° for 40 hr, leading to a mixture of about six products. The main component ($\sim$70%) showed ethylenic absorption in the nmr at about δ 5.8.

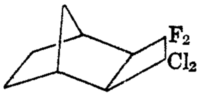
TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Structure	Olefinic H	Alkyl H	Secondary cyclic	Tertiary cyclic	Other
 3			3.24 t, $J = 3.74$ (2.00)		COOH, 12.32 s (1.02)
 7, 25% in $CHCl_3$		1.64 d, $J = 1.6$ (2.64)	3.35 octet, $J = 19.8, 13.5, 9.5$ (1.03); 2.41 sextet, $J = 13.6, 3.0$ (1.00)		COOH, 11.19 s (1.00)
 6, 50% in CCl_4		2.24 s (2.84), 1.52 d, $J = 1.3$ (3.00)	3.27 octet, $J = 20.7, 13.8, 9.9$ (0.98); 2.23 sextet, $J = 13.5, 3.0$ (0.99)		
 8	6.19 q, $J_{12} = 17.5, J_{13} = 9.6$ (1.00); 5.46 d, $J = 9.6$ (1.02); 5.45 d, $J = 17.4$ (1.05)		3.2 m (2.00), 10 lines		
 9	5.56 q, $J \simeq 1.5$ (0.99); 5.29 q, $J \simeq 1.5$ (1.01)		2.7 m (2.04)	3.5 t (0.98)	
 12	5.63 d, $J = 2.8$; 5.53 d, $J = 2.7$ (1.98)		3.3 m (2.02)		
 13	6.34 d, $J = 7.1$ (0.97); 5.92 t, $J = 7.4$ (1.03)		2.0–3.3 m (2.2)	3.6–4.2 m (1.05)	
 14	6.03 q, $J = 16.6, 10.5$ (0.99); 5.55 q, $J = 10.5, 1.8, 1.7$ (1.02); 5.47 q, $J = 16.7, 1.8, 1.9$ (0.99)	3.26 s (3.0)	2.6–3.1 q (1.97)		
 15	5.2–6.1 m (1.91)	2.1 m (2.06); 1.00 t, $J = 7.4, 7.0$ (3.00)	2.3–3.5 m (overlapping)	2.3–3.5 m (overlapping)	
	5.17 d, $J \sim 8$ (1.03)	1.87 d, $J \sim 1$ (3.0); 1.70 d, $J \sim 1.5$ (3.0)	2.5–3.2 m (1.86)	3.2–3.8 m (0.91)	

Norbornene, heated with 1122 to 110° for 60 hr and to 150° for 26 hr, yielded a product in about 92.5% purity to which structure **26** was assigned.

Norbornadiene at 105° yielded adducts **27** and **28** and, on further heating at 150° for 46 hr, **29**. Hydrogenation of **27** yielded **26**. The nmr spectrum of **28** is closely parallel to that of the higher melting 2,6-addition product of methyl azodicarboxylate to norbornadiene.[2]



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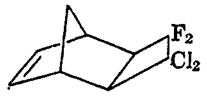

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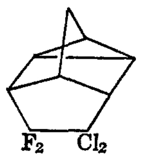

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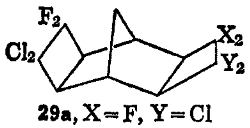
The product **29**, after two distillations, melted over a 40° range from 130 to 170°, as would be reasonable for a mixture of isomorphous **29a** and **b**.



29a, X = F, Y = Cl
b, X = Cl, Y = F

Discussion

Nmr Spectra.—Table III summarizes the nmr spectra determined in this work. Together with the analyses (Table IV) these spectra provide a basis of choice among 1,2, 3,4, and 1,4 adducts and between *cis* and *trans* configurations in side chains. Figure 1

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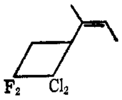
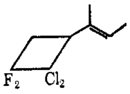
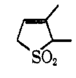
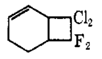
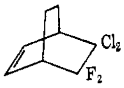
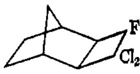
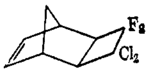
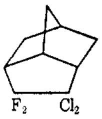
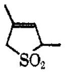
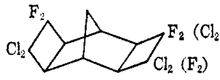
(2) S. J. Cristol, E. L. Allred, and D. L. Wetzel, *J. Org. Chem.*, **27**, 4058 (1962).

Table III
(*Continued*)

Structure	Olefinic H	Alkyl H	Secondary cyclic	Tertiary cyclic	Other
 **23**, 20% in CCl_4	5.7 q, $J = 6.5$ (0.97)	1.8 m (6.16)	2.7 m (1.98)	3.7 t (1.00)	
 **22**	5.2 q, $J = 6.5$ (1.00)	1.7 m (6.06)	2.6 m (2 .01)	3.2 t (0.98)	
 **18**, 50% in CCl_4	5.65 m (1.00)	1.80 m (3.28); 1.31 d, $J = 7.3$ (3.28)	3.58 m (2.0), overlapping	3.48 q, $J = 7.2$ (1.0), overlapping	
 **10**	6.14 d, $J = 11$ (0.96); 5.78 m, $J = 10, 3, 1$ (0.98)		1.5–2.3 m (4.00)	2.9–3.5 m (2.00)	
 **11**	6.3 m (1.73)		1.2–2.6 m (4.03)	2.8–3.5 m (1.97)	
 **26**			0.8–1.8 m (5.1), 1.8–2.3 m (1.2)	2.45 s unsharp 2.5–3.1 m (4.00)	
 **27**	6.23 s (1.97)		2.0 d, $J = 10$ (1.05); 1.4 d, $J = 10$ (1.02)	3.19 s unsharp (1.99), 2.5–3 m (1.97)	
 **28**, 60% in CCl_4			1.67 m (2.00)	2.62 s unsharp (1.16), 2.30 m (2.05), 1.4 m (2.7)	
 **21**	5.45 m (1.00)	3.5 (3.07), 1.77 m (3.13)	1.24 d, $J = 6.8$ (3.11)		
 **29**, 5% in CCl_4			2.23 s (1.91)	2.4–3.1 m (6.00), overlapping	

[a] Chemical shifts (ppm) are downfield from internal tetramethylsilane; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; J is given in cps. Figures in parentheses are numbers of protons involved as shown by integration of the nmr signal.

compares the spectrum of **28** with the analogous compound of Cristol, Allred, and Wetzel. In terms of the biradical mechanism, it appears that a biradical formed from 1122 at an *exo*-2 position of norbornadiene necessarily closes a four-membered ring at the *exo*-3 position while an initial attack at the *endo*-2 position is always followed by closure of a five-membered ring at the now accessible *endo*-6 carbon atom. The ratio of 14.7:1 in which these adducts are formed might be an indication of the degree of selectivity between *exo* and *endo* attack on this ring in a free-radical process, presumably dominated by steric factors. However, see the later discussion under Directive Effects.

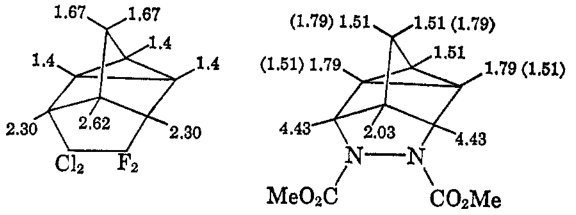


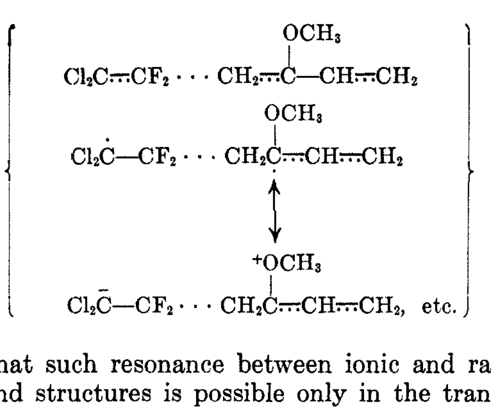
Figure 1.—Nmr assignments (δ values, internal standard tetramethylsilane, $\delta = 0.00$ ppm) of the adducts of 1,1-dichloro-2,2-difluoroethylene and dimethyl azodicarboxylate to bicyclo-[2.2.1]-2,5-heptadiene.

Directive Effects in Cycloaddition.—In part III[1c] it was noted that either methyl or chlorine at the 2 position of butadiene increases the rate of 1,2 cycloaddition and *retards* 3,4 cycloaddition. Methyl at the 1 position also accelerates 3,4 addition and retards 1,2 addition by a factor of at least 20. These effects were explained in terms of the biradical mechanism and the following properties of the groups: for the methyl group, the general hyperconjugative delocalization of the odd electron of a free radical on the adjoining carbon atom; for the chlorine atom, a similar delocalization through d orbitals; for both substituents, a hindrance to coplanarity of the transoid diene which diminishes the reactivity of the 3,4 double bond; for the methyl group, and presumably also for the chlorine atom, the kind of hindrance to direct attack at its adjoining carbon which is seen in free-radical attack (*e.g.*, on propenylbenzene relative to styrene).

If these effects were multiplicative, we might expect to be able to calculate the rate of addition to 2,3-dimethylbutadiene (relative to butadiene) by multiplying the relative rates at the two double bonds of isoprene, or 2.3 × 0.42 = 0.97. The relative rate found here is 0.66 × 1.36 = 0.90. By similar considerations we might calculate the expected isomer predominance in the cycloadditions of this paper as follows: *cis*-1-chlorobutadiene, 3,4 by at least 22:1; *cis*-3-methyl-1,3-pentadiene, 1,2 by 11:1; and *trans*-3-methyl-1,3-pentadiene, 1,2 by 8:1. In each case the selectivity is greater than the calculation suggests. If A and B of Tables I and II have the suggested structures, then the 3-methyl-1,3-pentadienes have in fact selectivity ratios of 48 for the *cis* and 33 for the *trans*, about four times those estimated.

The selectivity of 2-methoxybutadiene was at least 50:1 in favor of 1,2 addition. It does not seem possible to explain this high selectivity on the basis of the effects enumerated above, since α-alkoxy free radicals cannot be stabilized by either a d orbital or a hyperconjugation mechanism. The effect appears normal, however, if we attribute one more well-known property of free radicals to the biradical intermediates in cycloaddition. Whenever radicals are in the process of being formed or of reacting, the *transition state* is favored if it has contributing ionic structures.[3]

In additions of 1122 to a diene the *gem*-dichloroalkyl radical at one end is uncompromisingly electronegative, and effective dipolar contributions can come about only when there is potential cationic character in the allylic radical. This, of course, is strongly the case in 1,2 cycloaddition to 2-methoxybutadiene, and this seems a likely reason for the powerful directive effect of the methoxy group. It must be borne in mind that such resonance between ionic and radical-like bond structures is possible only in the transition state of a process in which the multiplicity remains that of the original reacting species. Reasons have been given for thinking that in the generation of a pair of radicals no unpairing of spins occurs until well after the transition state has been passed.[4]



$$\left\{ \begin{array}{c} Cl_2C{\cdots}CF_2 \cdots CH_2{\cdots}\overset{OCH_3}{C}{-}CH{\cdots}CH_2 \\ Cl_2\dot{C}{-}CF_2 \cdots CH_2\overset{OCH_3}{\dot{C}}{\cdots}CH{\cdots}CH_2 \\ \updownarrow \\ Cl_2\bar{C}{-}CF_2 \cdots CH_2\overset{^+OCH_3}{C}{\cdots}CH{\cdots}CH_2, \text{ etc.} \end{array} \right\}$$

It is now time to consider whether there is anything uniquely radical-like in the "biradical" intermediates which respond so strongly to ionic influences. Might the hyperconjugative effect which we attribute to the methyl group be an ionic one, the same as that which delocalizes charge in the tertiary butyl cation, and might the "d-orbital delocalization" by chlorine be only the ionic electron back-donation seen in the trichloromethyl anion? We shall report later on experiments now in progress to clarify these points, including studies of solvent effects. It is already clear, however, that the polar complementarity seen between dienes and dienophiles in the Diels–Alder reaction is of a higher order than any in additions of fluorinated olefins, and there are many points at which the effects in concerted 1,4 and stepwise 1,2 addition diverge. Chloroprene, mildly activated toward 1122, is slower than butadiene toward maleic anhydride by a factor of 10.[5] Important differences in solvent susceptibility and stereospecificity between 1122 and reagents related to tetracyanoethylene[6-9] make it probable at present that the "biradical" mechanism shown by the fluorinated olefins is different qualitatively from a mechanism proceeding through a dipolar ion.

The Addition of Sulfur Dioxide to Dienes.—This well-known reaction[10-13] is useful in the isolation of pure or highly enriched *trans* dienes from their *cis* isomers. The facts that the addition is exclusively of the 1,4 type and that *trans* olefins react much faster than their *cis* isomers are points classifying this reaction with the Diels–Alder in contrast to the 1,2 mechanism. One can recover the *trans* isomers by thermal decomposition of the cyclic sulfones, and the *cis* isomers from the residues after exhaustive reaction of isomer mixtures with maleic anhydride to remove the *trans* dienes.

Experimental Section

Elementary analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

The nmr spectra (Table III) were taken with a Varian Associates A-60 nmr spectrometer with a sweep time of 500 sec with carbon tetrachloride as a solvent and tetramethylsilane as an internal standard ($\delta = 0.00$ ppm).

Infrared spectra were taken with a Perkin-Elmer Infracord spectrophotometer.

The cycloadditions were carried out as described by Bartlett, Montgomery, and Seidel[1a] in sealed tubes containing small amounts of polymerization inhibitors. Only the temperatures and times of reactions varied from one case to another.

Table IV lists the elementary analyses of all the products described in this paper. Table V lists the properties used for characterization of the products, the yields, and purification methods used. In every case the purity of a product was judged by its behavior on vpc with the use of columns which experience has shown to be effective for the separation of isomers of these or related compounds. Numerals in parentheses following the

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(3) An example among radical–molecule reactions is the attack of chlorine atom upon substituted toluenes [G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956); *J. Org. Chem.*, **23**, 1407 (1958)]. An example involving generation of a radical pair is the concerted decomposition of substituted *t*-butyl phenylperacetates [P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960)].

(4) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(5) J. Sauer, *Angew. Chem.*, **74**, 352 (1962).

(6) C. A. Stewart, *J. Am. Chem. Soc.*, **84**, 117 (1962).

(7) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).

(8) J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962).

(9) C. J. Dempster, unpublished work in this laboratory.

(10) H. J. Backer and J. Strating, *Rec. Trav. Chim.*, **53**, 525 (1934).

(11) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 455 (1935).

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

(13) D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

TABLE IV

ELEMENTARY ANALYSES

	Calcd, %					Found, %				
Formula	C	H	Cl	N	F	C	H	Cl	N	F
$C_5H_4NClF_2O$	35.84	2.41	21.16	8.36		35.84	2.12	20.12	7.89	
2								20.93	8.66	
$C_7H_8Cl_2F_2O$	38.73	3.72	32.67			38.53	3.98	32.01		
6						32.46	3.75	34.15		
						39.70	3.90	32.71		
						39.65	3.69			
$C_6H_5Cl_3F_2$	32.54	2.28	48.03			33.40	2.41	47.92		
8						33.35	2.49			
						32.82	2.43			
$C_6H_5Cl_3F_2$	32.54	2.28	48.03			33.22	2.38	47.82		
9						33.14	2.47	47.68		
						33.05	2.40	49.47		
						32.46	2.32	49.04		
								46.29		
$C_6H_4Cl_4F_2$	28.16	1.58	55.42			28.34	1.81	55.36		
12										
$C_6H_5Cl_3F_2$	32.54	2.28				32.28	2.11			
13										
$C_7H_8Cl_2F_2O$	38.73	3.72				39.78	3.54			
14						39.02	3.64			
$C_8H_{10}Cl_2F_2$	44.67	4.69				45.19	4.76			
15						44.62	4.78			
$C_8H_{10}Cl_2F_2$	44.67	4.69	32.97			44.77	4.85	30.19		
23								33.29		
$C_8H_{10}Cl_2F_2$	44.67	4.69	32.97			44.87	4.65	32.71		
22										
$C_8H_{10}Cl_2F_2$	44.67	4.69	32.97		17.67	44.17	4.71	32.81		17.44
5						44.56	4.69			
$C_8H_8Cl_2F_2$	45.10	3.78				45.46	4.15			
11						45.03	3.88			
$C_8H_8Cl_2F_2$	45.10	3.78				45.38	3.71			
10										
$C_9H_8Cl_2F_2$	48.03	3.58	31.51			48.41	3.64	31.10		
27						48.40	3.36	31.48		
						48.17	3.70	31.22		
								31.10		
$C_9H_8Cl_2F_2$	48.03	3.58	31.51			48.49	3.73	32.24		
28										
$C_{11}H_8Cl_4F_4$	36.90	2.25	39.62			37.73	2.44	39.40		
29						37.89	2.49	38.94		

entries under "Vpc retention time, min" in Table V refer to Table VI which lists a number of specific sets of conditions for vapor chromatographic separations. *F* values are given in Table VII.

Degradation of 1,1-Difluoro-2,2-dichloro-3-methyl-3-isopropenylcyclobutane (5).—To a stirred solution of 3.23 g of **5** (15.0 mmoles) in 100 ml of acetone 25.3 g of finely powdered potassium permanganate (160 mmoles) was added at 25° in the course of 3 hr. After 2 days of stirring excess permanganate was destroyed with sodium bisulfite and the aqueous phase was extracted with ether. Acidic material was obtained by extracting the ether solution with aqueous sodium carbonate. After distillation under 20-mm pressure and recrystallization from pentane, the colorless product (270 mg) melted at 121.5–124.0° and depressed the melting point of authentic **7** to 92–96°. This acidic material was not further investigated. The neutral components were purified by distillation under 20 mm yielding 1.72 g of colorless ketone (**6**, 53%), mp 78.5–81.2°. Vpc gave no indication of impurities.

Conventional hypobromite treatment of the ketone (0.90 g, 4.15 mmoles) led to 0.84 g of colorless acid mp 100–123°. Its identity with authentic **7** was established spectroscopically. The authentic **7** was prepared by hydrolyzing the adduct of 1122 and methyl methacrylate. Distillation and two recrystallizations from pentane raised the melting point to 130.4–131.2°.

2,3-Dimethyl-1,3-butadiene was purchased from the Columbia Organic Chemicals Co. and was fractionated through a 32-cm Helipac column. The product boiled at 68°, $n^{25}D$ 1.4391.

cis- and *trans*-3-Methyl-1,3-pentadienes as well as 2-ethyl-1,3-butadiene were obtained by dehydrating with *p*-toluenesulfonic acid a sample of 3-methyl-1-penten-3-ol donated by the B. F. Goodrich Research Center. The alcohol (300 g, 3.00 moles) and 1.5 g of *p*-toluenesulfonic acid was heated until 210 g of mixed dienes and 42 ml of water had been collected by distillation. Vpc analysis (tris-2-cyanoethoxypropane column on 60–80 mesh Chromosorb P) indicated 16% 2-ethyl-1,3-butadiene, 30% *cis*- and 48% *trans*-3-methyl-1,3-pentadiene, and about 6% of unidentified compounds. Separation and purification of the olefins were carried out as indicated in Table V.

4-Methyl-1,3-pentadiene was prepared by the dehydration of 2-methyl-2,4-pentanediol (1010 g, 8.54 moles) with 1 g of iodine in the presence of 4 ml of aniline. The reactants were heated and the products were distilled. The organic portion of the distillate was separated, washed several times with water, and dried over sodium sulfate. About 0.5 g of di-*n*-butylammonium picrate was added to the mixture. Fractional distillation through a 32-cm Helipac column yielded two main fractions, 213 g of a mixture (4:1) of *trans*-2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene and 176 g of 2-methyl-1-penten-4-ol. In a number of preparations the ratio of the two dienes varied from 3:1 to 6:1, the larger ratio apparently being associated with longer distillation periods.

When the mixture of the two olefins was allowed to react with excess maleic anhydride, the *trans*-2-methyl-1,3-pentadiene reacted to the exclusion of its isomer which could be isolated, bp 76°, $n^{20}D$ 1.4700, from the residue.

1,3-Cyclohexadiene was purchased from the Aldrich Chemical Co.

cis-1-Chloro-1,3-butadiene was prepared by the method of Craig.[14] *trans*-1,4-Dichloro-2-butene (practical grade, Eastman

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[14] D. Craig, private communication, 1960.

TABLE V
DIENES, DERIVATIVES, AND CYCLOADDUCTS

Compd	Characterization	Yield, %	Purification method	Vpc retention time, min
2	Infrared spectrum 1695 cm^{-1}, mp 146.8–148.8°, mmp	27	Recrystn from CCl$_4$	
3	Mp 94.7–96.4°, mmp	80	Recrystn from pentane	
6	Mp 78.5–81.2°, homogeneous on vpc	53	Distn (20 mm)	
7	Mp 100–123°, spectrum identical with that of synthetic specimen, mp 130.4–131.2°	93	Distn (22 mm) syn; recrystn from pentane	
8	Bp 62.6–63.0° (14 mm), nmr		Vpc 1, 2	22
9	Nmr		Vpc 1, 2	31.5
10	Bp 80.2–80.8° (9 mm), nmr		Vpc 1a, 3a	32.4 (1a)
11	Mp 151–155° (sealed tube)		Vpc 1a, 3a, subl	39.6 (1a)
12	Mp 53–59°, homogeneous on vpc	69	Distn (23 mm)	
13	$n^{25.5}_{\text{D}}$ 1.4629, homogeneous on vpc	74	Distn (12 mm)	
14	Nmr		Dist (18 mm), prep vpc 8	37.2
15	Bp 72.0–72.6° (11.5–12.0 mm)	38	VPC 3	
16	97% pure by vpc 6	38	From sulfone, vpc 5, 7	
17	99.6% pure by vpc 6	78	Vpc 5, maleic anhydride on mixture, extn of residue	
18	Nmr	16	Distn (2 mm)	
21	Mp 40.6–41.8°	73	Recrystn from ether–pentane	
20	Vpc bp 75°	62	From sulfone	
23	Nmr		Vpc 8, 9	
22	Nmr		Vpc 8, 9	
26	Bp 108–109° (14–15 mm)		Vpc 3b	
27	Nmr		Vpc 13	40
28	Nmr, mp 54.6–55.8°		Vpc 13	56
29	Mp 135–165°	19.5	Distn (0.4 mm)	

TABLE VI
VAPOR CHROMATOGRAPHIC SEPARATIONS

Procedure	Column packing	Dimensions, ft in.	Temperatures, °C Inlet	 Column	 Detector	Flow rate, cc/min of He
1	Diisodecyl phthalate	6		120	210	
1a	Diisodecyl phthalate	6		160	210	48
2	Crosslinked diethylene glycol			156	238	170
3	Silicone SE 30			176	215	300
3a	Silicone SE 30			173	251	250
3b	Silicone SE 30		158	176	211	160
4	Silicone QF 1	20 × $^3/_8$		67	141	170
5	Silicone QF 1	20 × $^3/_8$		67	141	150
6	Tris-β-cyanoethoxypropane	10	120	48	245	60
7	Silicone QF 1	20 × $^3/_8$		28	109	170
8	Tris-β-cyanoethoxypropane	20 × $^3/_8$		119	225	80
9	Tris-β-cyanoethoxypropane	20 × $^3/_8$		128	222	130
10	β,β′-Oxydipropionitrile	10		32		
11	Carbowax 20 M (Autoprep)			83	124	220
12	Silicone 710	8 × 0.25		130		
13	Silicone QF 1			170	265	170
14	Diisodecyl phthalate on Chromosorb P	6 × 0.25		85	115	
14a	Diisodecyl phthalate on Chromosorb P	6 × 0.25		80	100	

TABLE VII
DETERMINATION OF F VALUES[a]

Compd	Wt, mg	Mol wt	M, mmoles	A	F	F_{av}
Isoprene adduct	601.3	201.04	2.9909	824.3	0.7414	
				889.0	0.7384	
				870.8	0.7361	0.7386
2,3-Dimethylbutadiene adduct	497.8	215.07	2.3146	646.6	0.7314	
				711.1	0.7144	
				695.1	0.7137	0.7199
Toluene	210.8	92.13	2.2880	467.5		
				502.2		
				490.4		

[a] Toluene is the standard.

Kodak Co.) was distilled under 20-mm pressure, bp 60–62°. Potassium hydroxide pellets (198 g of 85%) (3.0 moles) were heated to 100–120°, and *trans*-1,4-dichloro-2-butene (125 g, 1.00 mole) was added slowly with stirring to the molten potassium hydroxide. *cis*-1-Chloro-1,3-butadiene was distilled, collected, and dried over calcium chloride. Distillation gave 47.1 g (53%) of material, bp 66°, $n^{20}{}_D$ 1.4723. Treatment with maleic anhydride did not alter the physical properties of the *cis*-1-chloro-1,3-butadiene.

The 2-methoxybutadiene used was obtained in part as a gift from the late Dr. David Craig [bp 73.1–73.2° (730 mm), $n^{20}{}_D$ 1.4448] and in part prepared by the method of Petrov.[15] The latter material had an infrared spectrum identical with that of the former and similar physical properties, bp 74°, $n^{20}{}_D$ 1.4461.

The preparation of cyclic sulfones is illustrated by the reaction of the 3-methyl-1,3-pentadienes. A freshly distilled mixture (36.5 g) of the *cis* and *trans* isomers (0.445 mole, 27% *cis*, 73% *trans*), 250 g of sulfur dioxide (3.9 moles), small amounts of di-*n*-butylammonium picrate and pyrogallol, and 80 ml of absolute ether were sealed in a glass-lined steel autoclave. After 24 hr at room temperature the liquid part of the reaction mixture was separated from gummy material which was extracted subsequently with warm ether. From the combined ether solutions the solvent was removed; then at 125° bath temperature and 2-mm pressure, 10.2 g of a yellow oil was distilled which was shown by nmr (Table III) to consist of a single, fairly pure cyclic sulfone (16% of theoretical yield). Much decomposition occurred during the heating.

The recovery of the *cis* diene **16** from the cyclic sulfone **18** is also typical. Sulfone **18** (7.7 g) was heated to 150–180° and the products were distilled through a 5-cm Vigreux column, bp 67°. The yellow distillate was washed with aqueous sodium carbonate and water and dried, amounting to 1.65 g, 38%. Vpc (6, Table VI) showed the product to consist of *cis*-3-methyl-1,3-pentadiene (97%), *trans*-3-methyl-1,3-pentadiene (3%), and traces of lower boiling materials.

Rate Measurements.—The rate constant for addition of 1122 to 2,3-dimethylbutadiene was measured by observing the competition between this diene and isoprene in a mixture, the course of the reaction being followed by vapor chromatography. The solutions employed were prepared with a cooled (−20°), vacuum-jacketed, 15-ml volumetric flask. Portions (1 ml) of the solutions were transferred with a cooled syringe into heavy-walled ampoules (12.7-mm o.d., 2.3-mm wall thickness) cooled with ice water. To each of the ampoules 1 mg of di-*n*-butylammonium picrate had been added previously. The 1122 had been freshly distilled and was stored over molecular sieves, type 4A (Fisher). The dienes were also carefully distilled before use. The sealed ampoules were removed from the 82° bath at appropriate intervals 2–28 hr after immersion and stored at −20°. Analysis of 15–100-μl samples was carried out under conditions 14 and 14a of Table VI. Toluene was used as an internal standard. The F & M 300 gas chromatograph was equipped with a thermal conductivity detector and a Disc integrator which was employed to evaluate the peak areas.

To calculate the ratio of rate constants k_x/k_y the following formula was used

$$\frac{k_x}{k_y} = \frac{\log \dfrac{M_x{}^0 - F_x \dfrac{A_x}{A_{\text{standard}}} M_{\text{standard}}}{M_x{}^0}}{\log \dfrac{M_y{}^0 - F_y \dfrac{A_y}{A_{\text{standard}}} M_{\text{standard}}}{M_y{}^0}}$$

where $M_x{}^0$ designates the amount of competing species (x) in millimoles at the start of the experiment, F_x represents an experimentally determined conversion factor of x, and A_x is the measured peak area of the adduct of component x in integrator counts. Subscripts y and standard analogously refer to the second competing species y and to the standard (toluene), respectively. F takes into account the different thermal conductivities of the particular compound and the standard. Being defined by the equation

$$F_x = M_{\text{adduct x}} A_{\text{standard}}, M_{\text{standard}} A_x$$

it represents the ratio of peak areas of the standard and of the cycloadduct of x for equimolar amounts of the two.

Registry No.—1,1-Dichloro-2,2-difluoroethylene, 79-35-6; **3**, 1735-42-8; **7**, 1986-85-2; **6**, 10033-78-0; **8**, 10033-79-1; **9**, 10033-80-4; **12**, 10033-81-5; **13**, 10038-82-6; **14**, 10033-83-7; **15**, 10033-84-8; **23**, 10033-85-9; **22**, 10033-86-0, **18**, 10033-87-1; **10**, 10033-88-2; **11**, 10033-89-3; **26**, 10033-90-6; **27**, 10033-91-7; **28**, 10033-92-8; **21**, 10033-92-8; **29a**, 10039-50-6; **2**, 10033-93-9; **16**, 2787-45-3; **17**, 2787-43-1; **20**, 926-56-7; **29b**, 10033-96-2; 2,2-dichloro-1,1-difluoro-3-(2-methylpropenyl)cyclobutane, 10033-97-3; **5**, 10033-98-4; *cis*-1-chloro-1,3-butadiene, 10033-99-5.

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The Reaction of Rhodium Trichloride with Dienes

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The reaction of ethanolic rhodium trichloride with dienes gives rise not only to various complexes of rhodium(III), but also to catalytic reactions involving the addition of ethanol to the diene. The results obtained by various workers on the interaction of rhodium trichloride with butadiene are rationalized.

The reduction of rhodium trichloride by ethanol in the presence of olefins[1-3] has frequently been employed for the preparation of π complexes of rhodium(I). In the cases of acrylonitrile[4] and cyclododecatriene,[5] σ and π complexes of rhodium(III) were obtained, respectively.

The interaction of ethanolic rhodium trichloride with butadiene has been investigated by a number of workers[6-8] with a variety of results. We now wish to report the catalytic and stoichiometric results we have obtained with conjugated dienes and rhodium trichloride.

Results

The Reaction of Rhodium Trichloride with Isoprene.—When rhodium trichloride is heated in ethanol with

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