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Cycloaddition. XIX. Competing Concerted and Stepwise [2 + 4] Cycloaddition of the Dichlorodifluoroethylenes to Butadiene and 2,4-Hexadiene

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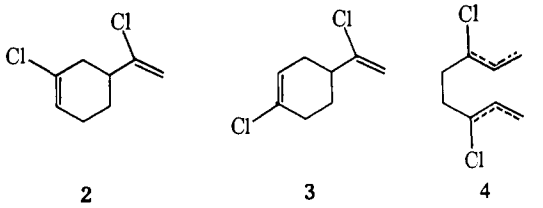
Abstract: The [2 + 4] cycloaddition of dichlorodifluoroethylenes to 1,3-dienes, though allowed as a concerted process by orbital symmetries, also occurs favorably by way of biradicals. Available criteria of mechanism are applied in detail to 1,1-dichloro-2,2-difluoroethylene (1122) and to *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene (1212) in their [2 + 4] cycloadditions to 1,3-butadiene and 2.4-hexadiene, and the competing mechanisms are sorted out. The 1122 isomer gives *less* [2 + 4] adduct with 2,4-hexadiene than with butadiene, a behavior compatible only with a stepwise mechanism having little or no competition from a concerted one. On the other hand, 1212 gives eight times as much [2 + 4] adduct with the hexadiene as with the butadiene, and the stereochemical retention index of the six-ring product is up from 4.5 for butadiene to 215 for 2,4-hexadiene, clearly indicating important competition from the concerted mechanism. The configuration of the methyl groups in the two sets of [2 + 4] products from 2,4-hexadiene is not randomized, a fact attributed to the rotation of the *cis*-allylic group being slower than the other rotations determining configuration. It is concluded that, among these reactions, only the addition of 1212 to 2,4-hexadiene involves any appreciable concerted character.

Ethylene and its halogen substitution products form a series of reagents exhibiting a wide range of reactivities and selectivities toward dienes. Butadiene reacts with ethylene to give a cross-adduct consisting 99.98% of cyclohexene.[2] Only through the concerted Diels–Alder mechanism could this result occur without substantial amounts of the [2 + 2] cycloadducts that are so much more characteristic of biradical mechanisms.[3,4]

At the other extreme, 1,1-dichloro-2,2-difluoroethylene ("1122") (**1**) adds to butadiene to give a vinylcyclobutane and, at 60°, less than 1% of a cyclohexene.[5] Trifluoroethylene is a borderline reagent, whose behavior toward dienes can be accounted for only by balanced capabilities for concerted [2 + 4] cycloaddition and biradical formation.[6a]

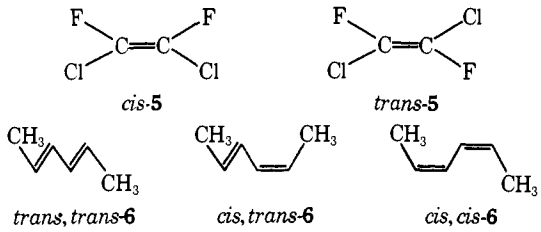
These facts do not allow the assignment of a mechanism to a cycloaddition by simply noting whether concert is allowed or forbidden by the orbital symmetry rules since stepwise reactions are always allowed and may compete even with normally favorable Diels–Alder mechanisms. We have noted, however, that in freely rotating dienes the amount of [2 + 4] product in a biradical reaction is limited by the diene's preference for an *s*-trans conformation.[5,7] A quantitative determination of how [2 + 4] cycloaddition to a diene is distributed between concerted and stepwise mechanisms should afford insight into the structural factors required for rapid reaction by one or the other mechanism.

A more specific criterion of mechanism than the amount of accompanying [2 + 2] addition is the effect of pressure on the rate of the [2 + 4] cycloaddition itself. Stewart[8] has shown that, in the dimerization of chloroprene, high compression favors relatively not all the [2 + 4] adducts but only those isomers (**2** and **3**) which *could not* have been formed by way of the most favored biradical (**4**); at atmospheric pressure, the biradical mechanism competes successfully where the concerted mechanism is allowed as well as where it is forbidden.



2 **3** **4**

A very general accompaniment of stepwise mechanisms is configuration loss. We have previously applied this criterion to the two centers of geometrical configuration in 2,4-hexadiene, 1,4-dichlorobutadiene, and their [2 + 2] cycloadducts[9–11] with 1122 and tetrafluoroethylene but, in those cases, the [2 + 4] cycloadducts were so minor as to escape detection. A second application of this criterion is to observe retention or loss of configuration in the *ene* component of a diene reaction. Application of this test to 1,2-dichloro-1,2-difluoroethylene ("1212") (*cis-5* and *trans-5*) and cyclopentadiene gave the simple answer that configuration was lost in the [2 + 2] product and retained in the [2 + 4] product.[12]

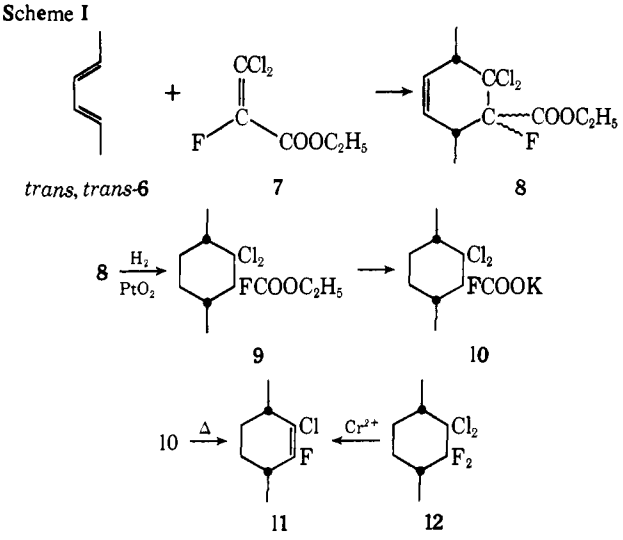


As a diene in the Diels–Alder reaction with ethylene, *trans-trans*-2,4-hexadiene (*trans,trans*-**6**) has been observed to be 12 times as reactive as butadiene under the same conditions.[2] The methyl groups, which favor the general donor character of the diene, are expected to have a retarding effect on biradical formation from the example of 2-butene, whose reaction with tetrafluoroethylene is only one-tenth as fast as that of ethylene.[13] In the present work, we have examined the cycloadducts of 1122 (**1**) and *cis*- and *trans*-1212 (*cis*-**5** and *trans*-**5**) to both butadiene and 2,4-hexadiene, seeking answers to the questions: Does the reaction of 1122 with 2,4-hexadiene yield any [2 + 4] cycloadduct and, if so, what is its configuration with respect to the methyl groups? In the reaction of the 1212 isomers with butadiene, will the halogen configuration of the [2 + 4] adduct be retained as with cyclopentadiene,[12] or lost, as expected for a stepwise mechanism? Then, with the 1212 behavior as a criterion, what is the mechanistic preference in the [2 + 4] addition to 2,4-hexadiene?

Results

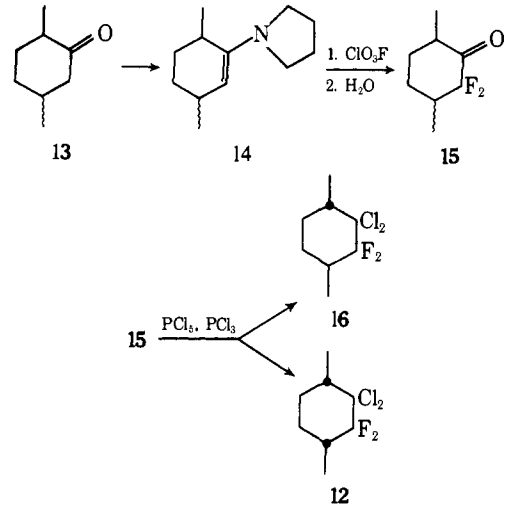
The Isomeric [2 + 4] Adducts of 1122 to the 2,4-Hexadienes. Careful vapor chromatography of the product of this cycloaddition revealed a peak at longer retention time than the [2 + 2] adducts, comprising less than 1% of the product. This material, isolated by preparative VPC on a Carbowax column, was shown to be a cross-adduct by its mass spectrum (parent peak, 214; P:(P + 2):(P + 4) = 56.3:36.7:7; calcd 57.4:36.7:5.9). That it is a cyclohexene and not a vinylcyclobutane is shown by the 1:1 ratio of the ethylenic and allylic hydrogens, while the clean AB quartet in the ^{19}F NMR spectrum is consistent with the material being a single geometric isomer. The cis configuration was established as shown in Scheme I. Ethyl 3,3-dichloro-2-fluoroacrylate

Scheme I

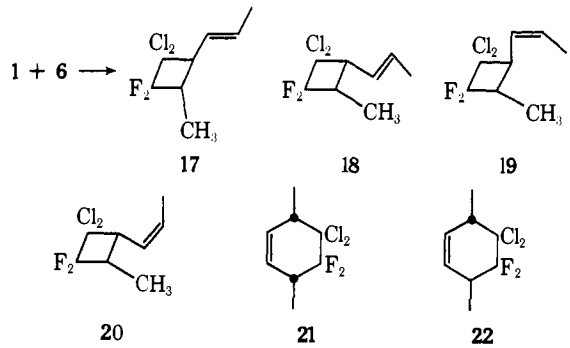


(7) added to *trans,trans*-2,4-hexadiene (*trans,trans*-**6**) gave only Diels–Alder product, which therefore had the two methyl groups cis; it was a mixture of the two configurations at the carboxyl. These mixed isomers could be converted by hydrogenation, hydrolysis, and decarboxylative elimination into the single isomer **11** of 1-chloro-2-fluoro-3,6-*cis*-dimethylcyclohexene, identical with the product resulting from hydrogenation and dechlorofluorination of the cycloadduct (mass spectrum, ir, NMR, VPC retention time).

Scheme II



Scheme III



Because the [2 + 4] cycloadduct was so nearly completely cis as to the methyl groups, the trans isomer was synthesized for comparison and to aid in the recognition of possible small amounts in the cycloadduct (Scheme II). A mixture of *cis*- and *trans*-2,5-dimethylcyclohexanones (**13**) was converted into the pyrrolidineenamines, fluorinated with perchloryl fluoride, and hydrolyzed to the fluorinated ketones. The *gem*-difluoro ketones (**15**) were converted by PCl_5 in PCl_3 to a mixture of the two stereoisomeric 2,2-dichloro-3,3-difluoro-1,4-dimethylcyclohexanes **12** and **16**, which could be separated by vapor chromatography and one of which (**12**) was identical with the hydrogenated cis cycloadduct. The new trans isomer was very similar to the cis in mass spectrum. A routine procedure was worked out for analyzing the 1122–2,4-hexadiene cycloadduct mixture in which the [2 + 2] products were analyzed first, and then the residue was hydrogenated over platinum oxide and subjected to further vapor chromatography.

Product Distribution in 1122 Cycloaddition to 2,4-Hexadiene. Thermal cycloadditions were carried out in sealed tubes at 79.5, 99.5, 120, and 153°, the product compositions being summarized in Tables I–IV and the structures shown in Scheme III. The distribution of [2 + 2] cycloadducts is consistent with previous studies on this system.[9] There is no detectable six-membered ring product from the *cis,cis*-2,4-hexadiene. From the trans,trans isomer, the cis [2 + 4] adduct, expected from a concerted process, varies from 0.46% of the total product at 79.5° to 1.1% at 153°. The trans six-membered ring product, formed with loss of configuration,

Table I. Cycloaddition of 2,4-Hexadienes and 1122 at 79.5°

	17	18	19	20	21	22
Trans,trans	82.9	16.4	<0.1	<0.05	0.46	~0.003
	83.1	16.6	<0.1	<0.05	0.46	~0.004
Cis,trans	47.2	13.7	33.3	5.8	0.07	~0.015
	46.3	14.7	33.2	5.8	0.08	~0.014
Cis,cis	<1	<0.2	76.0	22.8		
	<1	<0.2	76.6	22.1		

Table II. Cycloaddition of 2,4-Hexadienes and 1122 at 99.5°

	17	18	19	20	21	22
Trans,trans	80.5	16.9	1.80	0.22	0.64	~0.005
	80.7	16.6	1.86	0.25	0.61	~0.006
Cis,trans	44.6	15.2	33.6	6.5	0.115	~0.015
	45.6	15.3	32.2	7.0	0.116	~0.016
Cis,cis	2.4	0.76	75.0	21.8		
	2.2	0.80	74.5	22.5		

Table III. Cycloaddition of 2,4-Hexadienes and 1122 at 120.12°

	17	18	19	20	21	22
Trans,trans	77.2	17.1	4.1	0.80	0.80	~0.01
	78.8	16.2	3.4	0.78	0.79	~0.009
Cis,trans	46.7	15.5	31.3	6.3	0.17	~0.015
	47.7	16.0	29.6	6.5	0.18	~0.016
Cis,cis	5.5	1.9	70.5	22.1		

amounts to about 0.004% at the lowest temperature and about 0.02% at the highest. The *cis,trans*-2,4-hexadiene gives substantially less [2 + 4] adduct (0.08–0.24% over the temperature range) but, in this case also, it is the *cis*-dimethylcyclohexene that dominates, by about 10:1. Thus, despite the aptitude of the *trans,trans*-2,4-hexadiene for the Diels–Alder reaction, it gives only about half as much [2 + 4] cycloadduct as does butadiene; from the trans,trans starting material, the prevailing configuration of the cyclohexene is that expected from concerted reaction while, from the cis,trans isomer, the configuration is the opposite of that which a concerted reaction would give. This complicated picture will be further discussed after the results with 1212 have been reported.

Photosensitized Addition. A photosensitized cycloaddition was carried out by irradiating a mixture of *trans,trans*-2,4-hexadiene, 1122, and β-acetonaphthone at 2° for 4 days with a 450-W Hanovia lamp. The reaction led mostly to hexadiene dimers, with a mixture of cross-adducts whose composition is shown in Table V. The purpose of this experiment was to find out whether the amount of [2 + 4] adduct in the thermal experiments exceeded that obtained in a bona fide triplet biradical reaction. Here, too, no simple answer is at hand: the amount of *cis*-[2 + 4] product is *greater* by a factor of 4 in the photosensitized experiment than its value extrapolated to 2° from the thermal experiments. This is not accounted for by the known cis,trans isomerization occurring in the photosensitized reaction since the trans,trans diene starting material gives a larger amount of cyclohexenes thermally than any of its isomers. The reason for the disparity must be sought in a moderate selectivity of the excited sensitizer for transferring energy to the *s*-cis conformers of the diene,[6] which increases the proportion of eventual biradicals with cis-allylic groups and therefore capable of closing to a six-membered ring.

The [2 + 4] Adducts of 1212 to Butadiene. As a first step in product identification, a mixture of *cis*- and *trans*-1212 (46:54) was added thermally to butadiene by heating in a sealed tube at 190° for 24 hr. The two cyclohexene products were found in two overlapping VPC peaks of relative area

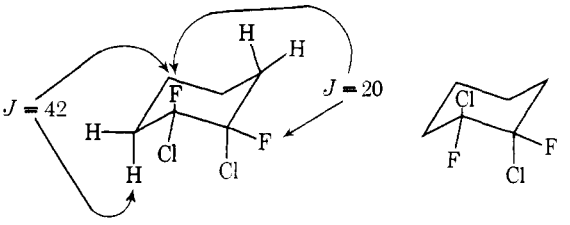
Table IV. Cycloaddition of 2,4-Hexadienes and 1122 at 153.25°

	17	18	19	20	21	22
Trans,trans	76	17.3	4.8	0.80	1.10	~0.020
	75.4	17.1	4.5	0.82	1.12	~0.015
Cis,trans	45.3	16.8	30.3	6.9	0.22	~0.020
	45.4	16.4	31.2	6.8	0.20	~0.023
Cis,cis	6.1	2.1	66.4	25.4		

Table V. Photosensitized Cycloaddition of 1122 to *trans,trans*-2,4-Hexadiene at 2°, 4 Days, with β-Acetonaphthone

Recovered diene					
Trans,trans: 74.2% Cis,trans: 21.7% Cis,cis: 4.1%					
Cycloadducts, %					
17	18	19	20	21	22
46.3	11.8	30.7	10.8	0.38	0.02

1.56:1 following, and well separated from, the four peaks of the [2 + 2] adducts. Both fractions gave correct elemental analyses, a parent peak in the mass spectrum at 186, and appropriate ratios of vinylic to saturated protons in the NMR (1:2 and 1:1). The [2 + 4] adduct fraction was hydrogenated and the resulting mixture of cyclohexanes examined by ^{19}F NMR in carbon disulfide at room temperature and at −100°. The room temperature spectrum showed two slightly broadened fluorine peaks, the downfield peak having 1.6 times the area of the other. At −100°, the fluorine spectrum separated into four peaks over a range of 850 Hz. At lowest field, 106.5φ, was a sharp singlet, next, a doublet (J = 20 Hz), a doublet (J = 38 Hz), and a quartet (J = 20, 42 Hz). Previous work on the proton and fluorine NMR spectra of chlorocyclohexanes[14,15] has indicated that, at equilibrium, appreciable amounts of chlorine are found in axial positions, that equatorial fluorine signals are likely to be at lower field than axial, and that vicinal axial-equatorial coupling of two fluorines is of the order of 20 Hz. Since a vicinal axial-axial J_{H-F} of 43 Hz has been observed,[16] the interpretation of these spectra falls into place in terms of structures **23, 24,** and **25,** and the conformation-



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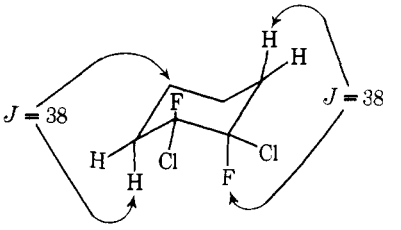
(singlet)



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al equilibration at −100° being slow on the NMR time scale. The ^{19}F NMR data are summarized in Table VIII.

The four peaks in the low-temperature fluorine NMR spectrum had integrated areas in the ratio 21.3:23.8:54:24, in accord with the assignment which would require the sec-

Table VI. Thermal Addition of *cis*- and *trans*-1,2-Dichloro-1,2-difluoroethylene (1212) to Butadiene at 180–190°

% *cis*-1212 Before rc	After rc	% [2 + 4] adducts	[2 + 4] adduct Composition % cis	% trans
99	97.5	2.1	57.5	42.5
1	1	2.4	23.0	77.0
46	45	2.2	39.0	61.0

ond and fourth peaks (due to the two fluorine atoms of **23**) to have identical areas, and the combined areas of the first and third to be related to those of the second and fourth as the room-temperature peak areas (1.575 vs. 1.6). It was now possible to determine by vapor chromatography the amount of cis- and trans- [2 + 4] cycloadduct in the mixture resulting from addition of the pure cis and trans 1212 isomers to butadiene.

Separation of the 1212 isomers was effected by the method of Wheland.[12,17] Samples of more than 99% isomeric purity were sealed, in fivefold excess, with butadiene in heavy-walled Pyrex tubes under vacuum and heated at 180–190° for 24 hr. The results are shown in Table VI.

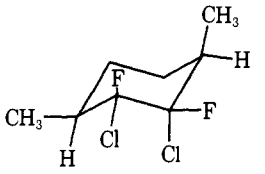
The extent of configuration loss in the [2 + 4] addition of 1212 to butadiene is characterized by the retention index *PQ*,[9] where

P = (retention/inversion) from cis reactant and

Q = (retention/inversion) from trans reactant

From the data in Table VI, $PQ = (57.5 \times 77)/(42.5 \times 23) = 4.5$, a figure comparable to the retention indices of some known stepwise [2 + 2] cycloadditions of 1212 in this temperature range: 8.0 for *trans*-cyclooctene[18] at 172°, 9.5 for cyclopentadiene[12] at 180–195°. In a case where the configuration is that of adjacent methyl groups, in the gas-phase cycloaddition of tetrafluoroethylene to 2-butene,[13] the loss of configuration during the reaction at 175° is greater ($PQ = 1.85$).

Cycloaddition of 1212 to *trans,trans*-2,4-Hexadiene. This product is capable of existing in 16 *dl* pairs of isomeric [2 + 2] cycloadducts and 2 meso isomers and 4 *dl* pairs of isomers as [2 + 4] cycloadducts. The present experiments were addressed to the limited objective of determining the halogen configuration in the [2 + 4] cycloadducts. The addition of mixed *cis*- and *trans*-1212 to *trans,trans*-2,4-hexadiene, under conditions similar to those of the butadiene reaction, gave a product which separated on TCEP into eight peaks at shorter and three at longer retention time. The combined first fraction was shown by elemental analysis and mass spectrum to consist of cross-adducts, and by NMR to have the right olefinic-allylic proton ratio to be [2 + 2] adducts. The three components of the second fraction were separately isolated, and each was shown by mass spectrum and NMR to be a [2 + 4] adduct (1:1 ratio of olefinic and allylic protons). For purposes of configurational assignment, these fractions were hydrogenated with platinum oxide as in the case of the butadiene adducts. Room temperature ^1H and ^{19}F NMR spectra showed that the hydrogenated first and third components had equivalent methyl groups and equivalent fluorine atoms. Of the four compounds, **26–29,** fitting this description, conformational freezing at low temperature should split the methyl signals and fluorine signals of **26** and **27** each into two of equal intensity, should split the signals of **29** into two of unequal intensity, and should result in such a predominance of one conformation in **28** as to amount to no splitting. The ^{19}F NMR at −100° splits the signals in the first and third hydrogenated isomers into two of equal intensity, indicating



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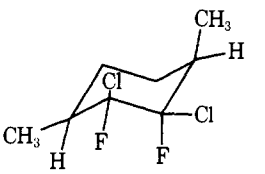

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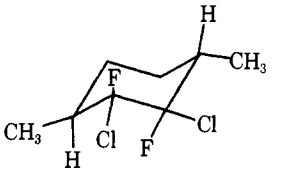

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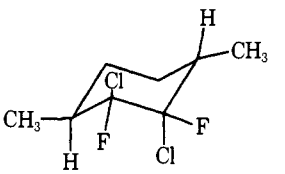

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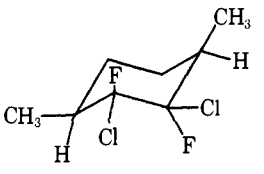
that these two isomers must have *cis*-methyl groups and cis halogen atoms (**26** and **27**).

The second of the three hydrogenated [2 + 4] adduct fractions showed nonequivalent methyl groups at room temperature by both proton and fluorine NMR. *cis*-Methyl groups would be rendered nonequivalent by a trans configuration of the halogen, as in **30;** *trans*-methyl groups would be similarly nonequivalent if the halogens were cis, as in **31.**



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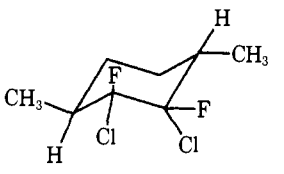

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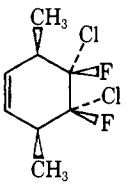
The most obvious difference between **30** and **31** is that in **31** both methyl groups may be equatorial. Since methyl has a stronger conformational preference than chlorine, this should make the low-temperature equilibrium between the conformers uneven for **30** and overwhelmingly one-sided for **31.** At −100°, the ^{19}F NMR spectrum of the hydrogenated middle [2 + 4] adduct showed two new, small doublets, in area about 4% of the others, with intermediate chemical shifts. This amount of a second conformer being compatible with that to be expected of structure **30,** and greater than any to be expected of **31,** the structure **30** is assigned to this hydrogenated cycloadduct, and the [2 + 4] product is found to consist of the three possible *cis*-3,6-dimethylcyclohexenes, **32, 33,** and **34.** There were no other peaks in the vapor



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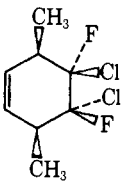

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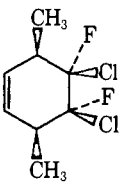

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chromatogram, and comparison with other separations made by this method makes it probable that any cycloadduct with *trans*-methyl groups was present to less than 1%. The splitting pattern in the low-temperature fluorine NMR spectrum is consistent in detail with these assignments (Table IX).

Table VII shows the results of thermal addition of *cis*- and *trans*-1212 to *trans,trans*-2,4-hexadiene at 180–190°.

Discussion

The reaction products of 1122 with butadiene—99% [2 + 2] cycloadducts—suggest that 1122 is a biradical-forming reagent which forms six-membered rings only because of the statistical occurrence of some cisoid biradicals.[5]

Table VII. Thermal Addition of 1212 Isomers to *trans,trans*-2,4-Hexadiene at 180–190°

Initial % *cis*-1212	Final % *cis*-1212	% [2 + 4] adducts	% *cis*- (32 + 34)	% *trans*- 33	*P*	*Q*
>99	>99	16.8	15.4	1.36	11.3	
<1	<1	19.4	0.97	18.4		19.0
46	45.5	16	6.72	9.3		

Table VIII. ^{19}F NMR Spectra of the Hydrogenated Mixed [2 + 4] Adducts of 1212 to Butadiene in CS_2

Temp, °C	Signal	Assignment
25	m, 113 ϕ (area 1.6)	Trans
	m, 116 ϕ (area 1.0)	Cis
−100	s, 106.5 ϕ (area 0.89)	Trans, conformation 24
	d, 111.2 ϕ, J = 20 Hz (area 1.0)	Equatorial F of cis
	d, 113.1 ϕ, J = 38 Hz (area 2.3)	Trans, conformation 25
	q, 114.6 ϕ, J = 42, 20 Hz (area 1.0)	Axial F of cis

In agreement with this view of 1122, its reaction with *trans,trans*-2,4-hexadiene is slower than with butadiene (opposite to the behavior of maleic anhydride)[19] and results in even less [2 + 4] cycloadduct. Yet, in contrast to the extensive loss of configuration in the [2 + 2] adducts, 99% of the newly observed [2 + 4] adduct has the two methyl groups in the cis configuration expected from a concerted cycloaddition. This stereoretentiveness is still 98% or more at 153° despite the fact that the "retained" product is the less favored one thermodynamically. We must examine the possibility that this product is formed by a concerted reaction suddenly taking precedence over the otherwise dominant stepwise process.

Whether or not the highly stereoselective formation of *cis*-3,6-dimethylcyclohexenes is a concerted process occurring in the presence of 200 times as much biradical formation, an explanation must be found why more of the biradicals do not cyclize to cyclohexenes with loss of configuration. There is no obvious reason why *trans,trans*-2,4-hexadiene should not exist in a cisoid conformation with a probability similar to that seen in butadiene, and form cisoid biradicals in a similar proportion. If it does, is there a reason why these biradicals should be both less prone to form six-membered rings and very much less likely to form them with configuration loss?

A study of the addition of 1122 to a series of cis-fixed dienes showed that a rigid cis geometry is not enough to guarantee formation of a six-membered ring by the biradical path.[20] From the sensitivity of the six-membered ring/four-membered ring ratio to small structural changes in the diene it is easy to believe that 1,4-dimethyl substitution on butadiene could reduce by a factor of 2 or 3 the proportion of cisoid biradicals that cyclize to six-membered rings.

The idea, however, that the [2 + 4] cycloadduct results 99% from a concerted Diels–Alder process is not supported by the products of cycloaddition to *cis,trans*-2,4-hexadiene. Here, too, the nonthermodynamically determined product with the methyl groups cis predominates, even though a concerted [2 + 4] mechanism would result in the methyl groups being trans to each other. It is true that the cis,trans isomer is very unreactive toward standard dienophiles, and it would obviously be possible for a concerted mechanism to be of overriding importance in the formation of the [2 + 4] fraction of the cycloadduct from the trans,trans isomer, but to become of very low relative significance in the cis,trans diene.

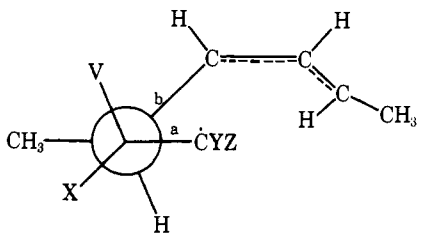
Table IX. NMR Spectra of the Hydrogenated [2 + 4] Cycloadducts 26, 27, and 30 of 1212 to *trans,trans*-2,4-Hexadiene

Isomer	Temp, °C	Nucleus	Signal
26	25	H	1.225 (dt, J = 7, 1.5 Hz)
			1.75 (m, broad)
			2.6 (m, broad)
	25	F	121 (s)
	−100	F	118.3 (d, J = 19.5 Hz)
			122.1 (dd, J = 28, 19.5 Hz)
27	25	H	1.265 (d, J = 7 Hz)
			1.68 (m, broad)
			2.50 (m, broad)
	25	F	106.5 (s)
	−100	F	103 (dd, J = 18.5, 14.5 Hz)
			114 (d, J = 18.5 Hz)
30	25	H	1.27 (d, J = 7 Hz)
			1.23 (d, J = 8 Hz)
			1.60 (m, broad)
			2.55 (m, broad)
	25	F	105
			125
	−100	F	105 (t, J = 12.5 Hz, area 1.0)
			125 (dd, J = 29, 12.5 Hz, area 1.0)
			106.4 (d, J = 12.5 Hz, area 0.04)
			114 (d, J = 12.5 Hz, area 0.04)

The results with *cis*- and *trans*-1212 give an assessment of the degree of concertedness based on the retention or loss of the configuration of the *halogens* in the dienophile. From Table VI, the fraction of [2 + 4] addition to butadiene at 180–190° is about the same as with 1122; the *PQ* of 4.5 for this fraction is consistent with a biradical mechanism, where the kinetically determined product of fully stereoequilibrated biradicals[9] would be trans/cis = $(Q + 1)/(P + 1)$ = 1.85, corresponding to 64.9% trans, 35.1% cis. Thus the [2 + 4] product of this reaction may be entirely the result of biradicals that do not reach complete stereoequilibration, or it may represent the simultaneous occurrence of a completely equilibrating biradical reaction with as much as 34–35% of stereospecific, concerted reaction.

From Table VII, it is immediately apparent that 1212, though an isomer of 1122, responds very differently to the change from butadiene to 2,4-hexadiene. The fraction of [2 + 4] cycloadduct has risen from 2 to 16–19%, as would be expected for a growing importance of a concerted mechanism. At the same time, the *PQ* is up to 215, clearly indicating competition between a stepwise and a dominating concerted mechanism. If the biradicals are reaching only the same degree of configuration loss as with butadiene, then this concerted reaction is 87.5% dominant from cis and 86% from trans; if the biradicals are reaching total randomization of the halogen configuration, these figures become 93.5 and 92.6%. Thus the addition of 1212 to 2,4-hexadiene presents an unequivocal case of competing mechanisms in the formation of the [2 + 4] adduct.

Now the occurrence of between 6.5 and 14% of stepwise mechanism, proved by the halogen configuration loss, is not accompanied by any detectable other configuration of the methyls than that expected of a pure concerted reaction. This is evidence that, in cisoid biradicals such as **35**, shown



35

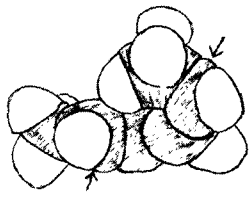
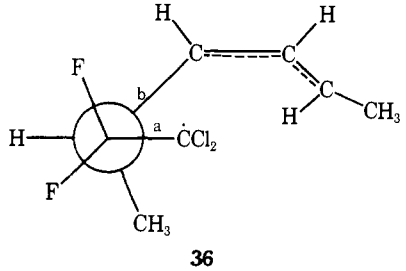


Figure 1. Schematic representation of the helical distortion of a cisoid diene with cis substitution. The arrows mark the directions of unhindered approach to the termini of the π system by an attacking reagent, leading to biradicals **36** and **37**.

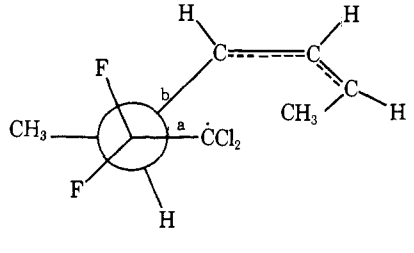
in Newman projection with the first-formed bond perpendicular to the paper, rotation about bond a is much faster than about bond b. The reasons for serious hindrance to rotation about bond b are obvious from the formula **35** and are borne out by examination of models.

These observations offer a resolution of the paradox mentioned earlier, that 1122, strongly predisposed to react by the biradical mechanism, still gives with *trans,trans*-2,4-hexadiene a 3,6-dimethylcyclohexene that is 99% cis; despite the large amount of rotation about bond b in the transoid biradical, this rotation in the hindered cisoid biradical is very slow compared with ring closure.

The fact that the *cis*-dimethylcyclohexene is also the chief [2 + 4] product from *cis,trans*-2,4-hexadiene, corresponding to an inversion of configuration, can be understood by reference to a special feature of *cis,trans*-2,4-hexadiene (*cis,trans*-**6**) and the biradical from it. The cis,trans diene cannot assume a coplanar cisoid conformation; the closest approach it can make to cisoid planarity is still somewhat helical since the *cis*-methyl group is pushed above or below the molecular plane by the interfering hydrogen atom, as shown schematically in Figure 1. As a result, at each end of the conjugated system, one face of the carbon atom, C-2 or C-5, is hindered by the presence of the group at the other end that cannot assume complete coplanarity with the rest of the molecule. When a biradical is formed by attack of 1122, either at the cis end of the molecule (**36**) or at the trans end (**37**), if this attack has been at



36



37

the less hindered face of the diene ("outside" the helix, Figure 1), the result is the development of a planar cis-allylic radical which is thrust behind the methyl group or hydrogen at the attacked end of the diene. If the subsequent rotation of bond b follows the direction of the lowest barrier, the first opportunity to close a six-membered ring in **36** will be with inversion. No such barrier being involved in the closure of a four-membered ring, it is easy to account for the sixfold smaller proportion of [2 + 4] adduct from the cis,trans than from the trans,trans isomer. It also appears from models, and would fit the product figures, that the biradical **37** from attack of 1122 at the trans end of the diene should give even less [2 + 4] product, although of the high rotation barriers at b here the only surmountable one should lead to *trans*-dimethylcyclohexene. From the distribution of [2 + 2] isomers in this case,[9] 58% of the biradical is formed by attack at the cis end (**36**).

Conclusion

In locating the dividing line between concerted and biradical mechanisms in the [2 + 4] cycloadditions of 1122, 1212, butadiene, and 2,4-hexadiene, we find that both 1122 and butadiene appear to react stepwise with both partners, while both a concerted and a stepwise component can be clearly identified in the [2 + 4] reaction of 1212 with 2,4-hexadiene, with the concerted component predominating by more than 6 to 1.

Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratories, Herlew, Denmark. ^{1}H NMR spectra were taken on either a Varian A-60 or HA-100. ^{19}F NMR spectra were taken in the HR mode on the Varian HA-100, and reported as ϕ values.[21] Determination of the coupling constants and chemical shifts for the ^{19}F NMR spectra employed audio-frequency side band modulation introduced by an internal oscillator. Infrared spectra were obtained by the use of a Perkin-Elmer Model 137-B spectrometer. Mass spectra were taken on an Associated Electrical Industries Ltd. Model MS 9 mass spectrometer. Vapor phase chromatograms were run with Hewlett-Packard F & M Models 700 and 7620 and Varian Aerograph Models 90-P. Peak areas were measured by a disk integrator and Hewlett-Packard digital integrator. If the baseline drifted, more reproducible results were obtained by cutting out and weighing the paper to determine the area under the peak. Table X describes the various vapor phase chromatography columns utilized.

2,4-Hexadienes (6), *trans,trans*-, *trans,cis*-, and *cis,cis*-2,4-hexadienes were purchased from Columbia Organic Chemicals Co., Inc. Analysis was accomplished by using column G at room temperature. The compositions of the three isomers were as shown in Table XI.

Preparation and Isolation of *cis*-4,4-Dichloro-5,5-difluoro-3,6-dimethylcyclohexene (**21**), A mixture of 5 g (0.061 mol) of *trans,trans*-2,4-hexadiene and 30 g (0.227 mol) of 1,1-dichloro-2,2-difluoroethylene (hereafter called 1122) was heated at 125° in a thick-walled sealed tube as previously described. The unreacted hexadiene and 1122 were evaporated under reduced pressure at room temperature. Distillation of the material gave 10 g (76%) of adducts [estimated bp 64° (40 mm)].

Isolation of the cis-1,4 adduct (50 mg) was achieved by preparative VPC using column C (column 130°, detector 170°, injector 160°, and helium flow 1 ml/sec). The 1,4 adduct (retention time 30 min) was nicely separated from the 1,2 adducts which gave a large unresolved peak (retention time 10–20 min).

Hydrogenation of *cis*-4,4-Dichloro-5,5-difluoro-3,6-dimethylcyclohexene 21 → 12, A mixture of 25 mg of VPC-collected *cis*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexane, 0.1 g of Merck zinc dust, 0.1 g of $Cr_2(SO_4)_3n\cdot H_2O$, 1 ml of water, and 1 ml of dimethyl formamide was stirred under nitrogen in a sealed thick-walled Pyrex tube containing a stirring bar. The tube was heated in a 95–110° oil bath for a day.

After cooling in dry ice–acetone, the tube was opened, and its sides were washed down with less than 1 ml of pentane. The tube was warmed until the liquefied contents could be vigorously shaken. Several milliliters of water was added after which the tube was again placed in dry ice–acetone. The pentane layer was decanted into a sample vial once the aqueous layer froze solid, and the VPC analysis was run using column C (column 130°, detector 170°, injector 160°, and helium flow 10 ml/10 sec.) There was obtained 12

Table X. VPC Conditions

Column	Liquid phase	Solid phase	Mesh	Length, ft	O.d., in	Chromatograph
A	20% Carbowax 20M	Chromosorb P	60–80	16	1/8	F & M 700
B	20% Carbowax 20M	Chromosorb W-AW	60–80	12	1/4	F & M 700
C	20% Carbowax 20M	Chromosorb W-AW	45–60	7	1/4	Autoprep 90-P
D	20% TCEP[a]	Chromosorb P	60–80	30	1/8	F & M 7620
E	25% TCEP	Chromosorb P	60–80	10	1/4	Autoprep 90-P
F	20% TCP[b]	Chromosorb W	60–80	30	1/8	F & M 7620
G	20% ββ'-ODPN[c]	Chromosorb P	60–80	17.5	1/8	F & M 7620
H	5% Me_2SO	Alumina	60–80	5	1/8	F & M 700
I	5% Me_2SO	Alumina	60–80	15	1/4	Autoprep 90-P

[a] TCEP = 1,2,3-Tris(2-cyanoethoxy)propane. [b] TCP = tricresyl phosphate. [c] ODPN = oxydipropionitrile.

Table XI. Composition of Initial Dienes

	Trans,trans	Cis,trans	Cis,cis
Trans,trans	99.7	0.3	0
Cis,trans	0.4	99.6	0
Cis,cis	0.3	1.4	98.3

mg (64%) of dehalogenated product (retention time, 19 min.).

Synthesis of Ethyl 3,3-Dichloro-2-fluoroacrylate (7). Ethyl 3,3-dichloro-2-fluoroacrylate (50 g) was synthesized according to the method developed by England, Lindsey, and Melby.[22]

Thermal Cycloaddition of Ethyl 3,3-Dichloro-2-fluoroacrylate to *trans,trans*-2,4-Hexadiene. A mixture of 9 g of ethyl 3,3-dichloro-2-fluoroacrylate, (0.0517 mol), 3 g of *trans,trans*-2,4-hexadiene (0.0366 mol), and 10 ml of benzene was sealed under vacuum in a heavy-walled Pyrex tube. After heating for 3 days at 185°, the tube was opened and the content distilled. There was obtained 3.5 g of a colorless liquid [estimated bp 90° (1 mm)]. VPC on column A at 200° (helium flow 1 ml/sec.) showed two peaks in a ratio of 1.7:1 with respective retention times of 47 and 56 min, corresponding to the two stereoisomers of 8.

The mass spectra of the two products, separated on column B at 200° both showed parent peaks at 256, equal to the calculated value for $C_{10}H_{15}O_2Cl_2F$.

The proton NMR and ir spectra of the mixture are consistent with the assigned structure. The room-temperature ^{19}F NMR of the mixture showed two absorptions whose areas were also in a ratio of 1.7:1 with respective ϕ values of 172 and 142.

Hydrogenation of the Ethyl 4,4-Dichloro-5-fluoro-3,6-*cis*-dimethylcyclohexene-5-carboxylates, 8 → 9. In 20 ml of ethyl acetate, 3 g of ethyl 4,4-dichloro-5-fluoro-3,6-*cis*-dimethylcyclohexene-5-carboxylate (0.0117 mol) was dissolved. To this was added 0.04 g of commercial platinum oxide catalyst. The mixture was hydrogenated at 27° (1 atm). In 3 hr, 300 ml of hydrogen was taken up and then the reaction stopped completely (theoretical uptake, 22.4 × 3/256 × 300/273 = 288 ml). After filtration, distillation gave 2.1 g of liquid [bp 90° (1 mm)]. The ir and the NMR no longer showed olefinic absorption.

Hydrolysis of Ethyl 1,1-Dichloro-2-fluoro-3,6-*cis*-dimethylcyclohexane-2-carboxylates, 9 → 10. Ethyl 1,1-dichloro-2-fluoro-3,6-*cis*-dimethylcyclohexane-1-carboxylate (2 g) (0.00775 mol) was added to 4 ml of a 10% ethanolic KOH solution. The mixture was stirred for 24 hr at 60°. The potassium salt precipitated. After filtration, the residue was dried under vacuum to a constant weight of 1 g (44%).

Decarboxylative Elimination of the Potassium Chloride from Potassium 1,1-Dichloro-2-fluoro-3,6-*cis*-dimethylcyclohexane-2-carboxylates, 10 → 11. A microdistilling tube containing 0.8 g (0.0027 mol) of potassium 1,1-dichloro-2-fluoro-3,6-*cis*-dimethylcyclohexane-2-carboxylate was evacuated to 0.1 mm, and the receiver was chilled with dry ice. The solid was heated at 180–190° for 3 hr. The material which distilled was 200–250 mg of colorless liquid. VPC of this material on column C (column 130°, detector 170°, injector 160°, and helium flow 1 ml/sec) gave only one peak (retention time 19 min). The ir and NMR of this material were superposable upon those of the hydrogenated and dehalogenated 1,4 cycloadduct of *trans,trans*-2-4-hexadiene and 1122.

***cis*- and *trans*-2,5-Dimethylcyclohexanone (13).** To a stirred mixture of 80 g (2.7 mol) of sodium dichromate and 65 g (35.3 ml, 0.063 mol) of concentrated sulfuric acid was added 50 g (0.40 mol) of 2,5-dimethylcyclohexanol in three portions. The reaction mixture was cooled in ice to keep the temperature below 68°. After ether extraction, washing with 5% NaOH and drying over anhydrous sodium sulfate, the ether was removed on a rotary evaporator, and the residue was distilled. A colorless liquid, bp 76–77° (27 mm) was obtained, yield 379 g (77%).

The infrared spectrum showed strong absorption at 5.83 μ. The NMR spectrum in carbon tetrachloride showed a complex multiplet from τ 7.4 to 8.8 (8 H) and a pair of doublets for the methyl groups from τ 8.9 to 9.2 (6 H). VPC analysis on column A at 110° showed two isomers to be present in the ratio 79:21 in order of increasing retention time.

***N*-(2,5-Dimethylcyclohex-6-enyl)pyrrolidine (14).** To a solution of 20 g (0.16 mol) of a mixture of the two isomers of 2,5-dimethylcyclohexanone in 120 ml of benzene was added 26 g (0.37 mol) of redistilled pyrrolidine. The reaction was refluxed, and the water formed was collected in a Dean-Stark trap. After 12 hr, no more water was formed and the reaction was stopped. The solvent was removed at reduced pressure and the residue distilled, bp 75° (2.5 mm). The ir exhibited a strong absorption 1660 cm^{-1} characteristic of the double bond stretching of enamines. The NMR in benzene solution showed a multiplet centered at τ 5.83 corresponding to the hydrogen on the double bond.

Synthesis of *cis*- and *trans*-2,2-Difluoro-3,6-dimethylcyclohexanone (15). Caution: Perchloryl fluoride was handled with the precautions described in Booklet 1819, "Perchloryl Fluoride", Pemsalt Chemical Corp., 3 Penn Center, Philadelphia, Pa.

In a 2-l. three-necked flask equipped with a gas inlet tube extending almost to the bottom of the flask, a thermometer, and a magnetic stirring bar were placed 5 g of enamine (0.028 mol) and 1 l. of dry ether. The flask was cooled in an ice–salt bath at −5 to −10°, and a stream of perchloryl fluoride was bubbled through the solution with vigorous stirring over a period of approximately 3 min, at such rate that the temperature of the reaction mixture did not rise above 0°. Stirring was continued for an additional 1 hr as the cooling bath melts. The solution was purged with nitrogen for 10 min. Then 200 ml of 10% HCl–water solution was added, and the mixture was stirred for 1 hr at room temperature before being placed in a 2-l. separatory funnel. The aqueous layer was separated, and then the ether layer was washed twice with 200 ml of water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator under reduced pressure. Distillation of the yellow mixture [70–85° (25 mm)] afforded 3.2 g of a colorless liquid.

A preparative VPC work-up on column E at 130°, followed by examination by mass spectrometry and NMR, revealed the presence of mono-, di-, and trifluorinated ketone as well as a small amount of starting material (~5%). The two desired *gem*-difluoro ketones (~25%) appeared as two overlapping peaks (retention times, 20 and 21.6 min) directly following the *trans*- and *cis*-2,5-dimethylcyclohexanones (retention times, 16 and 18 min).

By successive passings, each of the two isomeric *gem*-difluoro ketones could be isolated for analytical purposes. Both mass spectra showed a parent peak at 162, equal to the calculated value for $C_8H_{12}OF_2$. The ir showed strong carbonyl absorptions. Finally, the ^1H NMR indicated the geminal nature of the two fluorines.

For further treatment, 180 mg of the mixture of the two ketones was collected.

This fluorination reaction is very sensitive to reaction conditions. Below −30° only a mixture of 2-fluoro-3,6-dimethylcyclohexanones is formed. If we isolate them, prepare their corresponding

pyrrolidine enamines, and run a fluorination reaction at −40°, we only obtain a mixture of 2,6-difluoro-3,6-dimethylcyclohexanones.

The controlled monofluorination at temperatures below −30° is attributed to the insolubility of the ammonium salt formed which prevents further reaction. At higher temperatures, the white precipitate formed rapidly dissolves, probably because of its decomposition into the fluorinated enamine and perchloric acid, allowing then the reaction to proceed further.

Synthesis of *cis*- and *trans*-1,1-Dichloro-2,2-difluoro-3,6-dimethylcyclohexanes. (12 and 16). The mixture [180 mg (0.0011 mol)] of *cis*- and *trans*-2,2-difluoro-3,6-dimethylcyclohexanone was placed in 8 ml of PCl_3, and 0.6 g (0.029 mol) of PCl_5 was added. The mixture was stirred at room temperature for 8 days. It was then poured on ice, a few milliliters of CH_2Cl_2 was added, the solution extracted with $KHCO_3$ solution and dried over anhydrous magnesium sulfate, and the CH_2Cl_2 was partially evaporated under reduced pressure.

Preparative VPC using column C at 120° allowed the isolation of a few milligrams of *cis*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexane. Under these conditions, the trans counterpart and the monochlorinated substance had the same retention time. Column E at 120° effected their separation in milligram quantities.

The mass spectrum of *cis*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexane showed a parent peak at 216 equal to the calculated value of $C_8H_{12}Cl_2F_2$. The observed ratio of m/(m + 2)/(m + 4) was 56.2:36.8:7 (calculated, 57.4:36.7:5.9). The principal peaks and their intensities were 181 (17), 180 (10), 161 (18), 145 (100), 125 (42), 123 (45), 104 (48). This fragmentation corresponds to the loss of Cl, loss of HCl, loss of Cl and HF, loss of HCl and Cl, loss of Cl, HCl, and HF, loss of Cl, HCl, HF, and H_2 and loss of Cl, HCl, HF, F, and H_2.

The mass spectrum of the trans isomer was very similar. The observed ratio of m/(m + 2)/(m + 4) was 56.8:36:7. The fragmentation was identical, but the intensities were different: 181 (14), 180 (20), 161 (15), 145 (100), 125 (25), 123 (30), 104 (40).

Reaction of *trans,trans*-, *trans,cis*-, and *cis,cis*-2,4-Hexadienes with 1122 at Various Temperatures. The cycloadditions were run as in the preparative procedure described above. The tubes were heated for 24 hr in an oil bath, the temperature of which was maintained within ±0.01°. The 1,2 adducts were analyzed directly on column D at 150°. Retention times were: 19.6 (**17**), 20.4 (**19**), 24.4 (**18**), and 27.6 min (**20**). The 1,4 adducts were analyzed after hydrogenation of the reaction mixture. In a typical procedure, 0.2 g. (0.0093 mol) of the cycloadducts was dissolved in 5 ml of ethyl acetate. To this was added 15 mg of platinum oxide. The mixture was hydrogenated at 27° (1 atm). After the theoretical amount of hydrogen (23 ml) had been taken up, the reaction was stopped. The catalyst was filtered off and the solvent removed on a rotary evaporator. Column D was also used for the analysis of the *cis*- and *trans*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexanes. The sequence of the peaks was: unknown compound (48 min), trans (52.2 min), and cis (59.5 min).

The identification of the *cis*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexane originating from the *trans,trans*-2,4-hexadiene had already been described. In the case of the *trans,cis*-2,4-hexadiene, 1 mg of hydrogenated cis-1,4 adduct was isolated by preparative VPC on column C and was shown to have an ir spectrum which was superposable upon that of a sample of the authentic material.

The *trans*-1,1-dichloro-2,2-difluoro-3,6-dimethylcyclohexane was identified by comparison of its retention time with that of a sample of the authentic material using columns A, B, and D.

The Hewlett-Packard F & M Model 7620 equipped with a flame ionization detector was used for the analysis. Integrations were performed with a digital integrator. The ratios of cis- to trans-1,4 adduct were checked by the triangulation method. The relative areas were not corrected for the flame sensitivity of the adducts because of the shortage of 1,4 adducts.

In each case 1 μl of sample was injected. The conditions for all the runs were kept constant. The values were reproducible within 5%.

Photosensitized Reaction of *trans,trans*-2,4-Hexadiene and 1122. A Pyrex tube was charged with 1.5 g (0.018 mol) of *trans,trans*-2,4-hexadiene, 25 g (0.189 mol) of 1122, and 0.3 g (0.00176 mol) of freshly redistilled 1-acetonaphthone. The tube was degassed by two freeze–thaw cycles and sealed under vacuum. A 450-W Hanovia medium-pressure mercury lamp was used for the irradiation (4 days). The tube was strapped to a Pyrex well immersed in a water bath. The bath was kept at 2° by the use of a heat exchanger through which was passed cold methanol from a Lauda Kryomat Model TK30. Cold water was circulated through the Pyrex well.

The sample was then stripped of 1122 and the unreacted 2,4-hexadienes. VPC analysis using column G revealed the composition of the unreacted dienes to be trans-trans, 74.2%; cis-trans, 21.7%; cis-cis, 4.1%.

Trap-to-trap distillation afforded 200 mg of a colorless liquid comprising 2,4-hexadiene dimers and cross-cycloadducts. The analysis of the cycloadducts was performed in a manner similar to that for the thermal reactions. The adducts were identified by a comparison of the retention times with authentic materials on columns A and D.

Separation of *cis*- and *trans*-1212. Several approaches have been used[23-26] to separate *cis*- and *trans*-1212. The original paper[23] reported separation by distillation. Tiers and Lauterbur, however,[24] could not reproduce this separation. Craig and Evans[25] obtained 99.6% *trans*-1212 and 95.1% *cis*-1212 by a tedious fractional melting procedure in conjunction with distillation. The best method available so far has been developed by Wheland[17] using VPC. He found that rather volatile, highly polar liquid phases such as dimethyl sulfoxide, dimethylsulfone, and dimethylformamide on 80–100 mesh Alcoa F-20 chromatographic alumina are particularly successful. A high proportion of liquid phase relative to solid support led to reduced retention times with loss of resolution, whereas a low proportion of liquid phase led to extended retention times with blurring resolution. Thus about 5% by weight liquid phase such as dimethyl sulfoxide is sufficiently volatile so that the columns are not baked out but rather put into immediate use at 0–25°.

A VPC analysis of 1212 obtained from Peninsular Chemresearch, Inc., revealed two major components with roughly 5–10% of a third component that has the retention time of 1122. This common impurity in 1212 is removed by refluxing with sodium ethoxide in ethanol. The purified 1212 is then collected preparatively using column I at room temperature. Comparison with published ir spectra distinguishes the two isomers, *trans*-1212 (retention time, 4 hr) eluting before *cis*-1212 (retention time, 4.5 hr). Analytical VPC with column H at 50° (flow 1 ml/1 sec.) showed retention times of: trans, 21 min; cis, 24.5 min.

Addition of Butadiene to Mixed Isomers of 1212. A mixture of 1212 isomers (20 g, 0.1515 mol) of known composition (trans, 54%, cis, 46%) and butadiene (3 g, 0.0555 mol) was heated in a heavy-walled Pyrex tube for 24 hr at 189–190°. Fractionation of the products through a microcolumn gave 6.3 g (61%) of crude cycloadducts [estimated bp 147° (761 mm)]. Preparative VPC emptying column C at 100° (helium flow 1 ml/1 sec.) permitted separation of the 1,2 adducts (retention time, 12–24 min) from the 1,4 adducts (retention time, 52 min). Analytical VPC using column F at 120° (Table X) gave better separation and, in particular, allowed discrimination between the two 1,4 adducts. The retention times of the five peaks were respectively 34.5 min, 36.2 min, 37.5 min, 84.5 min, and 87 min.

Hydrogenation of the Butadiene–1212 Cycloadducts. In 40 ml of ethyl acetate was dissolved 2 g of distilled cycloadducts. To this was added 0.1 g of commercial platinum oxide catalyst. The catalyst was not hydrogenated before addition of the adduct. The mixture was hydrogenated at 27° (1 atm) pressure. In 2 hr, 280 ml of hydrogen was taken up and then the reaction stopped completely (theoretical hydrogen uptake 22400 × 2/186 × 300/273 = 265 ml). The catalyst was removed by filtration, the solvent was stripped off under reduced pressure, and the residue was trap-to-trap distilled under vacuum.

Preparative VPC on column C at 120° allowed separation of the hydrogenated 1,2 and 1,4 adducts for spectroscopic analysis (ir, ^1H NMR, and particularly ^{19}F NMR).

Thermal Cycloaddition of *trans*-1212 to Butadiene. 1212 from which the contaminating 1122 had been removed was separated into cis and trans isomers with column I at room temperature. Analysis on column H at 50° indicated the purified *trans*-1212 to be in fact 99% *trans*-1212 with 1% cis impurity.

About 0.15 g of this 99% pure *trans*-1212 was bulb-to-bulb distilled into a small heavy-walled Pyrex tube. To this was added 10

mg of butadiene. After sealing under vacuum, the tube was heated in an oven at 180–190° for 24 hr, then cooled, and opened.

The colorless solution was VPC analyzed as such without further treatment. Analysis of the recovered 1212 (column H at 50°) and of the cycloadducts (column F at 120°) has been reported in Table VI.

Thermal Cycloaddition of *cis*-1212 to Butadiene. About 0.15 g of 99% pure *cis*-1212 was bulb-to-bulb distilled into a small heavy-walled Pyrex tube. To this was added 10 mg of butadiene. After sealing under vacuum, the tube was heated in an oven (simultaneously with the *trans*-1212 butadiene run) at 180–190° for 24 hr, then cooled, and opened.

The colorless solution was VPC analyzed as such without further treatment. Analysis of the recovered 1212 (column H at 50°) and of the cycloadducts (column F at 120°) has been reported in Table VI.

Addition of *trans,trans*-2,4-Hexadiene to Mixed Isomers of 1212. A mixture of 1212 isomers (15 g, 0.114 mol) of known composition (trans 54%, cis 46%) and *trans,trans*-2,4-hexadiene (3 g, 0.0366 mol) was heated in a heavy-walled Pyrex tube for 24 hr at 180–190°. Fractionation of the reactants through a microcolumn gave 5 g (64%) of crude cycloadducts [bp 73–74° (15 mm)]. Preparative VPC, employing column C at 110° (helium flow, 1 ml/sec), permitted isolation of the 1,2 adducts as a whole (retention time, 12–28 min) and each of the 1,4 adducts (retention time, 38 and 47 min). Analytical VPC was done on column D at 150°. The retention times were: 1,2 adducts, 16–28 min; 1,4 adducts, 39, 42.5, and 47.5 min. Identification of the adducts was as described above.

Hydrogenation of Each of the 1,4 Cycloadducts of *trans,trans*-2,4-Hexadiene to Mixed Isomers of 1212. In a typical procedure, 40 mg of each of the three 1,4 cycloadducts isolated by preparative VPC was dissolved in 2 ml of ethyl acetate. To this was added 0.006 mg of commercial platinum oxide catalyst. The catalyst was not hydrogenated before addition of the adduct. The mixture was hydrogenated at 27° (1 atm). The catalyst was then removed by filtration, the solvent was partly removed under reduced pressure, and the hydrogenated adducts were isolated by preparative VPC on column C at 135°. About 30–35 ml of substance was then obtained. The NMR no longer showed ethylenic absorptions.

Thermal Cycloaddition of *trans*-1212 to *trans,trans*-2,4-Hexadiene. 1212 from which the contaminating 1122 had been removed was separated into cis and trans isomers with column I at room temperature. Analysis on column H at 50° indicated the separated *trans*-1212 to be in fact 99% *trans*-1212 with 1% cis impurity.

About 0.15 g of this 99% pure *trans*-1212 was bulb-to-bulb distilled into a small heavy-walled Pyrex tube. To this was added 10 μl of *trans,trans*-2,4-hexadiene. After sealing under vacuum, the tube was heated in an oven at 180–190° for 24 hr, then cooled, and opened.

The colorless solution was VPC analyzed as such without further treatment. Analysis of the recovered 1212 (column H at 50°) and of the cycloadducts (column D at 150°) is reported in Table VII.

Thermal Cycloaddition of *cis*-1212 to *trans,trans*-2,4-Hexadiene. About 0.15 g of 99% pure *cis*-1212 was bulb-to-bulb distilled into a small heavy-walled Pyrex tube. To this was added 10μl of *trans,trans*-2,4-hexadiene. After sealing under vacuum, the tube was heated in an oven (simultaneously with the *trans*-1212-*trans,trans*-2,4-hexadiene run) at 180–190° for 24 hr, then cooled, and opened.

The colorless solution was VPC analyzed as such without further treatment. Analysis of the recovered 1212 (column H at 50°) and of the cycloadducts (column D at 150°) is reported in Table VII.

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References and Notes

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