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The Kinetics of Addition, Dissociation and Isomerization in Two Diels–Alder Systems. A Test for “Molecule-Pair” Intermediates^{1a}

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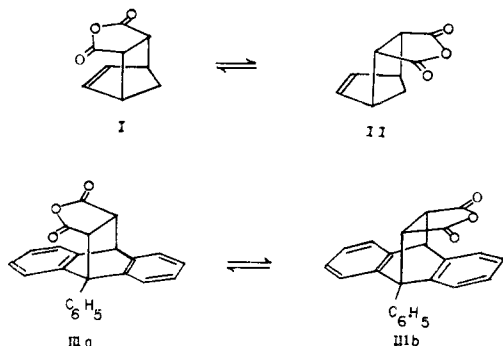
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The first-order rate coefficients for the dissociation of the 9-phenylanthracene–maleic anhydride adduct in *o*-dichlorobenzene, as measured by spectrophotometric assay of 9-phenylanthracene, by exchange with ¹⁴C-maleic anhydride, and by racemization, are identical, which indicates the absence of an internal isomerization pathway. Although an internal pathway had been demonstrated for the isomerization of the cyclopentadiene–maleic anhydride adduct, this cannot be attributed to a cage effect, since the second-order rate of combination of cyclopentadiene and maleic anhydride is too slow by six to nine powers of ten to be diffusion-controlled. The addition of 9-phenylanthracene to maleic anhydride is not catalyzed by ferric dipivaloylmethide, and the retrogression of the adduct has a normal pre-exponential factor. Both of the latter observations are consistent with retention of electronic multiplicity in the transition state.

Previous experiments² disclosed a mechanism for the stereochemical isomerization of the cyclopentadiene–maleic anhydride adducts that was independent of the dissociation of the adduct into the component addends. One of the conceivable detailed descriptions of the internal pathway of isomerization is reassociation of the diene–dienophile pair in a potential energy pocket in which the fragments reside long enough to permit stereochemical interconversion. The present paper reports the results of experiments designed to determine the scope of the internal isomerization by study of another system. The kinetics of the cyclopentadiene–maleic anhydride addition, which help to sharpen the interpretation of the non-dissociative isomerization, are also reported.

Results

Diels–Alder Addition in the 9-Phenylanthracene–Maleic Anhydride System.—Since the stereoisomeric adducts I and II in the cyclopentadiene–maleic anhydride system were chemically different, it was necessary to follow the behavior of both isomers independently.² In a system with appropriate symmetry properties, however, “isomerization” can be made equivalent to racemization, and the kinetics can be worked out by following the behavior of a single substance. For this reason (and others that will become apparent) we have studied the 9-phenylanthracene–maleic anhydride addition–retrogression.



(1) (a) This work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of said fund. We are also indebted to the Alfred P. Sloan Foundation for support of part of this work. (b) Alfred P. Sloan Fellow.

(2) J. A. Berson and R. D. Reynolds, *J. Am. Chem. Soc.*, **77**, 4434 (1955); J. A. Berson, R. D. Reynolds and W. M. Jones, *ibid.*, **78**, 6049 (1956).

In solvent *o*-dichlorobenzene, the reaction of 9-phenylanthracene with maleic anhydride, followed spectrophotometrically by observing the 368 m μ absorption of the diene, was first order in each component over a variation of more than 100-fold in the initial maleic anhydride concentration (Table I). The reaction reached equilibrium short of complete conversion to adduct III, and the rate coefficients were determined from eq. 1, in which a_e , b_e and c_e , are equilibrium concentrations of adduct, 9-phenylanthracene and maleic anhydride; b_0 and c_0 are initial concentrations; and a is the instantaneous concentration of adduct.

$$k_2 = \frac{2.3a_e}{t(b_0c_0 - a_e^2)} \log \left[\frac{aa_e^2 - a_e b_0 c_0}{ab_0 c_0 - a_e b_0 c_0} \right] \quad (1)$$

The equilibrium constants determined directly were in good agreement with the ratio of the forward and reverse rate coefficients (see below); at 152.4°, for example, $K = b_e c_e / a_e = 0.0115$, and $k_1/k_2 = 0.0114$.

The simple second-order behavior of this addition is to be contrasted with the results of other Diels–Alder additions of anthracene and maleic anhydride derivatives. For example, the second-order rate coefficient for the 9,10-dimethylanthracene–maleic anhydride addition³ decreased as the initial concentration of maleic anhydride was increased, the rate depression amounting to about 30% at 1.4 *M* maleic anhydride. This behavior was quantitatively explained³ in terms of an equilibrium between the addends and a molecular complex which competed with or preceded adduct formation. In our 9-phenylanthracene–maleic anhydride addition, although a molecular complex seemed to be formed (solutions containing both components were yellow), the second-order rate coefficient for the addition at 152.4° remained constant within experimental error up to 0.892 *M* maleic anhydride concentration $c_0/b_0 = 660$. Equation 2³ expresses the relationship between the experimentally determined rate coefficient (k_{obs}), the true second-order rate constant for adduct formation (k_a), the complex equilibrium constant [$K_x = (\text{complex})/(9\text{-phenylanthracene})(\text{maleic anhydride})$], and the concentration of maleic anhydride (c). From this equation and our estimated error of 5% in k_{obs} (*i.e.*,

$$(k_a/k_{obs}) - 1 = K_x c \quad (2)$$

$k_a/k_{obs} \leq 1.05$), a maximum value, $K_x = 0.056$ l.

(3) I. J. Andrews and R. M. Keefer, *ibid.*, **77**, 6284 (1955).

TABLE I
EQUILIBRIUM CONSTANTS AND SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION OF 9-PHENYLANTHRACENE WITH MALEIC ANHYDRIDE IN SOLVENT *o*-DICHLOROBENZENE

<i>T</i> , °C.	10 ³ <i>b</i> ₀ , moles/l.	10 ³ <i>c</i> ₀ , moles/l.	<i>k</i> ₂ , l. mole ⁻¹ min. ⁻¹	10 ² <i>K</i> , mole/l.
152.4	14.6	7.88	0.195	1.16
152.4	9.81	3.96	.235	..
152.4	10.1	12.40	.219	1.14
152.4	9.58	15.90	.211	1.15
152.4	20.5	19.80	.212	..
152.4	0.906	72.60	.205 ^a	..
152.4	1.01	76.60	.196	..
152.4	1.03	119.0	.190	..
152.4	1.35	892	.212	..
		Mean	0.208 ± 0.01	1.15 ± 0.01
132.1	0.906	105	0.0735	..
132.1	1.00	96.9	.0731 ^b	..
132.1	11.35	10.1	...	0.337
174.5	0.0856	11.1	.543	..
174.5	9.28	9.04	.566	3.41
174.5	2.04	1.80	...	3.18

^a In the presence of 0.833 *M* diethyl maleate; $-db/dt \cong 8.6 \times 10^{-4}$ l. mole⁻¹ min.⁻¹ (b) (diethyl maleate) at 152.4°.

^b In the presence of 4.75×10^{-5} *M* ferric dipivaloylmethide.

^c $K = b_e c_e / a_e$.

mole⁻¹, can be calculated. From data³ at two lower temperatures, K_x for the anthracene-maleic anhydride complex at 152.4° can be calculated to be 0.13, only about twice the K_x for the other system. At 152.4° and $c = 0.892$ *M*, k_a/k_{obs} for the anthracene-maleic anhydride addition would be 1.12, or just discernibly different from unity by our kinetic techniques. There is thus no reason to suspect that there is a drastic difference in complexing behavior between anthracene and 9-phenylanthracene, for even if the values of K_x were of the same order of magnitude at room temperature, a standard enthalpy change for complex formation in the 9-phenylanthracene system about the same as that (*ca.* -1800 cal./mole) in the anthracene system⁸ would ensure the virtual disappearance of any kinetic disturbance at 152.4°. It seems reasonable to assume, therefore, that the insensitivity of the rate coefficients to dienophile concentration in the 9-phenylanthracene case is largely attributable to the fortuitous circumstance that our experiments required high temperatures, the formation of adduct being immeasurably slow at room temperature.

From kinetic runs at three temperatures, the Arrhenius quantities of activation for the Diels-Alder combination of 9-phenylanthracene and maleic anhydride in solvent *o*-dichlorobenzene were $\log A = 6.2$ (A in sec.⁻¹ mole⁻¹ l.), and $E_a = 16.8$ kcal./mole. These values are to be compared with those ($\log A = 4.7 - 5.4$ and $E_a = 8.0 - 15.2$ kcal./mole)³ for other combinations of anthracene and maleic anhydride derivatives in solvent chloroform. In other cases of Diels-Alder additions, some change in rate and significant changes in activation parameters resulted from changes in solvent.^{3,4} The comparison of our results with those previously reported³ for similar additions in another

(4) (a) A. Wasserman, *Trans. Faraday Soc.*, **34**, 138 (1938); (b) M. Gillois and P. Rumpf, *Bull. soc. chim. France*, 1923 (1959).

solvent is therefore of doubtful significance. In this connection, we have tested for the possibility of a medium effect, which might cause concern at high maleic anhydride concentration, by examining the behavior of the rate coefficient for the 9-phenylanthracene-maleic anhydride addition in the presence of 0.833 *M* diethyl maleate. The rate was unaffected (Table I).

We have also found that the rate of the addition was unaffected by ferric dipivaloylmethide, a paramagnetic iron complex (Table I). Observations in the laboratory of Professor George S. Hammond⁵ have indicated that it is possible to accelerate singlet-triplet transitions with this reagent. The absence of any such acceleration in the addition and the finding that the retrogression of the adduct III has a normal pre-exponential factor (see below) are consistent with the view that the achievement of the Diels-Alder transition state does not involve a change in electronic multiplicity. The same conclusion has been reached^{4a} from examination of the pre-exponential factors for retrogression of several other Diels-Alder adducts. Thus, if "diradical" species⁶ are involved, they presumably are of the singlet rather than the triplet class.

Diels-Alder Retrogression in the 9-Phenylanthracene-Maleic Anhydride System.—If an internal mechanism exists by means of which interconversion of the enantiomeric forms of the 9-phenylanthracene-maleic anhydride adduct (IIIa, IIIb) can occur, the rate coefficient for the racemization should exceed that for dissociation into kinetically free addends. On the other hand, if the racemization and dissociation processes have the same rate-limiting step, the rate coefficients should be identical. We have now measured the rate of racemization of optically active III by polarimetry and the rate of dissociation by spectrophotometry and by radiochemical exchange, all in solvent *o*-dichlorobenzene.

Optically active adduct III was prepared by hydrolysis to the dibasic acid, resolution *via* the strychnine salt, and reversion to the anhydride. The racemization followed a first-order rate law, and the temperature-dependence (Table II) of the rate coefficient gave the equation

$$k_1 = 10^{14.5} \text{ sec.}^{-1} \exp \left(\frac{36.9 \text{ kcal./mole}}{2.3 RT} \right)$$

The kinetics of the dissociation of the adduct III to the equilibrium mixture were determined by following the optical density at 368 m μ . The reactions were again first order, rate coefficients being calculated from eq. 3. The first-order rate

$$k_1 = \frac{2.3 \log [(a_0^2 - a_e a)/(a - a_e) a_0]}{t [(a_0 + a_e)/(a_0 - a_e)]} \quad (3)$$

coefficients for dissociation at all three temperatures were identical with those for racemization (Table II).

(5) We are indebted to Professor Hammond for informing us of these results before publication, for a gift of ferric dipivaloylmethide, and for the suggestion of its use in this experiment.

(6) (a) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725 (1939); (b) *cf.* also C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 186; C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5811 (1958).

TABLE II
EQUILIBRIUM CONSTANTS AND FIRST-ORDER RATE COEFFICIENTS FOR THE DISSOCIATION, EXCHANGE AND RACEMIZATION OF THE 9-PHENYLANTHRACENE-MALEIC ANHYDRIDE ADDUCT (III) IN SOLVENT *o*-DICHLOROBENZENE

<i>T</i> , °C.	$10^3 a_0$, moles/l.	Method	$10^3 k_1$, min. ⁻¹	$10^3 K$, moles/l.
152.4	12.2	Polarimetric	2.46	..
152.4	~20	Polarimetric	2.30	..
152.4	8.56	Spectrophotometric	2.26	..
152.4	19.6	Spectrophotometric	2.36	1.07
152.4	^a	Isotopic exchange	2.37	..
152.4	^b	Isotopic exchange	2.37	..
132.1	0.865	Spectrophotometric	0.251	..
132.1	11.0	Spectrophotometric	..	0.338
132.1	11.6	Polarimetric	0.245	..
174.5	0.882	Spectrophotometric	18.6	..
174.5	18.2	Spectrophotometric	..	3.29
174.5	13.0	Polarimetric	18.5	..

^a Equilibrium mixture: $a = 30.0 \times 10^{-3}$ mole/l., $b = c = 18.6 \times 10^{-3}$ mole/l. ^b Equilibrium mixture: $a = 40.9 \times 10^{-3}$ mole/l., $b = c = 21.7 \times 10^{-3}$ mole/l.

In the spectrophotometric experiments, "dissociation" was taken to mean the appearance of the characteristic ultraviolet absorption of the diene. Another phenomenological criterion of "dissociation" of the adduct is isotopic exchange of one of the addends, derived from labeled adduct, with its unlabeled counterpart in solution. We have studied this situation with the aid of ¹⁴C carbonyl-

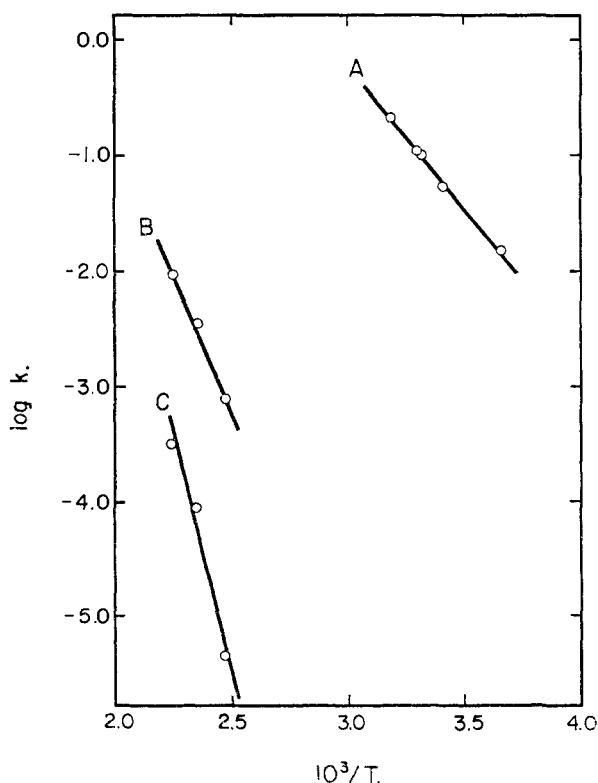


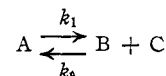
Fig. 1.—Arrhenius plot: A, cyclopentadiene-maleic anhydride addition in decalin; B, 9-phenylanthracene-maleic anhydride addition in *o*-dichlorobenzene; C, dissociation of the 9-phenylanthracene-maleic anhydride adduct in *o*-dichlorobenzene; units of k for A and B, sec.⁻¹ l.⁻¹ mole; for C, sec.⁻¹.

labeled adduct, prepared from 9-phenylanthracene and maleic anhydride-¹⁴C. At chemical equilibrium, the kinetics of all isotopic exchange reactions have a simple form: the rate of loss of activity is given by the well-known law of eq. 4,⁷ in which F is the fraction of activity exchanged, a_e and c_e are the total concentrations of each of the exchanging species at equilibrium (in our experiment, III and maleic anhydride) and R is the gross rate of exchange, that is, the velocity of reaction in either direction.

$$-\ln(1 - F) = \frac{Rt(a_e + c_e)}{a_e c_e} \quad (4)$$

Since the system is at chemical equilibrium, the concentration terms on the right of eq. 4 are constant; the exchange is thus a first-order process in the activity, regardless of the mechanism.

For dissociation of the adduct A to 9-phenylanthracene (B) and maleic anhydride (C) at chemical equilibrium, the velocity R may be expressed as



$$R = k_1 a_e = k_2 b_e c_e$$

In terms of concentrations of labeled and unlabeled species

$$-\ln(1 - F) = \ln \frac{(a_e^* - a_{\infty}^*)}{(a_e^* - a_{\infty}^*)}; \quad \frac{c_{\infty}^*}{a_{\infty}^*} = \frac{c_e}{a_e} \quad (5)$$

$$k_1 = \frac{2.3c_e}{t(a_e + c_e)} \log \frac{a_0^* - a_{\infty}^*}{a_e^* - a_{\infty}^*} \quad (6)$$

where the asterisked quantities represent concentrations of radioactive substances. Expressed in experimental quantities, that is, in ¹⁴C activities (γ) of the adduct, eq. 6 becomes

$$k_1 = \frac{2.3c_e}{t(a_e + c_e)} \log \frac{\gamma_0}{\gamma_0 - (\gamma_0 - \gamma)(1 + a_e/c_e)} \quad (7)$$

The exchange was followed by observing the ¹⁴C activities of samples of adduct recovered after various times from an equilibrium mixture of A, B and C in *o*-dichlorobenzene. The rate constant, k_1 , calculated from eq. 7 for data at 152.4°, was identical with those observed at the same temperature by the polarimetric and spectrophotometric techniques (Table II). The radioactivity balance observed in a reaction allowed to proceed to "infinite" time was satisfactory, the final specific activity corresponding to that expected from the equilibrium ratio of concentrations ($c_{\infty}^*/a_{\infty}^* = c_e/a_e$).

Diels-Alder Addition in the Cyclopentadiene-Maleic Anhydride System.—One of the conceivable detailed descriptions² of the internal isomerization of the cyclopentadiene-maleic anhydride adduct in solvent decalin involved recombination of a diene-dienophile pair within a solvent cage. For such a process to contribute substantially, the rate of the Diels-Alder addition would have to be fast enough to be competitive with that of diffusion of the partners away from each other. We have now found that the rate, although indeed quite fast, is still too slow by several orders of magnitude to give

(7) Cf. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 178-179, and references cited therein.

rise to appreciable cage recombination (see Discussion). The rate was measured over the temperature range 0.3–40° by two techniques: (1) by direct spectrophotometric assay of cyclopentadiene at 242 m μ , and (2) by a trapping technique which took advantage of the exceptionally high dienophilic reactivity⁸ of tetracyanoethylene and of the ability of the latter to form a red dye⁹ with dimethylaniline. The results of two methods agreed well (Table III) and showed the reaction to be first order in each component. A plot (Fig. 1) of $\log k_2$ vs. $1/T$ was linear and gave activation parameters $\log A = 7.85 \pm 0.4$ (A in sec.⁻¹ mole⁻¹ l.) and $E_a = 12.3 \pm 0.6$ kcal./mole. A kinetic test for complex formation was not feasible in this system because the relatively low solubility of maleic anhydride in decalin limited the range of concentrations that could be studied.

TABLE III
SECOND-ORDER RATE COEFFICIENTS FOR THE REACTION OF
CYCLOPENTADIENE WITH MALEIC ANHYDRIDE IN SOLVENT
DECALIN

T, °C.	10 ³ a ₀ , moles/l.	Method	k ₂ , l. mole ⁻¹ sec. ⁻¹
40.0	1.47	Direct	0.210
40.0	1.21	Direct	.208
30.0	1.86	Direct	.102
30.0	1.24	Direct	.108
28.7	..	Direct	(.094) ^a
28.7	2.09 ^b	Trapping	.0981
20.0	1.52	Direct	.0538
20.0	1.65	Direct	.0538
0.3	1.77	Direct	.0118

^a Extrapolated from the equation $\log k_2 = 7.85 - (12,300 \text{ cal./mole})/2.3RT$. ^b [Cyclopentadiene]₀ = 0.00212 mole/l.

Data for the cyclopentadiene–benzoquinone addition in solvent decalin are not available, and consequently a direct comparison of the dienophilic reactivities of maleic anhydride and benzoquinone, another reactive dienophile,^{4a} cannot yet be made. Nevertheless, a rough estimate is possible, since although the activation parameters for the benzoquinone addition are very sensitive to solvent, the second-order rate coefficients are not. If it is assumed that the rate in decalin is about the same as that measured^{4a} in benzene, the second-order rate coefficient for the cyclopentadiene–benzoquinone addition is about 1.7×10^{-3} l. mole⁻¹ sec.⁻¹ at 40°, or about one-hundredth that for the maleic anhydride addition. Cyclopentadiene is a far more reactive diene toward maleic anhydride than is 9-phenylanthracene. If the difference in solvents is again disregarded, the ratio of the second-order rate coefficients extrapolated from the data of Tables I and III is about 5.4×10^3 at 188.5°.

Discussion

There is no evidence for "molecule-pair" intermediates in the 9-phenylanthracene–maleic anhydride system. The rate coefficients are insensitive to the method by which "dissociation" is measured and are identical with that for racemization. (The steady first-order behavior of the race-

mization rate coefficient also argues against the incursion of a bimolecular four-center displacement mechanism with one maleic anhydride molecule replacing another bound to 9-phenylanthracene with inversion of configuration. This process would have manifested itself in autocatalytic behavior and a drifting rate coefficient as maleic anhydride accumulated during a run.) The simplest explanation of these findings is that every molecular act of racemization requires decomposition of the adduct into kinetically identifiable fragments that cannot be distinguished from the component addends.

In contrast, stereochemical interconversion of the isomeric cyclopentadiene–maleic anhydride adducts (IV and V) (in solvent decalin at 188.5°) occurs by two paths, only one of which passes through dissociated addends.² It now seems entirely unlikely that the internal isomerization can be ascribed to recombination of the fragments from a decomposed adduct molecule within a solvent cage, since the rate of the association is not fast enough to compete with diffusion of the partners away from each other. Thus, the activation energy, 12.3 kcal./mole, is much greater than that of binary diffusion activation energies in ordinary liquids, which typically fall in the range 3–5 kcal./mole.^{10a} Further, the actual second-order rate coefficient at 188.5° (extrapolated from the data of Table III) is about 125 l. mole⁻¹ sec.⁻¹, whereas diffusion-controlled processes in solution are expected to be faster than this by six to nine powers of ten^{10b} at the same temperature. If the internal mechanism involves fragmentation at all, the fragmented state must have special properties and would be better denoted as a "complex" rather than a "caged aggregate." This matter is further discussed below.

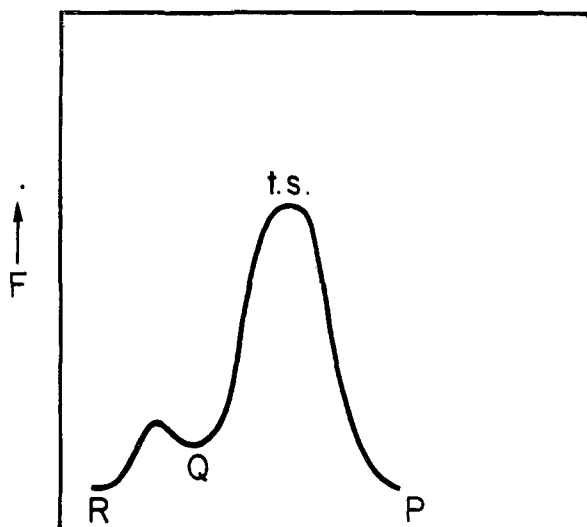
The remaining interpretations of the internal isomerization of the adducts IV and V may be divided into two categories: (i) mechanisms in which the bonds broken and re-formed are not identical with the characteristic diene–dienophile bonds (a and b) formed in the Diels–Alder addition itself; and (ii) mechanisms in which the Diels–Alder bonds are the ones broken and re-formed, but the fragments are held together by some sort of complexing force.

In category i are two mechanisms previously discussed²; one of these involves enolization, and the other involves cleavage of one of the Diels–Alder bonds followed by a hydrogen shift from C.7 to C.5 and re-cyclization. Also in category i is a process (suggested to us in two variants by Professors D. J. Cram and S. W. Benson) that involves cleavage of the bond c lying between the two carbonyl-bearing carbons. This mechanism might be imagined to give a common intermediate from either IV or V in which the stereochemistry at C.2 and C.3 was destroyed. The intermediate might be described in detail as resulting merely from homolysis of bond c (not necessarily with a change of multiplicity) or from actual formation of a double

(8) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(9) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).

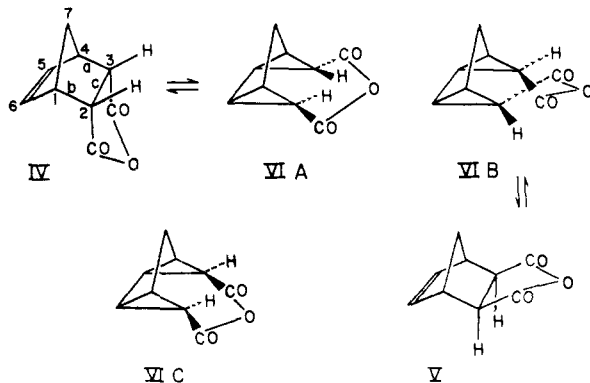
(10) (a) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 522–525; (b) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 493–502.



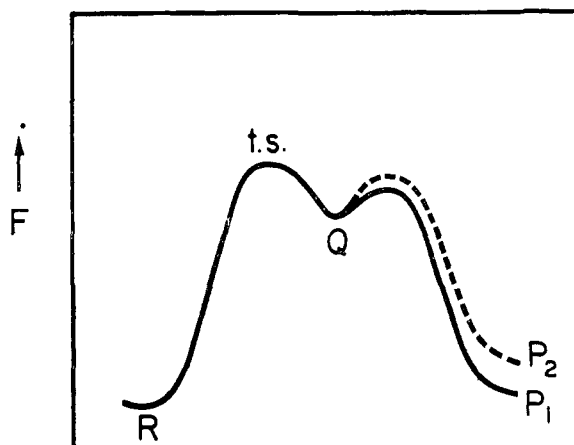
Reaction coordinate.

Fig. 2.—Energy diagram for a Diels-Alder reaction passing over a complex (Q) that is in rapid equilibrium with addends (R) and well below the rate-limiting transition state (t.s.); P represents adduct.

cyclopropane structure VI. Formation of VI in a *concerted* process does not automatically ensure the loss of stereochemical memory; cyclization with retention of configuration at both C.2 and C.3 would lead to *different* products (VIA and VIB) from IV and V. Only if cyclization occurs with retention at one asymmetric center and inversion at the other do IV and V give a common product (VIC).



A restriction is imposed on all mechanisms involving cleavage of bonds other than a and b: About half of the molecules of IV that are converted to V employ a dissociative mechanism, that is, a complete Diels-Alder retrogression.² Therefore, there would have to be a fortuitous correspondence between the rate of bond cleavages (a and b) leading to dissociation and the rate of bond cleavage (e.g., c) leading to non-dissociative isomerization. Such a coincidence is, of course, not impossible. If this explanation is the correct one, the non-dissociative isomerization occurs on a separate part of the potential energy surface from the Diels-Alder reaction proper, and conclusions regarding



Reaction coordinate.

Fig. 3.—Energy diagram for a Diels-Alder reaction passing over a complex (Q) that is close to the rate-limiting transition state (t.s.). Non-dissociative conversion of one adduct (P₁) to the other (P₂) through Q is competitive with dissociation to addends (R). The dotted curve represents part of the energy surface in a dimension other than the plane of the paper.

the mechanism of either of the processes cannot be drawn from a study of the other.

If the non-dissociative isomerization is assigned to category ii, the diene-dienophile complex (Q, Fig. 3) must be placed on the energy surface near the rate-limiting transition state. (We think it is reasonable to assume that a diene-dienophile complex in which bonds a and b are *both* sufficiently weak to allow stereochemical interconversion would be formed from the adduct by the same path used for dissociation.) This provides a useful conceptual distinction between the complex and the caged aggregate. Since by definition the energy of the caged aggregate in excess of that of the ground state cannot be greater than the small activation energy of diffusion, the caged aggregate must still acquire a major portion of the macroscopic activation energy (12.3 kcal.) in order to reach the rate-limiting transition state. Depending on whether the free energy for converting Q in Fig. 3 to P₁ is greater than or less than that for converting it back to R, the free energy of activation for the formation of Q from addends (R) is slightly less than or identical with the over-all free energy of activation for the rate-limiting process in the Diels-Alder addition.

Accepting for the moment the hypothesis that a complex provides a mechanism for internal isomerization in the cyclopentadiene case, we may inquire whether this complex should be considered to be structurally similar to those observed⁸ with anthracenes and presumably also formed with 9-phenylanthracene. If the complexes *are* similar, the non-dissociative isomerization in the cyclopentadiene case might be merely a consequence of the relatively compressed scale of energies produced by the low over-all free energy of activation; this would bring the complex and the rate-limiting transition state closer together than in the 9-phenylanthracene case and might permit the rates of dis-

sociation and isomerization to become competitive (Fig. 2 vs. Fig. 3). On the other hand, we cannot eliminate the possibilities that the two complexes are qualitatively different or that one or both of the energy surfaces contain more than one minimum.¹¹ Aside from the variations in the precise topography of the energy surfaces that may accompany a change from one diene-dienophile pair to another, we note that even within one system, the part played by complexing phenomena seems to depend on factors that are still imperfectly understood. For example, although the 9,10-dimethylanthracene-maleic anhydride addition shows definite evidence of complex formation in solvent chloroform,³ as evidenced by second-order rate coefficients that decrease with increasing initial dienophile concentration, no such behavior is observed in solvent acetone, where in fact, the second-order rate constants seem to increase slightly with increasing dienophile concentration.³

The present work shows that the internal isomerization observed² in the cyclopentadiene-maleic anhydride system is not attributable to what is ordinarily termed "cage re-combination." Whatever the mechanism of the internal isomerization, the process is not an invariable feature of Diels-Alder reactions, since it does not occur in the 9-phenylanthracene-maleic anhydride system.

Experimental

The 9-Phenylanthracene-Maleic Anhydride System. Materials.—A commercial *o*-dichlorobenzene (Eastman Kodak Co. white label) was fractionated at reduced pressure through a 1-ft. vacuum-jacketed Vigreux column and had b.p. 76° (28 mm.). Vapor chromatographic analysis showed that it contained about 0.5% of a contaminant having the same retention time as *p*-dichlorobenzene.

9-Phenylanthracene, prepared by the reaction of phenylmagnesium bromide with anthrone, was purified by crystallization from chloroform, chromatography on alumina, and recrystallization from petroleum hexane. It was obtained as faintly yellow plates, m.p. 153.5–157.5°, reported¹² m.p. 154–155°.

Maleic anhydride, m.p. 51.8–52.3°, was purified from a commercial sample by crystallization from chloroform and sublimation at reduced pressure.

The 9-phenylanthracene-maleic anhydride adduct (III) was prepared by dissolving 2.4 g. of 9-phenylanthracene and 2 g. of maleic anhydride in 10 ml. of *o*-dichlorobenzene, heating the orange solution for 1 hour and cooling. The crystals were collected, washed with benzene, and recrystallized twice from glacial acetic acid. The substance was obtained as white rhombs, m.p. 249–251° dec., reported¹⁸ m.p. 252°. In a similar manner, III-*carbonyl*-¹⁴C, m.p. 249–251°, was prepared from maleic anhydride-¹⁴C, obtained from Nuclear-Chicago on authorization of the Atomic Energy Commission.

Resolution of III.¹⁴—A suspension of 4.3 g. of the adduct in 230 ml. of 0.23 *M* aqueous potassium hydroxide was heated on the steam-bath, and 95% ethanol was added in small portions until a clear solution was obtained. After cooling and acidification, the precipitate was filtered off and dissolved in acetone. After having been dried over magnesium sulfate, the solution was filtered and treated with a solution of 4.0 g. of strychnine in the minimum quantity of chloro-

form. Crystals soon appeared, whereupon the mixture was allowed to stand for 3 days and then was filtered to give 4.5 g. of salt. This was dissolved in hot ethanol, acidified with concentrated hydrochloric acid, and treated with water to precipitate the acid. Crystallization from acetic anhydride gave III, softening at 234°, m.p. 244–247°, $[\alpha]_D^{20} - 50^\circ$ (*c* 0.0845, *l* 4, in *o*-dichlorobenzene). Repetition of the procedure using half the molar ratio of strychnine gave material of $[\alpha]_D^{20} - 80^\circ$. From the mother liquors, there was obtained material of m.p. 230–240°, $[\alpha]_D^{20} + 85^\circ$. No attempt was made to carry the resolution to completion.

Kinetic Methods. A.—Solutions were made up at room temperature and thermostated at reaction temperature in sealed ampoules. The rates of the forward and reverse reactions were indiscernibly slow at room temperature. The thermostatic temperature was controlled to better than $\pm 0.05^\circ$ and measured with National Bureau of Standards certified thermometers. Concentrations were corrected for the expansion of the solvent when necessary.

Spectrophotometric rates were determined by assay of 9-phenylanthracene. The ampoule containing reactants for each kinetic point was removed from the thermostat, plunged into ice-water, opened, and diluted to a convenient concentration with purified *o*-dichlorobenzene. The concentration of 9-phenylanthracene was calculated from the dilution factor, the observed optical density at 368 $m\mu$, and the extinction coefficient of pure 9-phenylanthracene in *o*-dichlorobenzene at 368 $m\mu$ (ϵ 10,000). The extinction coefficient of 9-phenylanthracene was unaffected by added maleic anhydride. Spectrophotometric measurements were made with a Cary model 14 recording spectrophotometer. Second-order rate coefficients for the addition reaction were computed from eq. 1, and first-order rate coefficients for the decomposition were computed from eq. 3. Illustrative kinetic runs are given in Tables IV and V.

TABLE IV

SAMPLE KINETIC RUN, 152.4°; DECOMPOSITION OF III
 $a_0 = 8.56 \times 10^{-3}$ mole/l., $b_0 = c_0 = 0$

Time, min.	Dilution	D_{368}	10^{3a} , moles/l.	10^3k_1 , min. ⁻¹
0	None	0.640	0.640	..
60	1/12.5	.885	11.1	2.33
120	1/25	.804	20.1	2.28
180	1/50	.559	27.9	2.31
240	1/50	.671	33.5	2.23
300	1/50	.772	38.6	2.25
360	1/50	.852	42.6	2.26
420	1/50	.910	45.5	2.25
1400	1/50	1.10	55.0	..

Mean 2.27 ± 0.03

TABLE V

SAMPLE KINETIC RUN, 152.4°; REACTION OF 9-PHENYLANTHRACENE WITH MALEIC ANHYDRIDE
 $a_0 = 1.98 \times 10^{-2}$ mole/l., $b_0 = 1.01 \times 10^{-2}$ mole/l.

Time, min.	Dilution	D_{368}	10^{3a} , moles/l.	k_2 , l. mole ⁻¹ min. ⁻¹
0	1/100	1.010
71	1/100	0.847	1.61	0.236
120	1/100	.780	2.28	.230
178	1/100	.731	2.77	.215
240	1/100	.690	3.18	.212
300	1/100	.661	3.47	.212
360	1/100	.639	3.69	.214
423	1/100	.620	3.88	.224
475	1/100	.618	3.90	.206
1452	1/100	.587	4.21	..
1810	1/100	.587	4.21	..

Mean 0.219 ± 0.008

Polarimetric rate coefficients were determined on kinetic solutions made up and thermostated as above by measuring the optical activity of the quenched solutions with a Rudolph polarimeter using a 4-cm. jacketed tube cooled with cir-

(11) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957), have discussed the possibility that more than a single type of complex may be formed from a given donor-acceptor pair.

(12) C. K. Bradsher, *ibid.*, **62**, 486 (1940).

(13) E. de B. Barnett, N. F. Goodway, A. G. Higgins and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934); cf. also C. Dufraisse, L. Velluz and C. Velluz, *Bull. soc. chim. France*, [5] **5**, 1073 (1938), and W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 481 (1938).

(14) We are indebted to Dr. W. M. Jones for collaboration on this experiment.

culating water from a thermostat. An illustrative kinetic run is given in Table VI. Initial concentrations of III were about $10^{-2} M$ in solvent *o*-dichlorobenzene. First-order rate coefficients were computed from the equation $k_1 = (2.3/t) \log (\alpha_0/\alpha)$.

TABLE VI

SAMPLE KINETIC RUN, 152.4°; RACEMIZATION OF III

Time, min.	α^{2D}	$10^3 k_1$, min. ⁻¹
0	-1.45°	..
60	-1.26	2.34
120	-1.11	2.22
194	-0.92	2.34
240	-.81	2.42
300	-.72	2.33
363	-.63	2.30
420	-.57	2.22
493	-.48	2.24

Mean 2.30 ± 0.006

Radioactive exchange measurements were carried out as follows: Solutions of mixtures of III-*carbonyl*-¹⁴C, 9-phenylanthracene and maleic anhydride in *o*-dichlorobenzene, gravimetrically adjusted to conform to equilibrium concentrations of the three species, were thermostated in sealed ampoules. Ampoules were removed at suitable time intervals, quenched in ice-water, opened, and delivered into 10-ml. portions of purified petroleum hexane, which precipitated III. The precipitate was washed with hexane, then with boiling water, dried, recrystallized from glacial acetic acid, and dried *in vacuo*. That this process produced pure III was shown by a control experiment in which non-radioactive III and radioactive maleic anhydride (31,000 c./min./mg.) were dissolved in *o*-dichlorobenzene; III was recovered from the mixture by the above procedure with an activity indistinguishable from background. Weighed samples (~10 mg.) were made up to 10.00-ml. solutions with reagent-grade toluene. A sample (5.00 ml.) of each solution was mixed with 5.00 ml. of scintillator solution [1,4-bis-2-(5-phenylxazolyl)-benzene, 0.811 g./l., and *p*-terphenyl, 5.757 g./l., in toluene] and the resulting solution counted in a liquid scintillation counter.¹⁵ Each sample was counted at least twice, and at least 40,000 counts were taken each time. The count rates for a given sample were reproducible to better than $\pm 1\%$. Sample count rates were 10,000-22,000 c./min. and backgrounds, determined before and after a set of counts and averaged, were 120 ± 5 c./min. The counting efficiency was about 80%. That true equilibrium mixtures were being examined was checked by determination of the optical density at 368 m μ of the final kinetic points. These did not vary from the optical density of the starting solution. First-order rate coefficients were computed from eq. 7. An accurate determination of the rate coefficient was critically dependent on the accuracy with which the original equilibrium mixture was prepared. In one run in which an inadvertently slightly inaccurate mixture (corresponding to an equilibrium constant 0.965×10^{-2} mole/l. instead of the correct value 1.15×10^{-2} mole/l.) was used, the observed k_1 was 1.67×10^{-3} min.⁻¹, about 30% below the correct value. The rate coefficient was quite steady during this run, and thus the kinetic data themselves provided no internal evidence of a disturbance. An illustrative kinetic run for an accurately adjusted equilibrium mixture is given in Table VII. Note that the "infinity" value of $\gamma = 11,585 \pm 60$ c./min./5 mg. corresponds closely to that expected, $\gamma = 11,460$ c./min./5 mg., from the equation $\gamma_\infty = \gamma_0 c_0/\alpha_0$.

The Cyclopentadiene-Maleic Anhydride System. Method I. Materials.—Decalin was purified from a commercial material (Eastman Kodak Co. practical grade *cis*-decalin) by washing with sulfuric acid and water, drying, fractionation through a 5-ft. Fenske column, and chromatography over silica gel. Vapor chromatography showed only two peaks which corresponded to *cis*- and *trans*-decalin.

Commercial dicyclopentadiene (Matheson, Coleman and Bell, technical grade) was cracked to the monomer by slow distillation through a 1-ft. vacuum jacketed Vigreux column.

(15) We are indebted to Dr. A. W. Adamson and Mr. A. Van Geet for advice on the use of this equipment.

TABLE VII

SAMPLE KINETIC RUN, 152.4°; RADIOACTIVE EXCHANGE OF III-¹⁴C AT EQUILIBRIUM $a_0 = 3.00 \times 10^{-2}$ mole/l., $b_0 = c_0 = 1.86 \times 10^{-2}$ mole/l.

Time, min.	Spec. act., γ , c./min./5 mg.	$10^3 k_1$, min. ⁻¹
Blank	18,463	..
0	18,529	..
60	16,216	2.55
120	14,816	2.41
180	13,807	2.38
240	12,991	2.50
300	12,688	2.29
360	12,300	2.34
420	12,142	2.21
480	11,939	2.26
1475	11,527	..
3045	11,642	..

Mean 2.37 ± 0.009

The fraction boiling at 40-40.5° was collected over Drierite and allowed to re-dimerize. This material was then cracked and fractionated as needed to give monomer of b.p. 40.0°.

Kinetic Methods.—The reaction was followed by measuring the change in light absorption by cyclopentadiene at 242 m μ with a Beckman DU spectrophotometer equipped with photomultiplier attachment. The temperature was controlled to $\pm 0.1^\circ$ by circulating water from a thermostat through a jacketed compartment (kindly supplied by Professor W. K. Wilmarth) housing the quartz absorption cells.

Compensation for the end absorption of maleic anhydride in the analytical region was achieved by using as reference a solution of maleic anhydride in decalin of a concentration equal to the initial concentration of the maleic anhydride in the reaction mixture. The spectrum of cyclopentadiene in decalin *vs.* decalin was the same as that (initially) of a solution of cyclopentadiene and maleic anhydride in decalin *vs.* maleic anhydride in decalin. The rate of dimerization of cyclopentadiene at the kinetic concentrations and temperatures was slow enough so that no correction was required, the spectrum of a decalin solution of the diene remaining unchanged in 24 hours at the temperature of our measurements. The longest reaction period for the diene-maleic anhydride addition was 5 hours. Apparent first-order rate coefficients, computed from the equation $k_1 = (2.3/t) \log (D_0/D)$, were plotted *vs.* time and extrapolated to zero time. The initial rate coefficients thus obtained were divided by the initial concentration of maleic anhydride to give second-order rate coefficients, k_2 . Within the limited range of concentrations imposed by solubility restrictions, the second-order coefficients were independent of the initial maleic anhydride concentration. An illustrative kinetic run is shown in Table VIII.

TABLE VIII

SAMPLE KINETIC RUN, 30.0°; REACTION OF CYCLOPENTADIENE AND MALEIC ANHYDRIDE IN DECALIN, $c_0 = 1.24 \times 10^{-3}$ mole/l.

Time, min.	D_{212}	$10^3 k_1$, min. ⁻¹	Time, min.	D_{212}	$10^3 k_1$, min. ⁻¹
0	1.22	(8.05) ^a	42	0.850	8.60
3	1.19	8.28	48	.782	9.27
6	1.16	8.40	54	.740	9.25
9	1.14	7.54	60	.694	9.40
12	1.11	8.22	66	.655	9.43
15	1.08	8.46	72	.611	9.58
18	1.05	8.34	78	.570	9.71
21	1.02	8.53	84	.534	9.83
24	0.992	8.61	90	.494	10.0
27	.968	8.53	102	.414	10.6
30	.941	8.66	120	.335	...
36	.880	9.08			

^a Extrapolated; $k_2 = 6.48$ min.⁻¹ l. mole⁻¹.

Method II. Materials.—Tetracyanoethylene, prepared according to literature procedures,¹⁶ was sublimed at 10^{-4} mm. and had m.p. 200–201°, reported¹⁶ m.p. 198–200°. Ethylene dichloride was chromatographed over silica gel. Acetonitrile was boiled with phosphorus pentoxide for 2 days and fractionated through a vacuum-jacketed Vigreux column to give material of b.p. 82°. N,N-Dimethylaniline was boiled for several hours with acetic anhydride, fractionated at reduced pressure, and stored in a nitrogen atmosphere.

Kinetic Methods.—The reaction was followed by quenching the unreacted cyclopentadiene in a cyclopentadiene-maleic anhydride-decalin mixture with excess tetracyanoethylene and measuring the remaining tetracyanoethylene by converting it to 4-tricyanovinyl-N,N-dimethylaniline,⁹ a red dye, which was determined spectrophotometrically at its absorption maximum 520 m μ . The red dye was formed only in polar solvents; in non-polar solvents, the reaction of tetracyanoethylene with N,N-dimethylaniline produced a blue color which faded when the solution was warmed and re-appeared upon cooling. The method was extremely sensitive to traces of impurities. Further, although the optical density of the red dye was reproducible ($\pm 1\%$) when the dye was prepared from a given batch of dimethylaniline, it varied within wide limits with different batches of amine.

Aliquots (2 ml.) of the reactant solution of cyclopentadiene and maleic anhydride in decalin were removed from the thermostat and delivered immediately into a standard solution (5 ml.) of tetracyanoethylene $1.82 \times 10^{-3} M$ in ethylene dichloride. Tetracyanoethylene reacts very quickly with the diene and a twofold excess of the cyano compound is ample for rapid quenching. The quenched solution was made up to 10.00 ml. with ethylene dichloride, 1.00 ml. of this solution was dissolved in acetonitrile, 1 drop of N,N-dimethylaniline was added, and the resulting solution was made up to 10.00 ml. with acetonitrile. The solution was allowed to stand overnight at room temperature, after which time the excess tetracyanoethylene had been converted to 4-tricyanovinyl-N,N-dimethylaniline. The extinction coefficient at 520 m μ of the dye was determined empirically from the initial gravimetric composition of the

(16) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

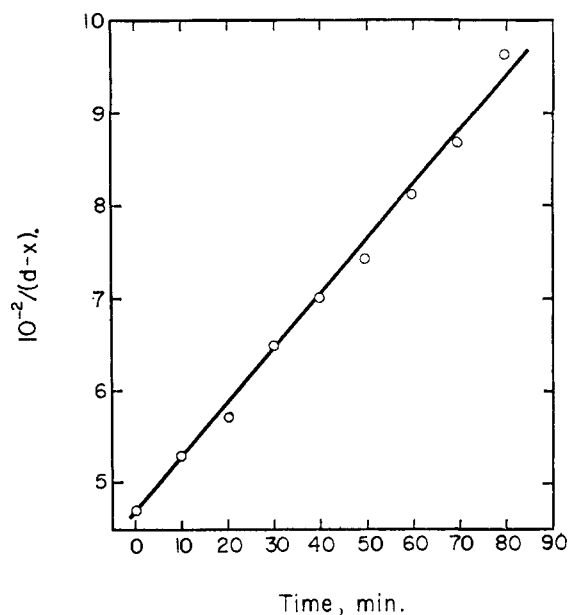


Fig. 4.—Kinetics of the cyclopentadiene-maleic anhydride addition in decalin at 28.7°; method II.

reactant mixture and the optical density and used throughout a run for the computation of the amount of tetracyanoethylene remaining. Figure 4 is a graph of the data obtained from a kinetic run at 28.7° in which the initial concentrations of diene and maleic anhydride were nearly equal ($2.12 \times 10^{-3} M$ and $2.09 \times 10^{-3} M$). In these circumstances, a plot of $1/(d-x)$ vs. time, where d is the average initial concentration of the reactants and x is the amount reacted, should be linear for a second-order process, with slope equal to the second-order rate coefficient, k_2 .¹⁷ From Fig. 4, $k_2 = 5.88 \text{ min.}^{-1} \text{ l. mole.}^{-1}$

(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., p. 19.

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The Mechanism of the Diels-Alder Reaction. The Stereochemistry of the *endo-exo* Isomerization of the Adducts of Cyclopentadiene with Acrylic and Methacrylic Esters¹

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The isomerization of the optically active *exo* adducts of cyclopentadiene with methyl acrylate and methyl methacrylate to the corresponding *endo* isomers occurs with partial racemization of the starting material and complete racemization of the product. The extent of the *exo* \rightarrow *endo* isomerization is in agreement with that expected from the extent of racemization of the *exo* starting material, the ratio of the rate constants for formation of the isomers from the component addends, and the assumption that isomerization requires fragmentation of the adduct to species in which both diene-dienophile bonds are broken. A triplet diradical transition state for the Diels-Alder reaction is difficult to reconcile with these and other observations. A two-step singlet mechanism is also unlikely. The results are satisfactorily encompassed by a four-center transition state. Whether this is symmetrical or lop-sided cannot yet be answered.

The original purpose of the experiments described in this paper was the elucidation of the stereochemistry of the internal *endo-exo* isomerization of Diels-Alder adducts. In the two Diels-Alder systems so far scrutinized² for the occurrence

of an internal isomerization, the phenomenon has been observed in one case^{2a} but not in the other.^{2b} At the outset of the present work, it was therefore not clear that any generalizations on the scope of the internal isomerization could be made, and experience provided us with no guide in our choice of a system. Our decision to investigate the adducts of cyclopentadiene with methyl acrylate and methyl

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(2) (a) J. A. Berson, R. D. Reynolds and W. M. Jones, *ibid.*, **78**, 6049 (1956). (b) J. A. Berson and W. A. Mueller, *ibid.*, **83**, 4940 (1961).