Cycloaddition. V. 2-Alkylbutadienes and 1,1-Dichloro-2,2-difluoroethylene. The Effect of Diene Conformation on Mode of Cycloaddition

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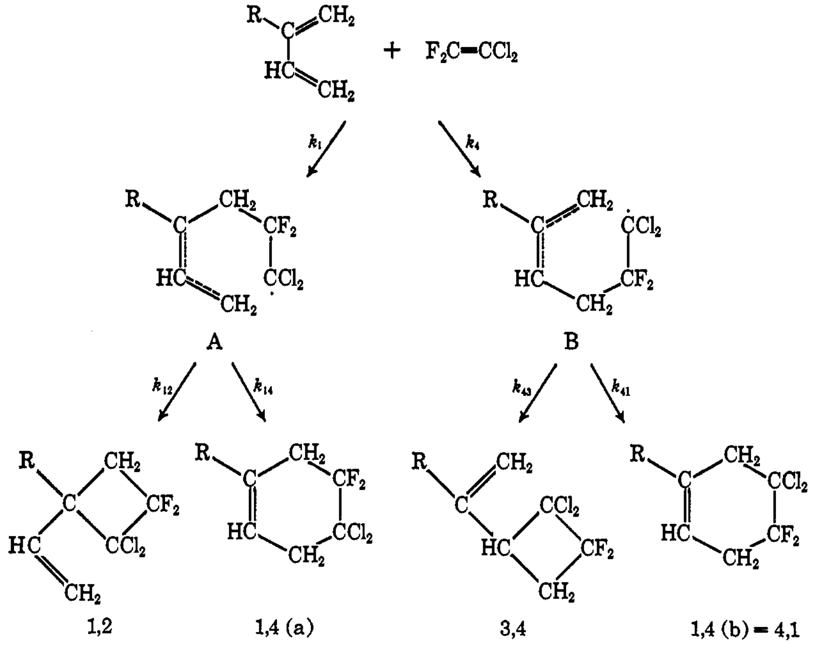
Abstract: The addition products of 1,1-dichloro-2,2-difluoroethylene to the 2-alkylbutadienes include some 1,4 adduct (1.6% in the case of isoprene) which increases in relative importance as the bulk of the alkyl group increases, 2-*t*-butylbutadiene yielding 45% of 1,4 adducts. Over this same range of substituents the ratio of 1,2 to 3,4 addition products falls from 5.4 for isoprene to 0.25 for 2-*t*-butylbutadiene. After a review of the evidence it seems probable that these 1,4 adducts arise not from an independent, concerted addition mechanism but by way of the same biradical intermediate previously implicated in the 1,2 and 3,4 addition. The two isomeric 1,4 adducts to 2-*t*-butylbutadiene could not be separated, but alkali treatment converted the mixture into a mixture of 3-fluoro-4-chloro- and 3-chloro-4-fluoro-*t*-butylbenzenes which were separated and independently synthesized. It is concluded that increasingly bulky alkyl substituents at the 2 position of butadiene (a) increase the population of the cisoid conformation of the diene; (b) increase the proportion of attack of the reagent at C_4 relative to C_1; and (c) increase the fraction of biradical which closes to yield a six-membered ring, the increase being much greater for that biradical formed by initial attack at C_1 than at C_4. With respect to these effects the neopentyl and phenyl groups appear less bulky than the isopropyl.

Fluorinated olefins have been observed to add to acyclic dienes with the apparent exclusive formation of vinylcyclobutanes by 1,2 cycloaddition rather than cyclohexenes by 1,4 addition.[1-3] This has been explained in terms of the intermediate formation of a biradical, together with the known preference[4,5] of butadiene for the *transoid* rather than the *cisoid* conformation and demonstrations[6] that an allylic radical initially formed with a *trans* configuration retains this configuration unchanged during its participation in a chain reaction. It is consistent with this general view that *cis*-fixed dienes, such as cyclopentadiene and

Scheme I



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(1) J. D. Roberts and C. M. Sharts, *Org. Reactions*, 12, 2 (1962).

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

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

(4) J. D. Roberts and C. M. Sharts, *Org. Reactions*, 12, 12 (1962).

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

(6) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, 83, 3877 (1961).

Table I. Preparation and Properties of Dienes

R	Characterization	Source or method	Ref
Ethyl	Bp 68°; vpc	Dehyd of 3-methyl-1-penten-3-ol; dist; vpc	*a*
n-Propyl	Bp 93.4–93.6° (768 mm)	Dec of cyclic sulfone (BFG)	*a*
Isopropyl	Bp 85–85.5°, $n^{25}\mathrm{D}$ 1.4340	3-Methyl-2-butanone + vinylmagnesium chloride; dehyd	7,[b,c]
t-Butyl	Cyclic sulfone, mp 81.7–82.7°	Pinacolone + vinylmagnesium chloride; purif *via* sulfone	7,[d]
Neopentyl	Bp 61.2–62.8° (87 mm), prep vpc (Carbowax M)	Diisobutylene + CH_2O + HOAc–HOAc	7,[e]
Phenyl	Used in mixture with α-methylstyrene	α-Methylstyrene + CH_2O + HOAc–HOAc	*f*

[a] I. M. Dolgopol'skiĭ, A. M. Tumanova, I. M. Dobromil'skaya, and M. F. Egudina, *Zh. Obshch. Khim.*, **28**, 1782 (1958). [b] R. Normant, *Angew. Chem.*, **67**, 760 (1955). [c] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957). [d] H. J. Backer and J. Strating, *Rec. Trav. Chim.*, **53**, 525 (1934). [e] A. T. Blomquist and J. C. Westfahl, *J. Am. Chem. Soc.*, **74**, 4073 (1952). [f] E. G. E. Hawkins and R. D. Thompson, *J. Chem. Soc.*, 370 (1961).

Table II. Vapor Phase Chromatographic Separations

Procedure no.	Column packing[a]	Temp, °C	Retention times, min
1	γ-Methyl-γ-nitropimelonitrile (MNPN)	120	1,2 and 3,4 adducts, 14.4; 1,4 adducts, 30
2	Bentone-34		Major, 118; minor, 134.8
3	Tris-β-cyanoethoxypropane	145	**3**, 53; **4**, 47; **5**, 59
4	MNPN	115	**6**, 20.5; **7**, 17.5; **8**, 38.5
5	Anal: diisodecyl phthalate (DIDP)	125	**9**, 39.2; **10**, 52; **11**, 69
	Prep: silicone QF-1	167	**9**, 20; **10**, 27; **11**, 30
6	Silicone QF-1	129	Major, 55; minor, 51; overlap
7	Tris-β-cyanoethoxypropane	120	(**13** + **14**), 42; 1,4 adducts, 24.8
	UCON LB-550X		**13**, 3.75 hr; **14**, 4 hr
8	15% FFAP, 5% Bentone[b]		**15a**, 26.5; **15b**, 25[b]
9	Tris-β-cyanoethoxypropane	115	**16**, 25; **17**, 14.5; **18**, 33
10	Carbowax 20M	170	**19**, 127; **20**, 88; 3,4 adduct, 182; 1,4 adduct, >206

[a] Liquid component. [b] See footnote *a*, Table V.

cyclohexadiene, do yield mixtures of 1,2 and 1,4 adducts with fluorinated olefins.

Craig, *et al.*,[7] observed what appeared to be steric accelerations of the Diels–Alder reaction between maleic anhydride and butadienes bearing bulky substituents at the 2 position. They suggested that 2 substituents larger than methyl hinder the transoid conformation of these dienes and accelerate the Diels–Alder reaction through an increase in the population of the cisoid conformation. Their examination of the infrared and Raman spectra of the dienes lent support to this interpretation.

Thus there were reasons to expect that 1,1-dichloro-2,2-difluoroethylene ("1122") might yield some 1,4 as well as 1,2 and 3,4 addition to suitably bulky 2-alkylbutadienes, whether this addition occurred through the terminal ring closure of a biradical (Scheme I) or by way of a concerted cycloaddition resembling the Diels–Alder reaction.

Results

The dienes were prepared by known methods as indicated in Table I. The cycloadditions were conducted with excess 1122 as solvent as previously described[2,3] except where indicated. The reactions were carried out in sealed tubes at 80° for periods from 21 to 48 hr. The products were fractionally distilled and the pure adducts isolated by vapor phase chromatography as summarized in Table II. The nuclear magnetic resonance spectra of the cycloadducts and their assignments are indicated in Table III.

Table IV shows the compositions of the cycloadducts obtained from seven 2-substituted butadienes. The results with the ethyl and larger groups prompted a new scrutiny of the cycloadducts from isoprene which led to the detection of 1.6% of the mixed isomers of the 1,4 cycloadduct. As seen from Table IV, this figure becomes 5% for 2-ethyl-, 16% for 2-isopropyl-, and 45% for 2-*t*-butylbutadienes. The neopentyl group, which in the work of Craig, *et al.*,[7]

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(7) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, 83, 2885 (1961).

appeared to be effectively more bulky than *t*-butyl, appears in Table IV to be only one-fourth as effective in promoting 1,4 cycloaddition of 1122.

Attending the increased amount of 1,4 addition is a rapidly shifting ratio between addition at the 1,2 and at the 3,4 positions. Thus the ratio of 1,2 to 3,4 adducts, which is 5.4 in the case of isoprene, undergoes a steady decrease until it reaches 0.25 in the case of 2-*t*-butylbutadiene.

Composition of the 1,4 Adduct. If the 1,4 adduct is produced according to Scheme I, since the CCl_2 end of the reagent always becomes the free-radical end,[2] the point of initial attachment of 1122 to the diene must determine the relative orientations of the chlorine and fluorine atoms in the 1,4 cycloadduct. It therefore appeared important to determine the isomeric composition of this adduct. The relatively abundant 1,4 cycloadduct of 2-*t*-butylbutadiene was chosen for the initial investigation.

In the original vpc separation of the adducts of 1122 to 2-*t*-butylbutadiene, a preparative separation of the 1,2 cycloadduct **13** from the mixed 1,4 products could not even be accomplished. It was found, however, that on treatment of this combined fraction with potassium *t*-butoxide in *t*-butyl alcohol, the cyclohexenes underwent complete conversion to aromatic compounds, while the cyclobutane component remained unaffected. Analytical vapor phase chromatography was then able to separate the resulting mixture of **13**, **15a**, and **15b**, and conditions were ultimately found (Table V) affording good resolution of the latter two components, each of which must arise uniquely from one of the two orientation isomers of the 1,4 adduct.

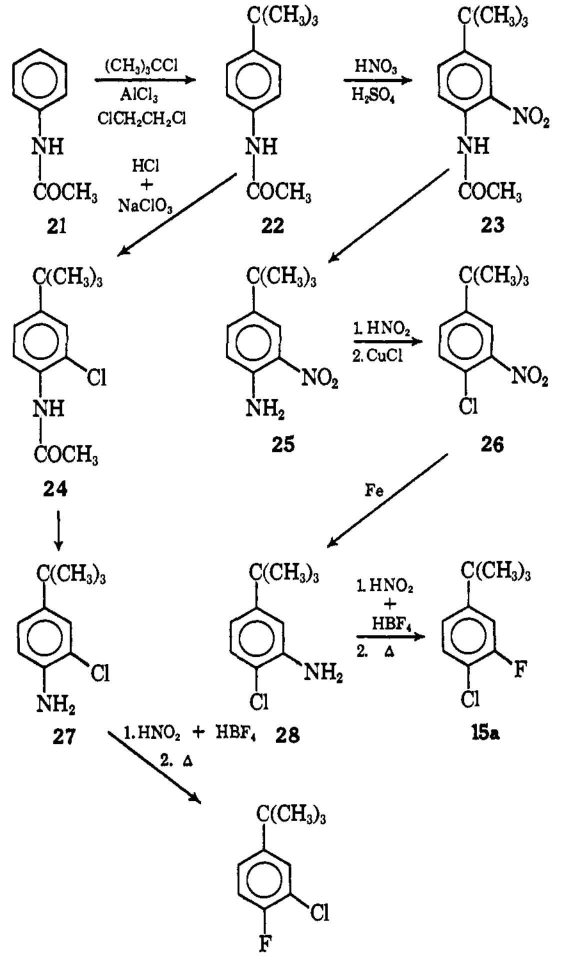
To establish the orientations of these two aromatized products, **15a** and **15b** were synthesized as shown in Scheme II. On vpc comparison, the synthetic compounds proved to have the same retention times as the components of the aromatized mixture with **15a**, 3-fluoro-4-chloro-*t*-butylbenzene, corresponding to the major component.

In the case of the 1,4 adducts of 1122 to isoprene a similar dehydrohalogenation to chlorofluorotoluenes was carried out; in this case one of the isomers, 3-chloro-4-fluorotoluene, was prepared independently and proved to be identical with the minor component of the isomer pair.

The 1,4 adducts of 1122 to 2-isopropylbutadiene were aromatized and their relative amounts determined by vpc separation of the aromatic isomers, but a synthetic preparation was not carried out. The orientations were assigned on the assumption that the isomer which prevailed in the more hindered *t*-butyl and less hindered methyl analogs would also be prevalent in the isopropyl case.

Mechanism of the 1,4 Addition. An increasing prevalence of the cisoid conformation in a conjugated diene would favor 1,4 cycloaddition by either of two mechanisms: (1) the normal, concerted Diels–Alder mechanism, which may proceed in a single step when a 1,2 cycloaddition may not;[8] (2) the formation of *cis* biradicals according to Scheme I, which would then allow competitive ring closure to cyclohexenes as well as to cyclobutanes. The present observations afford no compelling evidence as to which mechanism is operating. Pending the outcome of work now in progress, the available indications may be briefly summarized.

Scheme II



Toward most olefinic reagents the Diels–Alder mechanism is so strongly preferred that it assumes control to the exclusion of cyclobutane formation regardless of the conformational preference of the reacting diene. This is possible because the reactivity of the transoid diene by any concerted mechanism is zero. In the absence of biradicals or dipolar ions the reaction is entirely channeled through whatever cisoid diene is present at equilibrium (aided or unaided by complex formation with the dienophile). On the other hand, by the biradical mechanism, previous indications are that attack on the transoid diene is at least as easy as on the cisoid, and hence by this mechanism the ratio of 1,4- to 1,2-addition product can never exceed the ratio of cisoid to transoid diene in the conformational equilibrium.

Accordingly, one way in which competition of concerted addition with stepwise addition might show itself would be by cyclohexene:cyclobutane ratios in excess of the known or reasonably estimated cisoid:transoid ratios of the diene. A case in which this occurs is that of α-acetoxyacrylonitrile and butadiene,[9] which yield a mixture consisting of 84% 1,4- and 16% 1,2-

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(8) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

(9) (a) J. C. Little, *ibid.*, **87**, 4020 (1965); (b) K. E. Schueller, Thesis, Harvard University, 1966; (c) P. D. Bartlett, *Science*, **159**, 833 (1968).

Table III. Nmr Spectra of Cycloadducts[a]

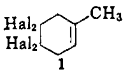
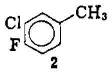
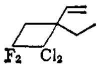
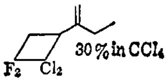
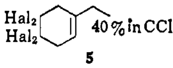
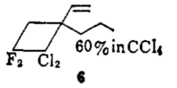
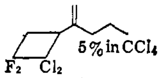
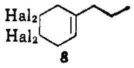
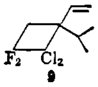
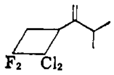
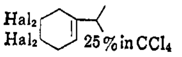
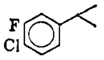
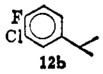
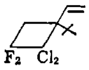
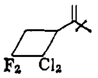
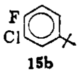
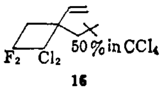
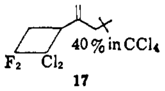
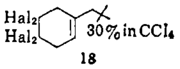
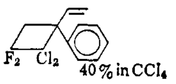
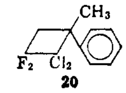
Compound	Vpc conditions[b]	Assignments, type of hydrogen: Olefinic	Alkyl, aryl	Secondary cyclic	Tertiary cyclic
 **1**	1	5.28 broad (1)	1.75 s (3)	2.45–3.22 m (4)	
 **2**	2		2.28 s (dil in CCl_4) 2.20 s (concd in CCl_4) (3) 6.70–7.15 (3)		
 **3**	3	5.86 q, J_{12} = 16.6; J_{13} = 10.3 (0.89) 5.30 d, J_{13} = 10.6 (0.94)[d] 4.96 d, J_{21} = 16.8 (1.09)[d]	1.8 q, J = 7 (1.94) 0.80 t, J = 7 (3.09)	2.5 m (2.00)	
 30% in CCl_4 **4**	3	5.05 q, J = 1.5 (0.94) 4.70 s, fine splitting (0.92)	2.2 q, J = 8 (1.9) 1.11 t, J = 7 (3.00)	2.7 m (1.9)	3.3 t (0.99)
 40% in CCl_4 **5**	3	5.2 m (1.00)	2.0 q, J = 7 (2.02) 1.03 t, J = 7 (3.18)	3.05 m 2.72 m (4.03) 2.47 m	
 60% in CCl_4 **6**	4	5.89 q (1.13), J = 16.8, 10.3 5.30 q (1.00), J = 10.5, 1.2 4.97 q (0.99), J = 17.0, 1.2	1.0 t (3.01) 1.6 m (4.07)	2.63 m (2.20)	
 5% in CCl_4 **7**	4	5.04 s (0.91) 4.70 s (0.91)	0.97 t (2.86), J = 6.9 1.55 m (2.20) 2.16 t (1.95)	2.64 m (1.93)	3.3 t (1.11), J = 10
 **8**	4	5.2 m (1.00)	1.94 t, J = 7 (1.98) 1.40 m (2.18) 0.87 t, J = 7 (3.02)	3.03 m 2.69 m (4.13) 2.44	
 **9**	5	6.11 q, J_{12} = 10.8, 10.7; J_{13} = 17.1 (1.02) 5.44 d, J = 10.6 (1.04) 5.11 d, J = 17.1 (1.04)	1.9–3.1 m (1 overlapping) 1.02 d, J = 6.8 (3.00) 0.73 d, J = 6.8 (3.00)	1.9–3.1 m (2 overlapping)	
 **10**	5	5.17 t, J = 1.2 (0.95) 4.88 d, J = 1.6 (0.97)	3.2 q, J = 6 (1, overlap) 1.13 q, J_{12} = 6.8, J_{1x} = J_{2x} = 2.0 (6.00)	2.3–3.0 m (2 overlapping)	3.4 t?, J = 10 (0.93)
 25% in CCl_4 **11**	5	5.32 m (0.96)	2.23 q, J = 7 (0.96) 1.05 d, J = 6.8 (6.00)	3.08 m 2.75 m (3.80) 2.52 m	
 **12a** +  **12b**	6	7 m (2.82)	2.8 m, $J \approx 7$ (0.88) 1.21 d, J = 6.9 (6.0)		
 **13**	7	6.18 q, J_{12} = 16.8; J_{13} = 10.4 (1.07) 5.28 d, J_{31} = 10.3 (1.00) 4.93 d, J_{21} = 16.9 (0.98)	1.11 s (9.44)	2.74 t, J = 11.4 (2.00)	
 **14**	7	5.40 s (1.13) 4.95 s (0.97)	1.16 s (9.00)	2.2–3.0 m (1.88)	3.3–3.8 t (unsharp), J = 10 (0.91)
 **15a** +  **15b**	8	7 m (3.00)	1.21 s (8.86)		
 50% in CCl_4 **16**	9	6.03 q, J_{12} = 17.1; J_{13} = 10.7 (1.07) 5.42 d, J_{31} = 10.6 (2.01) 5.20 d, J_{21} = 17.2	1.87 s (1.98) 0.95 s (9.16)	2.8 m (2.00)	
 40% in CCl_4 **17**	9	5.12 s (with fine splitting) (0.99) 4.94 d, J = 1.5 (1.02)	2.17 s (1.95) 0.98 s (9.00)	2.6 m (1.95)	3.5 t, J = 10 (0.98)
 30% in CCl_4 **18**	9	5.27 s unsharp (1.00)	1.92 s (2.33) 0.94 s (9.51)	3.13 m 2.83 m (3.6) 2.61 m	
 40% in CCl_4 **19**	10	6.25 q (with addl doublet spl, J = 1.5), J_{12} = 16.3; J_{13} = 10.3 (1.00) 5.06 d, J_{31} = 10.3 (1.02) 4.63 d, J_{21} = 16.9 (0.99)	7.1 m (5.13)	3.0 m (1.98)	

Table III (*Continued*)

Compound	Vpc conditions[b]	Assignments, type of hydrogen: Olefinic	Alkyl, aryl	Secondary cyclic	Tertiary cyclic
 **20**	10		7.1 m (5.00) 1.6 s (2.93)	2.8 m (1.91)	

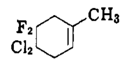
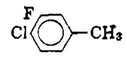
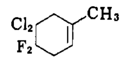
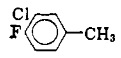
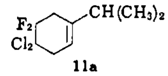
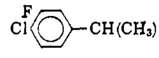
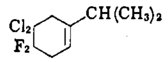
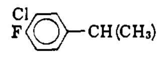
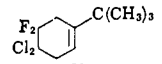
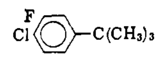
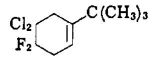
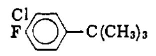
[a] Chemical shifts (δ) in parts per million (internal standard: tetramethylsilane, δ 0.00); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants (*J*) in cycles per second ; numbers in parentheses indicate number of H atoms based on peak areas. [b] See Table II. [c] In each formula containing the symbol "Hal_2," one Hal_2 refers to F_2 and the other to Cl_2. [d] With additional doublet splitting, *J* = 1.

Table IV. Thermal Cycloaddition of 1,1-Dichloro-2,2-difluoroethylene to 2-Substituted 1,3-Dienes at 80°

2 Substituent	% of prodt of addn at 1,2	3,4	1,4	Rel Diels–Alder rate[a]
Methyl	83	15	1.6	3.0
Ethyl	72	23	5	6.1
n-Propyl	73	23	4	. . .
Isopropyl	46	38	16	11.6
t-Butyl	11	44	45	29
Neopentyl	64	26	10	51
Phenyl	76	12	12	. .

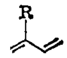
[a] Reaction with maleic anhydride,[7] [*k*(butadiene) = 1.0].

Table V. Composition of 1,4-Cycloadducts of 1122 to Isoprene and 2-Isopropyl- and 2-*t*-Butylbutadienes

Compound	Conversion prodt	% in mixt	Column
 **1a**	 **2a**	85	1
 **1b**	 **2b**	15	1
 **11a**	 **12a**	86	6
 **11b**	 **12b**	14	6
 **29a**	 **15a**	68.6[a]	8
 **29b**	 **15b**	31.4[a]	8

[a] We thank Mr. Ernest J. Bonelli of the Applications Laboratory, Wilkens Instrument and Research Co., Walnut Creek, Calif., for carrying out this analysis.

Table VI. Effect of 2 Substituents on Rate Ratios in Biradical Mechanism of Cycloaddition to Butadienes



R	k_1/k_4	k_{12}/k_{14}	k_{43}/k_{41}
CH_3	5.5	61	63
$(CH_3)_2CH$	1.5	3.3	17
$(CH_3)_3C$	0.72	0.36	3.1

addition products, although the fraction of the diene in the cisoid form is only about 6%.[10] In the present series, however, the fraction of 1,4 cycloaddition is always within the limits accountable by Scheme I, and thus no proof of mechanism is available in this way.

A second characteristic of the concerted mechanism is the preservation of configuration at the double bonds entering into cycloaddition. *trans,trans*-2,4-Hexadiene loses configuration at one of its double bonds in adding to 1122 (1,2 addition),[11] but retains its configuration in the Diels–Alder reaction with α-acetoxyacrylonitrile so that the methyl groups in the resulting cyclohexene are exclusively *cis* to each other.[9b,c] This criterion is also lacking in the present series, where none of the double bonds gives rise to geometrical isomerism.

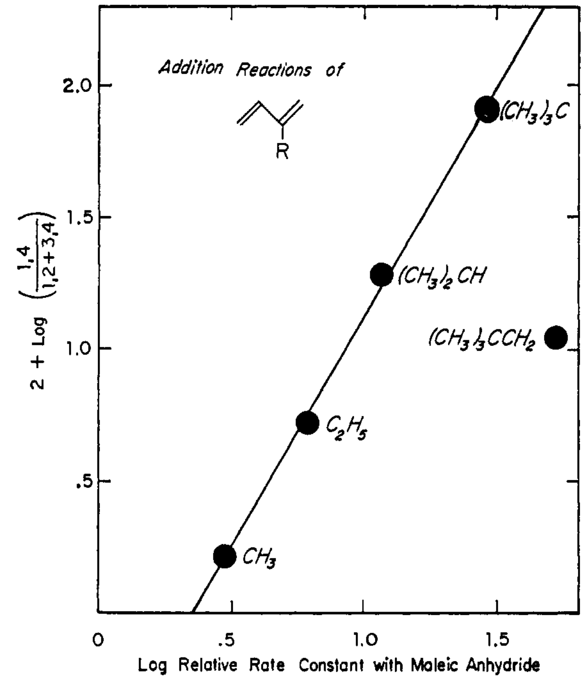


Figure 1. Different effects of 2-neopentyl group on 1,4 addition by maleic anhydride and by 1,1-dichloro-2,2-difluoroethylene.

A less precise but interesting consideration is the comparison which is available between the effects of bulky groups on the mode of addition of 1122 and the effects of these same groups on the rate of the *bona fide* Diels–Alder reaction with maleic anhydride.[7] If the mechanism of the 1,4 addition of 1122 is like that of maleic anhydride, one might expect the two effects to be parallel. They are indeed so (Table IV and Figure 1) except

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(10) J. S. Swenton and P. D. Bartlett, *J. Am. Chem. Soc.*, **90**, 2056 (1968).

(11) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *ibid.*, **86**, 626 (1964).

Table VII. Elementary Analyses

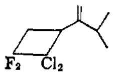
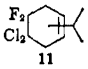
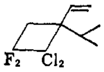
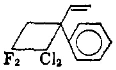
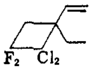
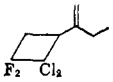
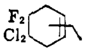
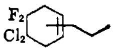
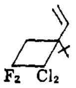
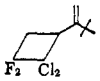
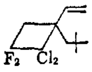
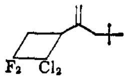
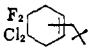
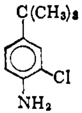
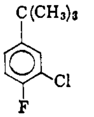
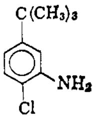
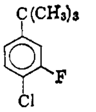
Compound	Calcd, % C	H	Cl	F	N	Found, % C	H	Cl	F	N
 10	47.18	5.28				48.52 47.17	5.61 5.49			
 11	47.18	5.28	30.95			47.72 47.57 47.70 41.87 47.16 46.96	5.16 5.43 5.36 5.35 5.77 5.19	23.28 30.62 30.73		
 9	47.18	5.28				47.35	5.34			
 12	62.62	5.84	20.54	11.01		62.83	6.05	20.67	10.87	
 mp 3.5–5° 19	54.78	3.83	26.95			54.49 54.82 55.49	3.77 3.70 4.01	27.06 26.82 27.39		
 3	44.67	4.69	32.97			44.81 44.88	4.68 4.57	33.95 33.79 32.65 32.56		
 4						45.42 45.57 45.90 45.86	4.81 4.60 4.85 4.69	34.08 34.38 34.37		
 5						44.70 44.91	4.82 4.60	33.66 33.30		
 8	47.18	5.28	30.95			48.01	5.49	30.52		
 29	49.40	5.80				49.93	5.84			
 13	49.40	5.80				49.50	5.78			
 14						49.98	6.08			
 15	64.34	6.48	19.00	10.18		63.99 64.12	6.81 6.76	19.00	10.34	
 16	51.38	6.27	27.58			52.00 52.08 51.95	6.16 6.46 6.36	26.25 27.90		
 17						52.22 52.05	6.69 6.31	27.01		
 18						52.51 52.31	6.31 6.45	27.71 27.46		
 27	65.39	7.68	19.30		7.63	64.79	7.30	19.68		8.31

Table VII (*Continued*)

Compound	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % F	Calcd, % N	Found, % C	Found, % H	Found, % Cl	Found, % F	Found, % N
 **15b**	64.36	6.47	19.00			64.86	6.63	18.88		
 **28**	65.39	7.68	19.30		7.63	64.29	7.26	19.96		8.09
 **15a**	64.36	6.47	19.00	10.18		64.84	6.62	19.39	9.59	

for the neopentyl group, which is almost twice as effective as the *t*-butyl in enhancing the rate of the Diels–Alder reaction, but yields less than one-fourth as much 1,4 addition of 1122 as does the *t*-butyl. This fact would require special explanation if the mechanisms of the 1,4 addition were regarded as being similar for maleic anhydride and 1122.

If the 1,4 adducts owe their origin to the same biradical mechanism as the 1,2 adducts, according to Scheme I, then we can use the product compositions to deduce the relative rates of the competing steps at three points in the mechanism.

In Scheme I the relative rates of initial attack at C_1 and C_4 are measured by the ratio k_1/k_4, which is indicated by the product ratio

$$\frac{[1,2] + [1,4(a)]}{[3,4] + [1,4(b)]} = \frac{k_1}{k_4}$$

The relative rates of four-ring and six-ring formation from biradical A are given by

$$k_{12}/k_{14} = [1,2]/[1,4(a)]$$

and from biradical **B** by

$$k_{43}/k_{41} = [3,4]/[1,4(b)]$$

Table VI lists these quantities for isoprene, 2-isopropylbutadiene, and 2-*t*-butylbutadiene. We observe that as the bulk of the 2 substituent increases, the initial attack shifts slowly from C_1 toward C_4, the ratio k_1/k_4 decreasing by a factor of 7.7 between methyl and *t*-butyl substituents. Following attack of 1122 at C_1 (in biradical A), the relative rates of 1,2 and 1,4 ring closure decline by a factor of about 170 from methyl to *t*-butyl; the same ratio in biradical B declines by a factor of 20. These effects cannot all be due to the change from prevalent transoid to prevalent cisoid conformation of the diene. It would seem that little if any of the determination of the initial point of attack can be due to this cause, but it may well be a direct parallel effect of increasing hindrance near the two ends of the conjugated system.

Experimental Section

Preparation of Dienes. The methods used are summarized in Table I and are illustrated by the preparation of 2-ethylbutadiene. The dehydration of 300 g of 3-methyl-1-penten-3-ol (donated by the B. F. Goodrich Research Center, Brecksville, Ohio) by distillation with *p*-toluenesulfonic acid (1.5 g) yielded 210 g (83%) of a mixture of dienes. Vapor phase chromatography on a tris-β-cyanoethoxypropane column at 40° indicated 16% 2-ethylbutadiene, 30% *cis*- and 48% *trans*-3-methyl-1,3-pentadienes, and about 6% of unidentified compounds. Fractional distillation through a 32-cm Helipac column at a 50:1 reflux ratio cleanly separated the 2-ethylbutadiene, bp 68°, from the mixture of 3-methyl-1,3-pentadienes, bp 77–78°. The study of the latter fraction has been described in part IV of this series.[3] The 2-ethylbutadiene was purified by preparative vpc using a silicone OF-1 column at 67°.

Not only in the preparation of this diene, but also in its reaction with 1122, some positional rearrangement of the double bond occurred. This may be due to small amounts of acid generated by the attack on the halo olefin by water, which is very difficult to eliminate entirely from this low-boiling material.

Cycloadditions. The cycloadditions to the dienes were all carried out at 80° in sealed tubes in the presence of small amounts of di-*n*-butylammonium picrate, with excess 1,1-dichloro-2,2-difluoroethylene (1122) as the solvent. The essential feature of the product analysis was the vapor chromatographic separation; the conditions had to be worked out for each case and checked by the use of various columns. Table II lists the vpc conditions used in the several cases. In Table III these conditions are referred to by number to indicate how each product was separated, and the nmr spectra of the products are summarized and their assignments indicated.

In a few cases the cyclic sulfone of the diene was used directly instead of the diene; in these cases the temperature was 120° instead of 80°, the higher temperature being required to decompose the sulfone. In these cases the product composition showed only the small differences to be expected from the higher temperature (67, 28, and 5% instead of 73, 23, and 4% for 1,2, 3,4, and 1,4 adducts, respectively, for 2-*n*-propylbutadiene).

The partial isomerization, presumably acid induced, referred to above is illustrated by the cycloaddition of 1122 to 2-ethylbutadiene. In addition to the normal adducts reported in Table IV, there were formed two other compounds (1.4 and 1.8%, respectively), whose vpc retention times and nmr spectra showed that they were the main adducts of the two 3-methyl-1,3-pentadienes (**22** and **23** of ref 3). Presumably because of more effective drying, the cycloaddition to 2-*n*-propylbutadiene was not attended by such isomerization.

Synthetic Preparation of the Chlorofluoro-*t*-butylbenzenes. In the synthesis of 3-fluoro-4-chloro-*t*-butylbenzene (**15a**) and 3-chloro-4-fluoro-*t*-butylbenzene (**15b**) according to Scheme II acetanilide (**21**) was first converted into *p*-*t*-butylacetanilide (**22**) by the method of Carpenter, *et al.*[12] One recrystallization from benzene gave **22** melting at 171.5–173° (sealed tube) (lit.[12] 171–172°). This product was identical by mixture melting point with one obtained by way of the nitration of *t*-butylbenzene. The chlorination of **22** to 3-chloro-4-acetamino-*t*-butylbenzene (**24**) was effected by

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[12] M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).

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

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

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

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

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

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

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

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

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

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

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

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

John S. Swenton and Paul D. Bartlett

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

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

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

Results

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

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

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

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