

adiene, norbornene). The n.m.r. spectrum consisted of a sharp signal at τ 3.84 (relative area 1.0) and a complex absorption extending from τ 6.2 to 8.3 (relative area 2.6). The relatively poor integration is reasonably attributed to a contaminant. The most revealing feature of the spectrum was the sharp signal at τ 3.84, which is also observed in all the model compounds of norbornene structure. The n.m.r. spectrum of the other cycloadduct consisted of a complex multiplet centered at τ 4.05 (relative area 1.0), which had the distinct appearance of an AB spin-spin system, and

complex absorptions at τ 6.3 (relative area 1.0) and 7.3 (relative area 1.0). Figure 4 shows the characteristic absorptions of the two products in the unsaturation region, compared to a model norbornene derivative.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Cycloaddition. II. Evidence of a Biradical Intermediate in the Thermal Addition of 1,1-Dichloro-2,2-difluoroethylene to the Geometrical Isomers of 2,4-Hexadiene¹

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Under conditions where the geometrical isomers of 2,4-hexadiene, as well as their 1,2-adducts with 1,1-dichloro-2,2-difluoroethylene, undergo no stereoisomerization, the *cis-cis*-diene yields two isomeric adducts, the *trans-trans*-diene yields another two adducts, and the *cis-trans*-diene yields a mixture of all four. It is shown that each addition to a *cis* or *trans* double bond is accompanied by stereochemical isomerization at the site of the addition so as to approach, but not attain, a cyclobutane mixture 82% *trans* and 18% *cis* at the ring at 80°. This nonstereospecific addition shows that the reaction proceeds by way of a bifunctional intermediate. From the quantitative product compositions it is calculated that the internal rotation of this intermediate from a "cis" to a "trans" conformation occurs 10 times as fast as its ring closure to cyclic product. Since the rate constant for the rotation is estimated to be of the order of 10^{11} sec.⁻¹, it follows that the half-life of the bifunctional intermediate is of the order of 10^{-10} sec.

Introduction

Several facts established in part I of this series² lend special interest to the cycloaddition of fluorinated olefins to the geometrical isomers of 2,4-hexadiene. First, the general effects of methyl groups and chlorine atoms as substituents in butadiene appear to be uniquely consistent with a two-step addition mechanism by way of a "biradical" intermediate (as opposed to a dipolar ion or a charge-transfer complex). Second, the retention of configuration during addition to *cis*- and *trans*-piperilynes to yield *cis*- and *trans*-propenylcyclobutanes indicated that, if an allylic radical is formed during the addition sequence, it retains its configuration, and the same would be expected to be true of the nonparticipating double bond in the case of 2,4-hexadiene. Third, none of the dienes investigated in part I afforded a test of one of the most obvious possibilities of a "biradical" mechanism, namely, the loss of configuration at the participating double bond through free rotation in the bifunctional intermediate. There is much evidence that cycloaddition of the Diels-Alder type proceeds with complete retention of configuration at the participating double bonds and often with a very striking degree of preference between the *endo* and *exo* configurations in the product.³

Similar observations of complete retention of configuration have been made in 1,2-cycloadditions involving reactants which are active dienophiles in Diels-Alder reactions. Thus, in the addition of *cis*- and *trans*-2,3-dicyanohexafluoro-2-butene to the geometrical isomers of propyl propenyl ether, there is complete retention of configuration in both reactants.⁴ With reactants of this type in solution, however, there is very little evidence of biradical character in the addition reactions, whether they be of the 1,2- or the 1,4-type, since ionizing power of the solvent is important.^{5a,b} The nondienophile

character of 1,1-dichloro-2,2-difluoroethylene ("1122"), observed in part I in its addition to monosubstituted butadienes continues to be emphasized in its reaction with the three geometrical isomers of 2,4-hexadiene.

Isomeric Composition of 2,4-Hexadiene.—2,4-Hexadiene as supplied,⁶ was shown by vapor phase chromatography (using an F & M Model 300 instrument with an 8-ft. column packed with β,β' -oxydipropionitrile on 60-80 mesh Chromosorb-P) to be a mixture of three isomers present to the extent of 56.1, 37.8, and 6.0% in the order of their elution. Subsequent evidence is consistent only with the normal assignment of *trans-trans*, *trans-cis*, and *cis-cis* configurations in the order named. It was found that the first and principal component could be fully removed from the mixture by the reaction with excess maleic anhydride at room temperature for 14 hr. The resulting mixture gave just two peaks on vapor chromatography and consisted of 85.8% of the *trans-cis* and 14.2% of the *cis-cis* isomer. When the more powerful dienophile, tetracyanoethylene (TCNE), was allowed to react with the three-component mixture of 2,4-hexadiene isomers at 40° for 22.3 hr., the recovered diene consisted of the *cis-cis* isomer (with the longest retention time) in a purity of 97% and free from its geometrical isomers. Irradiation of a dilute ethanol solution of the three-component mixture with a Hanovia mercury lamp using a Pyrex filter and benzophenone as sensitizer gave a mixture in 85% recovery which now showed 29.6% *trans-trans*, 46.3% *trans-cis*, and 24.1% *cis-cis*. Pure *trans-trans*- and *trans-cis*-2,4-hexadienes were prepared by preparative vapor phase chromatography (Beckman Megachrom using a single 24-ft. stainless steel column packed with tricyanoethoxypropane on 45-60 mesh Chromosorb-P). This procedure easily separated the *trans-trans* isomer from the others, but the pure *trans-cis* was obtained only by a series of careful fraction cuttings on small samples in which the *cis-cis* came out as a shoulder on the *trans-cis* peak. The first two isomers were thus obtained in a purity greater than 99%. The *cis-cis* isomer was freed from the others by means of tetracyanoethylene.

(1) Presented at the National Organic Symposium, Columbus, Ohio, June 18, 1963.

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

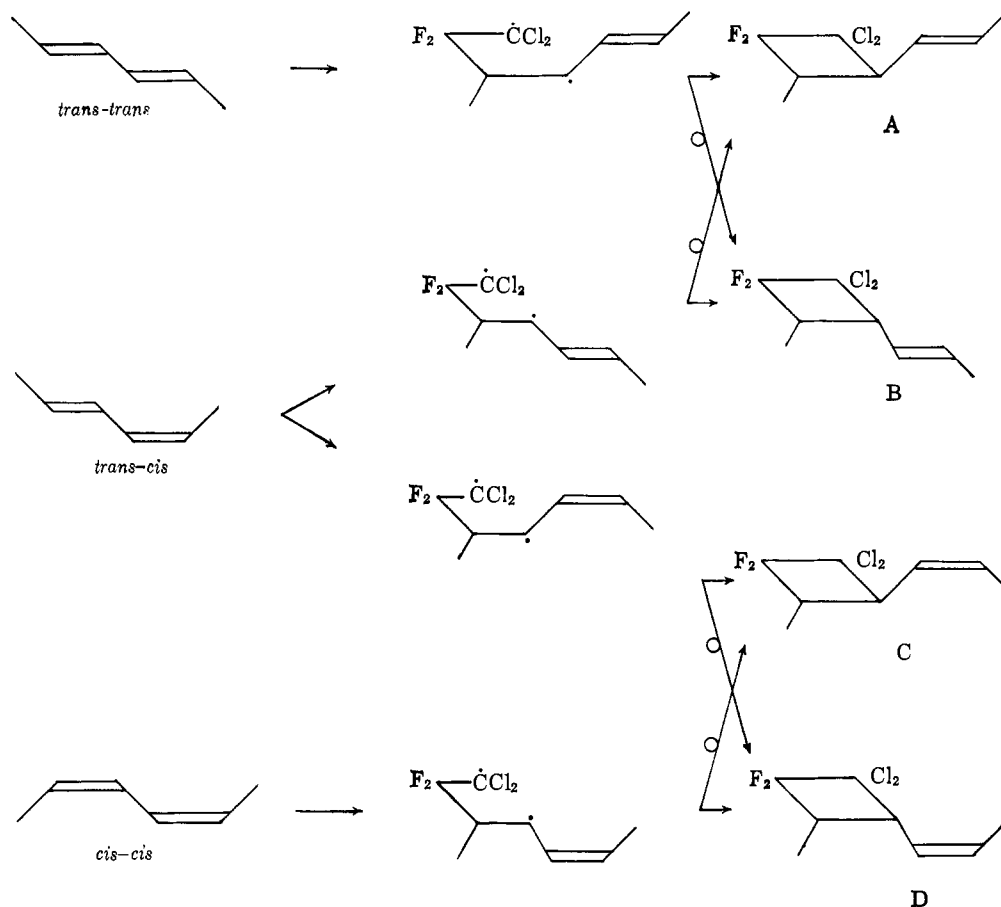
(3) K. Alder and M. Schumacher in "Fortschritte der Chemie Organischer Naturstoffe," Vol. X, I. Zechmeister, Ed., Springer Verlag, Vienna, 1953.

(4) S. Proskow, private communication. Compare S. Proskow, H. E. Simmons, and J. I. Cairns, *J. Am. Chem. Soc.*, **85**, 2341 (1963).

(5) (a) C. A. Stewart, Jr., *ibid.*, **84**, 117 (1962); (b) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962).

(6) Donated by the du Pont Co. through the kindness of Dr. Clare Stewart.

CHART I
PRODUCT ISOMER DISTRIBUTION BY A TWO-STEP MECHANISM WITH ROTATION IN A BIFUNCTIONAL INTERMEDIATE



Control experiments showed that there was no thermal interconversion of the hexadiene isomers when they were heated singly at the temperature and for the period of time used in the cycloaddition reactions.

The cycloadditions reported in this paper were conducted at 80.05° for 16 hr. and at 100.62° for 8.5 hr. Samples of unconverted diene recovered from these addition reactions showed small amounts of isomerization which could not account in any way for the large effects observed upon the products. For example, when 1.07 g. of *trans-trans*-2,4-hexadiene containing 2% of the *trans-cis* isomer was heated with 20 g. of 1122 in an oven at 80–90° for 47 hr. (about three times the usual period), the recovered 2,4-hexadiene now showed a *trans-cis* isomer content of 7%.

Cycloadditions with Isomer Mixtures.—In exploratory experiments, before the pure geometrical isomers were available, cycloadditions of 1122 to 2,4-hexadiene were carried out in sealed tubes using the original three-component isomer mixture and also using the two-component mixture recovered from the reaction with maleic anhydride. In both cases, four well-resolved peaks were observed on the vapor chromatogram. The retention times in each vapor chromatogram corresponded exactly to those in the other, but the compositions of the products from the two-component and three-component hexadiene mixtures were different by as much as 22% in one isomer and 25% in another. That these four peaks represent isomers of the cycloaddition product was established by analysis of a product mixture for carbon, hydrogen, fluorine, and chlorine (see Experimental part). In each case, the product mixture was resubjected to the conditions of the cycloaddition and the average change in the proportion of a component during this treatment was 0.9%.

Relation of Product Composition to Mechanism.—There are eight possible 1,2-addition products of 1122 and 2,4-hexadiene. The isomers A, B, C, and D of Chart I have the chlorine and fluorine atoms oriented as in all the addition products described in part I. Reversal of this orientation would afford the further isomers A', B', C', and D' (not shown). Chart I shows the course of events to be expected if the cycloaddition is initiated by the formation of an open bifunctional ("biradical") intermediate capable of rotation about its single bonds and if the reversed orientation of Cl and F never occurs.

Charts II, III, and IV indicate product distributions on certain other assumptions. Completely stereospecific *cis*-addition with normal Cl-F orientation would yield the distribution of Chart II, while stereospecific *cis*-addition with mixed Cl-F orientation would yield the eight isomers as shown in Chart III. Both of these schemes are out of accord with the facts of the preliminary experiments. Indeed, the only other scheme affording the observed pattern of product distribution is that of Chart IV, based on the improbable assumption that during the addition the configuration of the *propenyl side chain* becomes equilibrated, no changes occurring in the configuration of the double bond to which addition occurs.

CHART II

PRODUCT ISOMER DISTRIBUTION FOR ADDITION WITH RETENTION OF CONFIGURATION

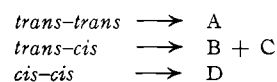


CHART III

PRODUCT ISOMER DISTRIBUTION FOR ADDITION WITH RETENTION OF CONFIGURATION BUT NONSPECIFIC ORIENTATION OF CF_2 AND CCl_2 ($A' = A$ BUT WITH Cl' 'S AND F' 'S INTERCHANGED, ETC.)

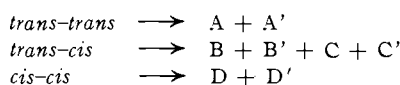
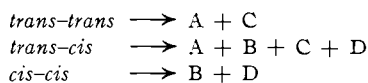


CHART IV

PRODUCT ISOMER DISTRIBUTION FOR TWO-STEP MECHANISM WHICH RETAINS CONFIGURATION AT RING, BUT ISOMERIZES CONFIGURATION OF SIDE CHAIN



Cycloadditions with Pure Geometrical Isomers.—

When the three pure geometrical isomers of 2,4-hexadiene were subjected to cycloaddition under the same conditions, the results shown in Table I were obtained. Again the same four retention times were observed on vapor phase chromatography, but it now becomes clear that only the 2,4-hexadiene isomer of intermediate retention time to which we have assigned the *trans-cis* configuration is capable of yielding all four cycloaddition products while the other two geometrical isomers of the diene yield different pairs of reaction products. This fact is a simultaneous confirmation of the configuration of the *trans-cis*-hexadiene and of the fact that an intermediate is involved which produces isomer mixtures corresponding to either Chart I or Chart IV.

TABLE I

ISOMER DISTRIBUTION IN CYCLOADDUCTS FROM $\text{Cl}_2\text{C}=\text{CF}_2$ AND 2,4-HEXADIENE

Diene isomer	T, °C.	Product isomers, %			
		I	II	III	IV
<i>trans-trans</i>	80.05	0	84.2	15.8	0
		0	83.2	16.8	0
<i>trans-cis</i>	80.05	34.2	44.2	13.7	7.9
		36.0	43.7	13.8	6.6
		35.5	43.7	14.1	6.7
<i>cis-cis</i>	80.05	75.9	0	0	24.1
		76.0	0	0	24.0
<i>trans-trans</i>	100.62	0	82.3	17.7	0
		0	82.1	17.9	0
<i>trans-cis</i>	100.62	33.2	44.9	14.5	7.4
		33.2	46.6	13.8	6.4
		37.3	44.8	12.1	5.8

Although the results with piperylene cited in part I seemed to establish satisfactorily the absence of stereoequilibrium in the side chain double bond, we nevertheless confirmed this by an experiment on the two-component adduct of 1122 to *trans-trans*-2,4-hexadiene. In the experiment in question, this adduct showed two peaks on vapor chromatography with areas in the ratio of 5.09 to 1, the peak with the shorter retention time being the larger. This product was hydrogenated at 27° under one atmosphere pressure and absorbed 1.2 times the calculated hydrogen in 20 min., at which point the hydrogen absorption stopped completely. The hydrogenated product on vapor chromatography showed two new peaks in the ratio of 5.00 to 1, the larger peak corresponding to the shorter retention time.

In similar fashion a mixture of the adducts I-IV from the addition of 1122 to the mixed isomers of 2,4-hexadiene was subjected to catalytic hydrogenation. The ratio of v.p.c. peak areas for $(\text{III} + \text{IV})/(\text{I} + \text{II})$ was 0.237 and 0.223 in two experiments before hydrogenation. The two peaks after hydrogenation were in the ratios of 0.229 and 0.251, respectively. It is thus clear

that the two isomeric addition products of *trans-trans*-2,4-hexadiene possess different geometries in the cyclobutane ring as demanded by Chart I, and not identical ones according to Chart IV.

With this point established we can see that Table I affords with high probability a complete assignment of the configurations of all the cycloadducts. There can be no serious doubt of the configurations of the initial dienes of which the least polar (by vapor chromatography) is also the most reactive in the Diels-Alder reaction where it is known⁷ that *trans*-piperylene is very much more reactive than *cis*. The most polar of the dienes is also the one which fails to react with tetracyanoethylene and the remaining diene is the one which gives four cycloadducts. Accordingly, adducts I and IV must have *cis*-propenyl side chains while adducts II and III have *trans*-propenyl side chains. The ring configurations form a consistent picture if it be assumed that the *trans*-1,2-disubstituted cyclobutanes are preferred over the *cis*. This will give the assignments II = A, III = B, I = C, and IV = D.

We then note that product isomers I and IV do not occur in quite the same ratio when formed from *cis-cis* as from *trans-cis*-hexadiene. The preferred isomer is more highly preferred when the double bond to which addition is occurring is already *trans* (product ratio 5 to 1 instead of 3 to 1). Likewise, of the isomers II and III, the preferred isomer is the more predominant when formed from *trans-trans*-hexadiene by addition to a *trans* double bond rather than when formed from *trans-cis*-hexadiene by addition to a *cis* double bond. This is the pattern to be expected of a reaction proceeding through a bifunctional intermediate in which ring closure competes with rotation about the bond which was originally double.

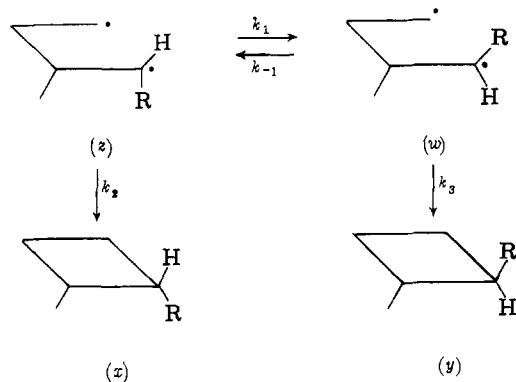
Discussion

One other fact about relative reactivities is shown by Table I. If, in the case of *trans-cis*-hexadiene, we compare the sum of products I and IV with the sum of products II and III, we shall have a measure of the relative rates of addition of 1122 to the *cis* and the *trans* double bonds. In the three examples given, the ratios of rates of addition to the *cis* and the *trans* double bonds are 1.37, 1.35, and 1.37. It is thus somewhat easier for the reagent to initiate reaction at a *cis* double bond neighboring a *trans* double bond than at a *trans* double bond neighboring a *cis* double bond. In part III⁸ we have some rate measurements indicating that in the piperylenes, where the addition is to the configurationless 3,4-double bond, the rate of addition to *cis*-piperylene is greater than that to *trans*-piperylene by the factor 1.40. It is thus more favorable in cycloaddition to have the participating double bond neighboring a *cis* than a *trans* configuration. The preference shown for the *cis* double bond in *trans-cis*-hexadiene is thus exhibited over a slight barrier imposed by the neighboring *trans* configuration. If we make an appropriate correction for this, we conclude that the inherent preference of 1122 for reaction at a *cis* rather than a *trans* center is by a factor of 1.9.

Competitive Reactions of the Intermediate.—The competition between internal rotation and ring closure in the intermediate is such that rotational equilibrium is approached but not attained before the occurrence of ring closure. This fact makes it possible to estimate quantitatively the relative rates of these competing processes. For this purpose let us define rate constants as

(7) D. Craig, *J. Am. Chem. Soc.*, **72**, 1678 (1950).

(8) P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).



Here z and w are the instantaneous concentrations of those groups of rotamers of the bifunctional intermediate which will close to *cis* and to *trans* configurations at the cyclobutane ring, respectively, and the concentrations of these cyclic products are x and y . The rotation is treated as a reaction proceeding over a low energy barrier, with the forward and reverse rate constants k_1 and k_{-1} . Under these conditions the steady-state concentration of that rotamer which has the opposite configuration from the original diene will be determined only by the rate constants shown. That is, starting with addition to a *cis* double bond,

$$(dw/dt)_{cis} = k_1z - (k_{-1} + k_3)w \cong 0, \text{ and}$$

$$(z/w)_{cis} = (k_{-1} + k_3)/k_1$$

In this case

$$\left(\frac{dx}{dy}\right)_{cis} = \frac{k_2(z)}{k_3(w)}_{cis} = \frac{k_2(k_{-1} + k_3)}{k_1k_3}$$

Hence at any time

$$(x/y)_{cis} \equiv p = k_2(k_{-1} + k_3)/k_1k_3 \quad (1)$$

Starting with addition to a *trans* double bond

$$(dz/dt)_{trans} = k_{-1}w - (k_1 + k_2)z \cong 0, \text{ and}$$

$$(w/z)_{trans} = (k_1 + k_2)/k_{-1}; \text{ then}$$

$$\left(\frac{dy}{dx}\right)_{trans} = \frac{k_3(w)}{k_2(z)}_{trans} = \frac{k_3(k_1 + k_2)}{k_{-1}k_2}$$

and at any time

$$\left(\frac{x}{y}\right)_{trans} \equiv q = \frac{k_3(k_1 + k_2)}{k_{-1}k_2} \quad (2)$$

It is useful to express eq. 1 and 2 in terms of the ratios of related rate constants, $a = k_{-1}/k_1$; $b = k_2/k_1$; $c = k_3/k_2$. The equations then become

$$p = (a/c) + b \quad (3)$$

$$q = (c/a)(1 + b) \quad (4)$$

From eq. 3 and 4 we obtain the rate constant ratios in terms of the experimental quantities p and q

$$a/c = (p + 1)/(q + 1) \quad (5)$$

$$b = (pq - 1)/(q + 1) \quad (6)$$

It is evident from eq. 3 and 4 that the fraction (a/c) represents the *cis/trans* product ratio which would exist under conditions of complete rotational equilibration before ring closure, leading to identical product compositions from both directions. As appears from Table II, the experimental values of p and q are independent of the isomer taken as starting material, and accordingly a/c and b have been evaluated from averages.

At 80° the average of five determinations of p is 0.316 with a mean deviation of 0.0036 or 1.1%; the average of five values of q is 5.07 with a mean deviation of 0.35, or 6.9%. The less precise values at 100.62° have an average of $p = 0.296$ and $q = 5.05$, not significantly different from those at 80°, and hence not permitting any

TABLE II

DETERMINATION OF RELATIVE RATE CONSTANTS FROM DATA OF TABLE I

Hexadiene isomer	Temp., °C.	p	q	a/c	b	
<i>trans-trans</i>	80.05		5.33			
			4.93			
<i>trans-cis</i>	80.05	0.310	4.33			
			.314	5.46		
			.324	5.30		
<i>cis-cis</i>	80.05	.317				
			.315			
Average	80.05	0.316	5.07	0.217	0.099	
<i>trans-trans</i>	100.62		4.65			
			4.60			
<i>trans-cis</i>	100.62	0.322	4.45			
			.296	5.12		
			.271	6.45		
Average	100.62	0.296	5.05	0.214	0.082	

estimate of the differential activation energies except that they are small.

In the first of two limiting cases, it might be considered that the preference for a *trans* product reflects only a lower average energy of the rotamers which close to *trans* product by 0.47 kcal./mole, and that $k_2 = k_3$, in which case $a/c = a = 0.22$ and the energy minima associated with rotation of the biradical lie at unequal levels. Bothner-By, Naar-Colin, and Günther⁹ have concluded from n.m.r. evidence that in the analogous compound 3-methyl-1-butene the three rotational minima are about equally populated. This would correspond to our a being equal to 1 and $c = 4.5$, meaning that the hindrance to formation of a *cis* structure sets in only as the ring begins to be closed. In either case the value of b , 0.10, is the ratio of the rate of the slower ring closure to that of the faster rotation in the biradical.

The Nature of the Intermediate.—The property of a "biradical" which is important for the phenomena of stereoequilibration here reported is simply the absence of significant bonding between the carbon atoms to which the "radical" character is attributed. The "virtual diradical" intermediate,² which is considered to have one fully and one partially formed bond, is a useful concept in either of two cases: (a) where the formation of the true biradical from the reactants is thermally too unfavorable to be compatible with the observed reaction rate, or (b) where the orientation in the products requires biradical forces to operate but where there is an absence of free rotation in the intermediate and stereospecific addition. In the presence case the evidence of rotation suggests a fully free biradical; we may inquire whether the formation of such a biradical could occur with a plausible energy of activation. The heat of polymerization of gaseous tetrafluoroethylene to solid linear polymer¹⁰ is $\Delta H = -42$ kcal./mole at 660°. This is to be compared with the corresponding figure for ethylene at 400°, -24.7 kcal./mole. The amount of destabilization of the double bond by fluorine substitution so indicated, 17 kcal., is supported also by the difference in heats of reaction of the two olefins with HBr, 16.2 kcal., and with Cl₂, 15.8 kcal.¹¹ The following components are then appropriate for a bond energy calculation

(9) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(10) C. R. Patrick, "Advances in Fluorine Chemistry," Vol. 2, Butterworth, London, 1961, p. 22.

(11) Reference 10, p. 27.

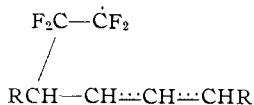
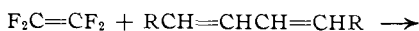
Fluorinated C=C, 147^{12a} - 16 = 131 kcal.

C—C single bond, 83 kcal.^{12b}

Resonance energy of allylic radical, 25 kcal.^{12c}

Resonance energy of diene lost, 3.5 kcal.

Then for



$$\Delta H = -3 \times 83 - 25 + 131 + 147 + 3.5 = +7.5 \text{ kcal/mole}$$

Thus the formation of a biradical is thermochemically favorable enough so that no partial formation of the second bond is required for feasibility. We have made this calculation for tetrafluoroethylene because of the availability of thermal data. Less extensive data indicate less destabilization in the double bond of 1,1-dichloro-2,2-difluoroethylene,¹³ but this may be offset by an estimated 8 kcal. of resonance energy in an RC-Cl₂ compared to an RCF₂ radical (resonance energy of CCl₃[•], 12; of CF₃[•], 0).^{12c}

In part I it is shown that the structure of the products from chloroprene, isoprene, and the piperylenes requires a nonpolar intermediate and not a dipolar ion, and this conclusion is reinforced by the effects of structure on rate observed in part III. We conclude from this that the bifunctional intermediate has two sites each with an unpaired electron.

If we assume that there is no force between these radical sites to limit rotation, it appears from a model that the rotation which leads to the stereoequilibrium should have only a barrier similar to that in propylene. (It is known that barriers to rotation are quite insensitive to substitution until the point of real steric hindrance is reached.¹⁴) If we take this barrier as equal to about 3 kcal., neglect solvent effects, and apply simple transition state theory, we estimate that the rotation should have a rate constant k_1 of the order of $(kT/h) \exp(3000/RT)$ or $1 \times 10^{11} \text{ sec.}^{-1}$ at 80°. From our value of b , which is k_2/k_1 , k_2 would then appear to be about $1 \times 10^{10} \text{ sec.}^{-1}$. When a biradical of four atoms in the chain reacts at such a first-order rate, it corresponds approximately to two separate comparable radicals reacting with a bimolecular rate constant of about $2 \times 10^{10} \text{ l./mole sec.}^{15}$ These are all maximal values but their magnitudes are not unreasonable. The resonance energies of the two radicals should be largely offset by their complementary polar character. The bimolecular equivalent rate constant in question is about 700 times that^{16,17} for coupling of identical radicals of the vinyl acetate type.

A somewhat comparable biradical for which rate information is available is the trimethylene biradical produced from thermal ring opening of cyclopropane.¹⁸ For the ring closure of this species Benson¹⁹ has assigned Arrhenius parameters which correspond to a rate constant at 80° of $8 \times 10^7 \text{ sec.}^{-1}$. This ring closure involves primary, unstabilized radicals but operates

against a higher strain barrier than does the closure of a cyclobutane ring.

Reactions of methylene afford a case partially parallel to the stereochemistry of addition of 1122 to 2,4-hexadiene. Singlet methylene, resulting from thermal or direct photochemical dissociation of diazomethane, has two characteristics that cannot be separated, in that it is a high-energy species as well as possessing the electrophilic reactivity of a singlet carbene.^{20,21} It is now clear that no biradical need be involved in reaction of the singlet methylene with *cis*-2-butene, but that the reaction can begin with an association of the methylene with both of the carbon atoms of the double bond. On the other hand, triplet methylene, produced by benzophenone-photosensitized decomposition of diazomethane, yields a mixture of stereoisomeric dimethylcyclopropanes from *cis*-2-butene,²² a result rather analogous to the one in the present case.

If we assume that singlet methylene was absent in these experiments we may apply our treatment to the estimation of the competing rate constants in the 2-methyl-1,3-butanediyl biradical. Anet, Bader, and van der Auwera,²³ using a gas-phase system and producing triplet methylene by collisional deactivation of the photochemically produced singlet, obtained similar product compositions from *cis*- and *trans*-2-butenes, the ratio of which presumably corresponds to our parameter a/c which is not likely to be very different in the liquid phase. This enables us to conclude that under Hammond's conditions, where $p = 2$, if $a/c = 0.17$, $b = 1.83$, so that ring closure of the 2-methyl-1,3-butanediyl biradical is about 18 times as rapid, relative to its rate of internal rotation, as is that of the biradical in our cycloaddition reaction.

The gas-phase work of Anet, *et al.*, since it appears to establish equilibrium between the *cis* and *trans* isomers, can by itself afford only a maximal value of the competition ratio b . If we use the same estimate of a/c taken from the average *cis-trans* composition of the product from *cis*- and *trans*-2-butenes and assume that the *cis* content of the product from the *cis* is not in error by more than 50% of its value, we conclude that p for this case is less than 0.25 and b is less than 0.08.

Any attempt to compare the competitive rate constants in our cycloaddition reactions with those in the reactions of triplet methylene brings up the fundamental question of the relationship of the spins of the electrons in the intermediate biradical. In cycloaddition the biradical is formed in a thermal reaction between two molecules whose spins are all paired. The biradical must accordingly be formed with the spins of its odd electrons antiparallel, loosely analogous to an excited singlet state. In contrast, when triplet methylene adds to an olefin, the resulting biradical must initially have the spins of its odd electrons parallel, as in the excited triplet from which it is formed. The same should be true of the cycloaddition intermediates in the photosensitized dimerization of dienes,²⁴⁻²⁶ if this involves reaction between an excited triplet and a ground-state molecule.

When two single electrons are in orbitals of different energies involving the same set of atoms, as in photo-

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(24) G. S. Hammond, A. Fischer, and N. J. Turro, *ibid.*, **83**, 467 (1961).

(25) N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962).

(26) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

excited anthracene, the singlet and triplet states are separated by a substantial energy increment, and transitions between them are characteristically slow. Studies of competitive modes of deactivation of excited singlets lead to rate constants of the order of 10^7 to 10^9 for the intersystem crossing to the lower-lying triplet. Far less information is available concerning the spin inversions in pairs of unconnected free radicals which collide, it being generally supposed that such a collision cannot result in combination unless the electron spins are antiparallel as the radicals approach each other. In an assembly of randomly spin-oriented free radicals in a magnetic frame of reference this restriction can make not more than a twofold difference in the rate constant for radical combination.

However, in the case of a biradical whose odd electrons are insulated from each other by a sequence of saturated atoms, the behavior of the species might depend critically upon the severity of the restriction upon spin inversion. Since ring closure must occur between a specific pair of atoms, a "triplet" biradical, *i.e.*, one generated with its spins parallel, must undergo inversion of one of those spins before it can form a ring. Should the spin relaxation be slower than the rate of intermolecular coupling of radicals of this type "triplet" biradicals would necessarily react with one another to form polymer instead of undergoing ring closure.

In comparing our "singlet" tetramethylene biradicals with the "triplet" trimethylene biradicals of Anet and of Hammond, we find that the latter in solution appear to close more rapidly than ours (to less stereoequilibrated products), while the trimethylene radicals in the gas phase seem to close more slowly. There is certainly no indication that in solution the triplet origin of the trimethylene type radical presents any limitation to its ring closure. Despite the scanty nature of the evidence, it seems clear that in the gas phase either rotation in the biradical is faster, or spin inversion is slower than in solution, or both. If solvent molecules have any effect on either process, it should be in this direction. We are carrying on further experiments to compare the behavior of biradicals having their origin in spin-paired and spin-unpaired systems.

Experimental

The Photochemical Isomer Redistribution of 2,4-Hexadiene.—

Anhydrous ethanol was prepared by method (a) of Fieser.²⁷ (Commercial absolute ethanol was avoided in order to prevent contamination of the dienes with benzene.)

A solution of 16.4 g. (0.200 mole) of 2,4-hexadiene isomers⁸ (*trans-trans*, 56.1%; *trans-cis*, 37.8%; *cis-cis*, 6.0%) and 27.3 g. (0.15 mole) of benzophenone made up to 1.0 l. with absolute ethanol was placed in a Hanovia apparatus equipped with a 500-w. lamp and a 2-mm. Pyrex filter sleeve. The isomers were irradiated for 4.5 hr. The ethanol and the 2,4-hexadiene were distilled away from the benzophenone with a rotary evaporator. The ethanol solution was poured into water and the 2,4-hexadiene isomers collected. The isomers were washed several times with water, dried over calcium chloride, and distilled through a semi-micro column.²⁸ The 2,4-hexadiene (13.0 g., 85% recovery), b.p. 82–83°, obtained in this manner had the composition: *trans-trans*, 29.6%; *trans-cis*, 46.3%; *cis-cis*, 24.1%. Analysis of the dienes was accomplished by using an 8-ft. (0.25 in. o.d.) β,β' -oxydipropionitrile (20% liquid phase on 60–80 mesh Chromosorb-P) column.

Reaction of 2,4-Hexadiene Isomers with Maleic Anhydride.—To a mixture of 50 g. (0.51 mole) of maleic anhydride and 25 ml. of acetone was added 25.0 g. (0.305 mole) of 2,4-hexadiene (*trans-trans*, 56.1%; *trans-cis*, 37.8%; *cis-cis*, 6.0%). The solution became warm but did not boil, cooled gradually, and was stirred at room temperature for 14 hr. The unreacted dienes were recovered by distillation with steam. The nonaqueous distillate was washed several times with water, dried over anhydrous calcium chloride, and distilled. A two-component mixture of

dienes was obtained (9.62 g., 87% recovery); v.p.c. analysis showed that the mixture was 85.8% the *trans-cis* isomer and 14.2% the *cis-cis* isomer.

***trans-trans*-2,4-Hexadiene and *trans-cis*-2,4-Hexadiene.—**Eight 6-ft. (5/8 in. o.d.) stainless steel columns for the Beckman Instruments Megachrom preparative gas chromatograph were packed with 26% (w./w.) 1,2,3-(2-cyanoethoxy)-propane on 45–60 mesh Chromosorb-P. It was not possible to achieve a clean separation of the three isomeric 2,4-hexadienes. Under the column conditions employed (a single 24-ft. column, 40 p.s.i. inlet pressure, 1.0 p.s.i. back pressure, 45°), *trans-trans*-2,4-hexadiene had a retention time of 34 min., while *trans-cis*-2,4-hexadiene came at 40.5 min. *cis-cis*-2,4-Hexadiene appeared as a shoulder on the *trans-cis* isomer peak at 44 min. By the appropriate cutting of fractions and provided that a small sample was injected (0.6 cc), the *trans-trans* and *trans-cis* isomers could be obtained in greater than 99% purity. Recovery under these conditions was 50–70% when liquid nitrogen was used to cool the fraction collectors. Better recovery was observed using larger samples, but the resolution drops off sharply with an increase in sample size.

***cis-cis*-2,4-Hexadiene.—**In a 250-ml., round-bottomed flask were placed 17.50 g. (0.213 mole) of 2,4-hexadiene isomers (86% *trans-cis* and 14% *cis-cis*), 40.0 g. (0.312 mole) of tetracyanoethane, 100 ml. of Fisher reagent acetone, and 0.10 g. of di-*n*-butylammonium picrate. The solution was heated at 40.16° for 22.3 hr. The flask, containing the reaction products, was connected to a vacuum line, cooled with a Dry Ice-acetone mixture, and evacuated (0.015 mm.). The volatile reaction products were transferred to another flask immersed in a Dry Ice-acetone slurry by closing off the vacuum system from the vacuum pump and withdrawing the coolant from the flask containing the reaction products. The distilled products were poured into water and the organic phase collected. After several washings, the reaction products were dried over anhydrous calcium chloride. The yield of *cis-cis*-2,4-hexadiene was 1.56 g. (64%). Analysis by v.p.c. (22°, 8-ft. column, 0.25 in. o.d., of 20% 1,2,3-(2-cyanoethoxy)-propane 60–80 mesh Chromosorb-P) revealed that the other two isomers were absent but that 3% of other impurities were present.

The infrared absorption spectra of the pure 2,4-hexadiene isomers show marked differences. Each one has a strong doublet at 3.4 and 3.5 μ and a moderate to strong peak at 6.9 μ . However, the strongest peak in spectrum of the *cis-cis* isomer is a broad one at 14.6 μ . It is absent in the *trans-trans* and is weakened in the *trans-cis* and shifted to 14.2 μ . The *trans-cis* isomer has a unique peak of medium intensity at 12.10 μ , and the *trans-trans* is characterized by an absorption at 10.04 μ which is more than twice as intense as any other peak in its spectrum. The *trans-cis* absorbs strongly at 10.10 and 10.50 μ , while the *cis-cis* is transparent in this region.

Addition of 1,1-Dichloro-2,2-difluoroethylene to Mixed Isomers of 2,4-Hexadiene.—A mixture of 2,4-hexadiene isomers (0.503 g., 0.00612 mole) of known composition (*trans-trans*, 31.6%; *trans-cis*, 43.2%; *cis-cis*, 25.2%), 1,1-dichloro-2,2-difluoroethylene (10.5 g., 0.079 mole), and 50 mg. of di-*n*-butylammonium picrate was heated in a heavy-walled Pyrex ampoule for 22.1 hr. at 50.05°. Fractionation of the reactants through a microcolumn gave 0.540 g. (41%) of crude cycloadducts (estimated b.p. 64° at 40 mm.). The mixture of cycloadducts was isolated in high purity employing v.p.c. (0.10-ml. injections on the 8-ft. (0.25 in. o.d.) 1,2,3-(2-cyanoethoxy)-propane column at 160°). The collected material, 0.192 g., was redistilled to remove any non-volatile contaminants such as the liquid phase of the chromatographic column. The remaining cycloadducts, 0.131 g., were shown to be present in at least 99.8% purity by v.p.c. analysis. The composition of the mixture was: I, 34.3%; II, 45.7%; III, 10.7%; IV, 9.3%.

Anal. (by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.): Calcd. for $C_8H_{10}Cl_2F_2$: C, 44.67; H, 4.69; Cl, 32.97; F, 17.67. Found: C, 44.95, 44.79; H, 4.88, 4.73; Cl, 32.46, 32.42; F, 17.45, 17.33.

The Reactions of *trans-trans*-, *trans-cis*-, and *cis-cis*-2,4-Hexadienes with 1,1-Dichloro-2,2-difluoroethylene.—About 0.08 g. (0.100 ml., 0.001 mole) of each isomeric 2,4-hexadiene was placed in a separate ampoule of about 1.8-ml. capacity prepared from heavy-walled Pyrex tubing, with 1.5 g. (1.00 ml., 0.011 mole) of 1,1-dichloro-2,2-difluoroethylene, and 10 mg. of di-*n*-butylammonium picrate. The ampoules were heated for the appropriate periods of time (16.3 hr. at 80.05°, 8.5 hr. at 100.62°), and the relative amounts of the isomeric cycloadducts determined by v.p.c., employing an F & M Model 300 gas chromatograph equipped with a disk integrator. The isomeric cycloadducts were difficult to separate cleanly. Under the column conditions employed (8 ft., 0.25 in. o.d., column of 20% tricresyl phosphate on 60–80 mesh Chromosorb-P, 90°, 120 cc./min.) the retention times of the various isomers were: I, 31.0 min.; II, 33.5 min.; III, 38.3 min.; IV, 42.6 min. The results of the analyses are reported in Table I.

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Hydrogenation of the Cycloadducts of *trans-trans*-2,4-Hexadiene and 1,1-Dichloro-2,2-difluoroethylene.—For this experiment an adduct was used which was prepared by heating for 47 hr. in an oven at 80–90°. The adduct, analyzed on an 8-ft. column, 0.25 in. o.d., packed with 20% 1,2,3-tris- β -cyanoethoxypropane (helium flow 60 ml./min., 115°) contained isomers II and III in a ratio of 5.09 to 1 (retention times 14 and 18 min., respectively).

In 40 ml. of glacial acetic acid was dissolved 0.35 g. of the twice-distilled cycloadduct. To this was added 0.037 g. of commercial platinum oxide catalyst. The catalyst was not hydrogenated before addition of the adduct. The mixture was hydrogenated at 27° and 1 atm. pressure. In 20 min. 48 ml. of hydrogen was taken up and then the reaction stopped completely (theoretical hydrogen uptake: $22.4 \times 0.35/2.5 \times 300/273 = 40$ ml.). The catalyst was removed by filtration and 200 ml. of water was added. The mixture was extracted seven times with 10-ml. portions of *n*-pentane. The solution was dried over magnesium sulfate and the *n*-pentane distilled off through a short Holtzmann column. The number and ratio of products was determined by v.p.c. (8 ft., 0.25 in. o.d., 20% 1,2,3-tris- β -cyanoethoxypropane column, helium flow rate 60 ml./min., 130°). Two product peaks at 5 and 7 min. were found, the area under the

peaks having a ratio of 5.00:1 (the one with the shorter retention time is the larger).

Hydrogenation of the Four-Component Adduct Mixture.—By a similar procedure, 0.149 g. of a four-component mixture of adduct isomers was hydrogenated with 0.015 g. of commercial platinum oxide. The hydrogen uptake was 24.4 ml., complete in 45 min. In a blank experiment an equal weight of the catalyst took up 6.8 ml. of hydrogen. The uptake by the sample was therefore 24.4 – 6.8 = 17.6 compared with a theoretical 17.0.

In the analyses, isomers I and II were determined together in an imperfectly resolved peak at 34 min. on 1,2,3-tris- β -cyanoethoxypropane and 47 min. on tricesyl phosphate. Isomer III had retention times on these columns of 42 and 59 min., and isomer IV of 48 and 63 min., respectively. The product had two peaks at 17 and 25 min., respectively, on the tris- β -cyanoethoxypropane column. The ratio of the second to the first peak in three determinations was 0.229, 0.251, and 0.251, from an initial mixture with (III + IV)/(I + II) ratios of 0.237 and 0.223.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Cycloaddition. III. Kinetics and Reactivity in the Addition of 1,1-Dichloro-2,2-difluoroethylene to Dienes. The Biradical Mechanism

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In 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene to dienes, both 2-methyl and 2-chlorine substitutions are mildly activating for addition to the 1,2-double bond and deactivating for addition to the 3,4-double bond. *cis*-Piperylene is slightly more reactive than *trans*-piperylene. Terminal methyl substitution slows cycloaddition much as it does free radical polymerization. Cyclopentadiene is attacked 70% as fast as butadiene instead of being 1350 times as reactive, as it is toward maleic anhydride in the Diels–Alder reaction. These facts are regarded as consistent with the two-step biradical mechanism supported in parts I and II; and they emphasize that the mechanism of the Diels–Alder reaction is entirely different from that of addition of haloolefins, even when (as in the case of cyclopentadiene) the latter yield chiefly 1,4-addition products.

Introduction

One of the most direct ways to study the difference between the reaction of dienes with dienophiles (1,4-addition in the Diels–Alder reaction) and the reaction of the same dienes with 1,2-cycloaddition reagents would be to observe the effects of structural variations upon the rates of these two differing processes. It was shown in part I of this series that the orientation of an unsymmetrical reagent¹ such as 1,1-dichloro-2,2-difluoroethylene (“1122”) is consistent with the hypothesis that the point of initial bond formation is that which leads to the most favorable biradical intermediate. It was shown in part II that cycloaddition to geometrically isomeric dienes proceeds through a stage permitting free rotation about the axis of the double bond to which the addition is taking place.² Although the addition reactions of typical dienophiles can be discussed in terms of a possible bifunctional intermediate,³ the stereospecificity commonly associated with these reactions⁴ indicates that, if biradicals are involved, they have rather different properties from the biradicals of ref. 2 and the possibility remains open that only one transition state is traversed by the reactants in the course of a Diels–Alder reaction.

In the present paper we have compared the rates of 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene to a series of dienes whose reactivities toward maleic anhydride have already been compared.^{5,6}

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Experimental

Materials.—The sources and preparations of the compounds have been described in parts I¹ and II.²

Procedure for Kinetic Runs.—Rate measurements were made employing an ampoule technique and following the rate of appearance of cycloadducts by vapor phase chromatography.

Ampoules having a capillary neck and a volume of 1.6–1.8 ml. were prepared from heavy-walled Pyrex tubing (12.7 mm. o.d., 2.3 mm. wall thickness) and were oven annealed. Another type of ampoule, which was used in making density measurements, had a second capillary constriction immediately above the first.

A concentrated solution of inhibitor (di-*n*-butylammonium picrate or hydroquinone) in methylene chloride was prepared. A volume of solution containing 10 mg. of inhibitor was added to each ampoule by syringe. The methylene chloride was removed under reduced pressure and the ampoules were stored in a desiccator until used. It was necessary to place the inhibitor in each ampoule rather than add it to the reactants, since the inhibitors used were of limited solubility in the cold reactants.

The solutions were prepared by weight in a vacuum-jacketed volumetric flask of about 15.0 ml. The solutions were 0.5–1.5 *M* in 1,3-diene and the 1,1-dichloro-2,2-difluoroethylene was employed as the solvent (8.0–8.5 *M*). Diene dimerization was minimized by using the fluoroolefin as solvent, which also permitted lower reaction temperatures. The dimer of 1,1-dichloro-2,2-difluoroethylene represented less than 0.3% of the reaction products at 80°. All of the components of the solutions were placed in an ice bath prior to weighing. The cooling facilitated the transfer of these liquids by syringes fitted with long needles.

The volumetric flask was weighed and cooled by washing with 1,1-dichloro-2,2-difluoroethylene. The diene (enough for 0.5–1.5 *M* solution) and the internal standard (purified toluene, cumene, or *t*-butylbenzene) were weighed out, and the solution was made up to 15.0 ml. with 1,1-dichloro-2,2-difluoroethylene. An amount of internal standard was added which provided a v.p.c. peak area corresponding to 40% of the peak area of the theoretical yield of cycloadduct. By adding the internal standard to the reactants it was possible to eliminate quantitative transfers and the large errors accompanying them.

About 1.2 ml. of the reactant solution was added to each of the standard ampoules and an amount to the modified ampoule which was just sufficient to bring the solution up into the capillary neck at the reaction temperature (the solution expanded about 10% upon being heated from 0 to 80°). The ampoules were sealed off at the capillary neck and placed in an oil bath maintained at