Method II. Materials.—Tetracyanoethylene, prepared according to literature procedures,[16] was sublimed at 10^{-4} mm. and had m.p. 200–201°, reported[16] 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 mμ. 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 1.82×10^{-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 mμ 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).
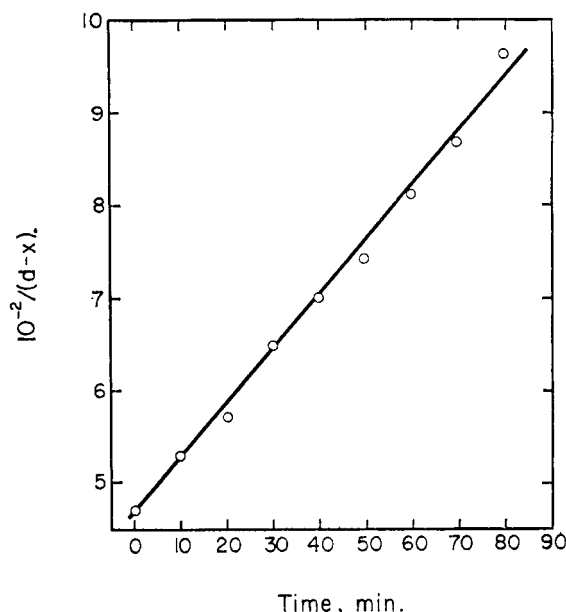

Fig. 4.—Kinetics of the cyclopentadiene–maleic anhydride addition in decalin at 28.7°; method II.

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 (2.12×10^{-3} M and 2.09×10^{-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, $k_2 = 5.88$ min.$^{-1}$ 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.

The Mechanism of the Diels–Alder Reaction. The Stereochemistry of the *endo-exo* Isomerization of the Adducts of Cyclopentadiene with Acrylic and Methacrylic Esters[1]
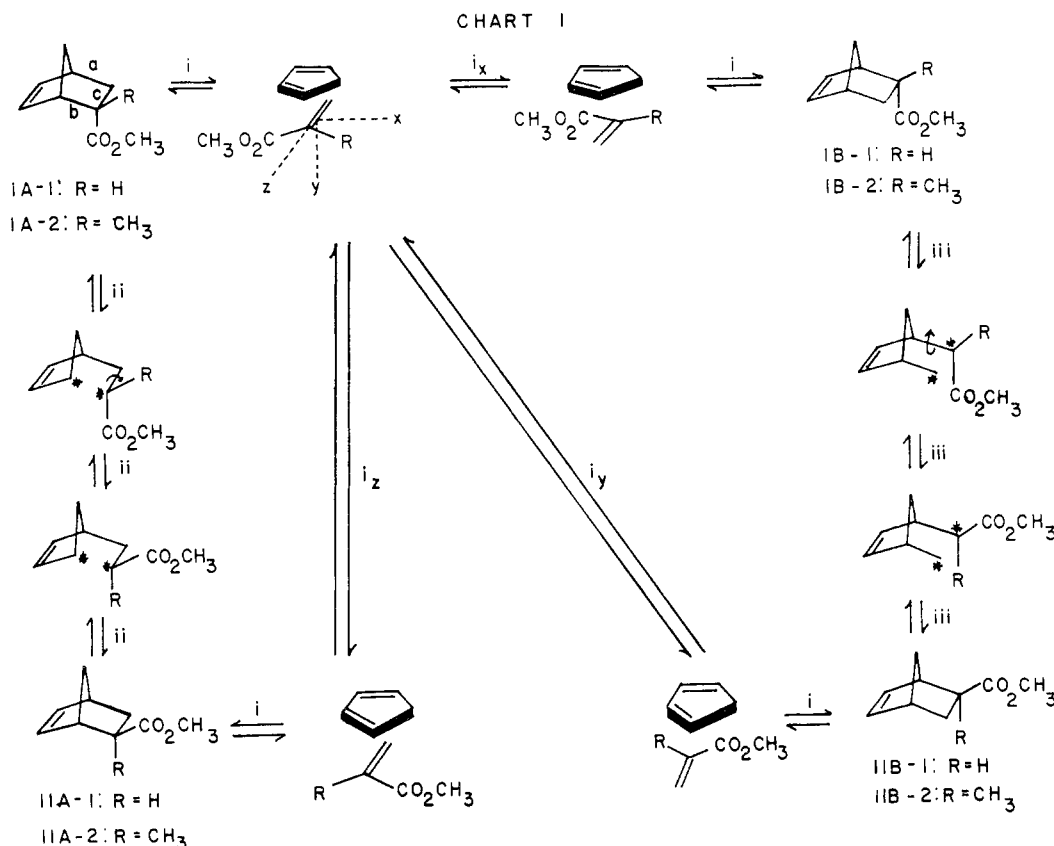
By JEROME A. BERSON AND ALLEN REMANICK

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* → *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 scrutinized[2] for the occurrence

(1) (a) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We are also indebted to the Office of Ordnance Research Contract No. DA-04-495-ORD-532 for support of part of this work. (b) For a preliminary report, see J. A. Berson, A. Remanick and W. A. Mueller, *J. Am. Chem. Soc.*, **82**, 5501 (1960).

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

(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).

CHART I

IA-1: R = H
IA-2: R = CH$_3$

IB-1: R = H
IB-2: R = CH$_3$

IIA-1: R = H
IIA-2: R = CH$_3$

IIB-1: R = H
IIB-2: R = CH$_3$

methacrylate was based largely on the anticipation that the effects we sought to demonstrate would be conveniently discernible if present and that the results would bear upon the more general question of the mechanism of the Diels–Alder reaction itself, regardless of the outcome of the study of the internal isomerization.

Disregarding the precise nature of the bonding in the intermediates, one may imagine three detailed non-dissociative processes by which an *endo*-adduct I may be converted to the *exo* isomer II, or *vice versa*: (i) fragmentation into a complex or caged aggregate by cleavage of bonds a and b, rotation of one partner with respect to the other, and recombination; (ii) cleavage of bond b, rotation, and re-cyclization; (iii) cleavage of bond c, rotation, and re-cyclization (see Chart I; the asterisks represent the termini of broken bonds). By paths ii and iii, optically active IA would be converted to optically active IIA of the same stereochemical series, *i.e.*, both paths would produce a result that is stereochemically indistinguishable from simple epimerization. In path i, although an infinite number of rotations of the fragments relative to each other can be imagined, they may each be reduced conceptually to rotations about one of the three Cartesian axes x, y, z. Rotation i_x which would not result in *endo–exo* isomerization but in conversion to the mirror image, would merely racemize the starting system. Rotations i_y and i_z would both cause isomerization, the tumbling rotation i_z leading to an enantiomer (II) epimeric with the starting material IA, and the sliding rotation i_y leading to the antipodal stereochemical series IIB. Although preservation of optical activity in such an experi-

ment would clearly imply the existence of an internal mechanism, the converse is not true, since the conversion could still be partially internal and lead to racemic product if i_x were fast or if a fortuitously appropriate combination of the other internal paths co-existed. Finally, a mechanism for the isomerization that passed through completely dissociated fragments would produce totally racemized product.

Results

The information necessary to establish the relative and absolute configurations and magnitudes of rotation in the 2-methyl-5-norbornene-2-carboxylic acid and the 5-norbornene-2-carboxylic acid series were available from previous correlations.[3,4] That part of the results needed to follow the arguments of this paper is reproduced in Table I. The preparations of the optically active *exo*-methyl esters followed the previously reported[3,4] procedures.

Preliminary experiments with racemic materials demonstrated that thermal isomerizations of methyl 2-*endo*-methyl-5-norbornene-2-*exo*-carboxylate and methyl 5-norbornene-2-*exo*-carboxylate to the corresponding *endo* isomers occurred in decalin solution (0.3–0.4 M) at 171°. In the methacrylate series (I-2, II-2), the adducts were recovered by extraction with methanol, saponification, separation of *endo* material from *exo* by formation of the iodolactone of the *endo*-acid, regeneration of the acids, and re-esterification with diazomethane. In the acrylate (I-1, II-1) series, where saponification would have caused epimerization *via* an enol,

(3) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961).

(4) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

separation of the isomeric esters was achieved by preparative vapor chromatography. To prevent thermal racemization of the products (see below), the pyrolyses in the optically active series were run to only a few per cent conversion. The isomerizations were accompanied by retrogression to the addends, since polymers of the dienophile were observed as side products.

TABLE I

ABSOLUTE CONFIGURATIONS[a] AND MAXIMUM ROTATIONS, $[\alpha]_D$

| Compound	R	X	$[\alpha]_D$	Compound	R	X	$[\alpha]_D$
IA-1a	H	CO₂H	−144°	IIA-1a	H	CO₂H	−17.1°
IA-1b	H	CO₂CH₃	−141	IIA-1b	H	CO₂CH₃	−28.7
IA-2a	CH₃	CO₂H	−107	IIA-2a	CH₃	CO₂H	−67.3
IA-2b	CH₃	CO₂CH₃	− 96.5	IIA-2b	CH₃	CO₂CH₃	−65.2

[a] The signs of rotation given in the table are those corresponding to materials of the indicated absolute configurations (A). The enantiomeric series is designated by the index B. Carbons 1, 2 and 6 in both formulas are to be considered as lying close to the observer, while carbons 3, 4, and 5 are remote.

When these procedures were applied to the mixture obtained from a pyrolysis of optically active *exo*-methacrylate adduct (IIB–2b), some unexpected experimental difficulties arose. It has usually been assumed that iodination of a mixture of *endo* and *exo* Diels–Alder adduct acids forms an iodolactone (*e.g.*, III) derived only from the *endo*-acid and leaves the *exo*-acid unchanged. The *exo*-acid retains its carboxyl function under these conditions while the *endo*-acid is converted to a neutral substance, and this has been the basis for a widely used method for the quantitative separation of such isomers.

III
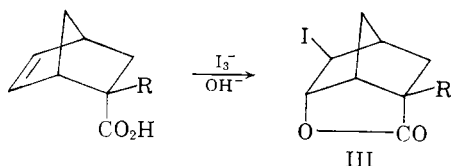
From the thermal isomerization of methyl 2-*endo*-methyl-5-norbornene-2-*exo*-carboxylate, $[\alpha]_D$ +60.4°, prepared from the corresponding acid, $[\alpha]_D$ +62.5°, an ester mixture was obtained which, after saponification, was subjected to iodolactone separation. The acidic fraction had $[\alpha]_D$ +58.1° (7% racemization) and gave vapor chromatographically pure *exo*-ester upon re-methylation. The neutral fraction was de-iodinated with zinc, and a sample of the resulting acid, $[\alpha]_D$+ 10.8°, which should have contained no *exo* material, was methylated. The resulting ester, however, was contaminated with 18.5% of a substance which had the same vapor chromatographic retention time as the *exo*-ester. That this contaminant probably was the *exo*-ester was evident from the following experiment. Re-formation of the iodolactone from the acid mixture $[\alpha]_D$ +10.8°, careful chromatography of the lactone, and regeneration of the acid with zinc

gave pure *racemic endo*-acid (at least 99.9% homogeneous), the identity and purity of which were established by its m.p. and by vapor chromatography of the methyl ester. A mixture of 81.5% of racemic *endo*-acid and 18.5% of *exo*-acid of $[\alpha]_D$ +58.1° should have had $[\alpha]_D$ +10.8°; this figure is in precise agreement with the value found for the original mixture of acids. Apparently, the iodolactonization procedure gave a neutral material from the *exo*-acid; this substance was carried along with the normal iodolactone and re-appeared as an acidic contaminant after the zinc reduction. We have no direct evidence for the composition of the neutral substance, but it seems not impossible that it contains the Wagner–Meerwein rearrangement product IV, although regeneration of the *exo*-acid

IV
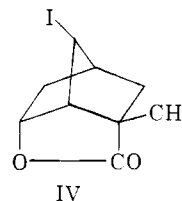
from IV would require an unprecedented reversal of the rearrangement in the zinc reduction. In an examination of the behavior of pure *exo*-acid toward the conditions of iodolactonization, we have found that a small amount of neutral material is in fact formed, but it is apparently a complex mixture. These disturbances may well have escaped notice in previous applications of the iodolactonization procedure because it has been common practice to recrystallize the iodolactone. When this technique must be sacrificed for fear of optical fractionation, as was the case in our experiments, other precautions to remove the contaminant must be exercised.

The optically active *endo*-ester IB–2b, (+)-methyl 2-*exo*-methyl-5-norbornene-2-*endo*-carboxylate, racemized only slowly, 5.9% of the optical activity being lost in a control run under the same conditions used in the thermal isomerization experiment with the *exo*-ester. The complete racemization observed in the *endo*-ester generated by pyrolysis of *exo*-ester is therefore an integral part of the mechanism of isomerization.

Similar results were observed in the acrylate series, although experimental difficulties made the data slightly less reliable than those in the methacrylate series. Pyrolysis of (+)-methyl 5-norbornene-2-*exo*-carboxylate, IIB–1b, $[\alpha]_D$ + 22.8°, gave a mixture of esters from which pure *exo*-ester was recovered with $[\alpha]_D$ +22.6° by preparative vapor chromatography of a methanol extract of the decalin solution. The amount of *endo*-ester present was so small that it could not be isolated in a quantity sufficient for direct polarimetric examination. A vapor chromatographic fraction enriched in the *endo*-ester was, however, separated. It had $[\alpha]_D$ +9.64 ± 0.25° and consisted of 54.0 ± 0.5% *endo*-ester and 46.0 ± 0.5% *exo*-ester. The specific rotation of the *endo*-ester calculated from these data was −1.4 ± 0.6°, corresponding to about 1% inversion of configuration (*i.e.*, IIB − 1b → IA − 1b) and 99% racemization. Because of the possibility of contamination of this fraction by optically

active impurities (see Experimental), we do not consider this result to be reliably different from 100% racemization. Again, a control experiment showed that racemization of optically active *endo*-ester under the pyrolysis conditions was too slow to account for any significant part of the observed loss of activity in the *exo* → *endo* conversion.

In an attempt to set up conditions under which the rate of recombination of addends from a fragmented adduct molecule might become diffusion-controlled, we have studied the isomerization of the *exo*-adduct of methyl methacrylate and cyclopentadiene in a viscous medium. Under these conditions, the rate of diffusion of the partners out of the solvent cage in which they are generated might be expected to become slower than in non-viscous media, while the rate of recombination within the cage would not be expected to change materially. If the rotations within the cage were stereospecific, some preservation of optical activity in the isomerized product might be observed. A 0.324 M solution of the (−)-*exo*-ester (IIA − 2b) in solvent methyl methacrylate was warmed with 0.1% of benzoyl peroxide to produce a hard, glassy polymer. This was pulverized, sealed in glass tubes and heated for eight hours at 171°. Under these conditions, only a slight softening of the material was noted; the viscosity in such a system must have been enormous. Although the recovery of adduct was only 19% (possibly because part of the material was incorporated into a co-polymer with methyl methacrylate), it was sufficient to permit separation of the isomers by the iodolactone method. The recovered *exo*-ester was 60% racemized, and the recovered *endo*-ester was completely racemic. It is not entirely clear, however, that the system was fundamentally different from those in which non-viscous media were used. We have no assurance that the adduct was molecularly dispersed in the medium, and if there were clusters of adduct molecules distributed through a viscous matrix, the adduct in each region could have served as its own non-viscous solvent. The experiment therefore offers only negative evidence for the absence of a stereospecific cage recombination. The possibility remains open that a cage process does occur but is stereochemically non-specific.

There are strong indications that the isomerizations reported here pass through an intermediate state in which *both* of the diene–dienophile bonds are broken. If this intermediate state is one that is stereochemically indeterminate, molecules will return from it to racemic *exo*-adduct X or proceed to isomerized, racemic *endo*-adduct N in the same ratio $(k_N/k_X$ or $k_N'/k_X')$ that these adducts are formed from addends. For the purpose of the present discussion, microscopic reversibility en-

sures that it is irrelevant whether the intermediate state is an aggregate of some sort $(\overline{D.M})$ that has lost stereochemical integrity or is actually identical with dissociated addends. When racemization of X by return of racemic N can be neglected, which is the case at the low over-all X → N conversions studied here in solvent decalin, this scheme predicts that the % of X converted to N will be the product of (k_N/k_X) and the % racemization of X. If one assumes that the rates of formation of X and N have the same kinetic dependence on the concentrations of D and M, the ratio (k_N/k_X) is just the ratio N/X given by the kinetically controlled product composition when D and M are allowed to undergo Diels–Alder addition. This ratio in solvent decalin for the temperature of the isomerization runs (171°) is now available by extrapolation of data[5] at other temperatures. The satisfactory correspondence between the % conversion calculated on the above basis and that found experimentally is indicated in Table II. In the methacrylate series, the data are for the conversion of X to N. In the acrylate series, where the % racemization of X in the X → N conversion under the conditions used is too low to be useful, the result reported in Table II is for the reverse reaction, N to X, in which case the kinetic ratio used for the calculation was (k_X/k_N). Table II also indicates results for the run in "solvent" polymethylmethacrylate, where there is a substantial discrepancy between the observed and calculated values. This is expected, since the (k_N/k_X) ratio is known to be solvent-dependent[5] and since the necessary condition of low % conversion was not satisfied in this experiment. If it is assumed that the (k_N/k_X) ratio in polymethylmethacrylate is not very much different from that in decalin, the discrepancy is in the direction expected for some contribution to the racemization of X by return of racemic N.

The isomerizations, at least in solvent decalin, are most simply interpreted in terms of a fragmentation of the adduct into two pieces. The only alternative, namely a fortuitous combination of one-bond-breaking processes (ii and iii of Chart I) producing retention of configuration balanced by an exactly equal contribution of cleanly configuration-inverting fragmentation (i_y of Chart I), seems unlikely. Not only would the relative contributions of each of the paths in question have to balance precisely, but the distribution of each intermediate in its return to the adducts would have to balance at the observed kinetic ratio of products. The data do not distinguish between completely dissociated addends (D + M) and a stereochemically random aggregate or complex $(\overline{D.M})$ as the proper representation of the intermediate state. The presence of an incompletely dissociated addend-pair $(\overline{D.M})$ would be detectable by a labeling experiment like the one used in another system[2a]; conversion of labeled X to N in the presence of ordinary dienophile would give N with a higher proportion of the label than it would have if formed by complete dissociation. We were dissuaded from attempting this experiment by the observation that methyl methacrylate poly-
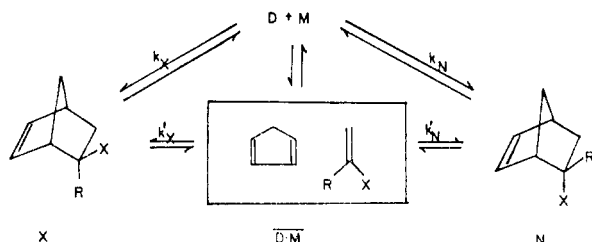
(5) J. A. Berson and W. A. Mueller, *Tetrahedron Letters*, No. 4, 131 (1961).

TABLE II

RACEMIZATION AND CONVERSION IN THE THERMAL ISOMERIZATION EXPERIMENTS, 171°

Adduct starting material	Solvent	% rac. of starting material	Kinetic ratio	Conversion, %	
				Calcd.	Found
endo-Acrylate	Decalin	17.0	0.37[a]	6.3 ± 0.3	7.5 ± 1.0
exo-Methacrylate	Decalin	7.0	.67[b]	4.7 ± .3	5.6 ± 1.0
exo-Methacrylate	Polymethylmethacrylate	60.2	.67[b]	40.4 ± .3	32.1 ± 0.5

[a] X/N extrapolated from data of ref. 5.   [b] N/X extrapolated from data of ref. 5.

merized very rapidly under the conditions of the isomerizations.

Discussion

Despite intensive efforts devoted to its study, the mechanism of the Diels–Alder reaction remains a subject of debate.[6-9] In part, this is attributable to the nature of the reaction itself. Although catalytic,[10,11] solvent[5,12,13] and structural[14] effects are observed and are important in practical applications, the reaction is nevertheless relatively unresponsive to many of the influences that dramatically alter the rate and course of most organic processes. There is general agreement that the rate-determining step in adduct formation is bimolecular, but the structure of the transition state and, in particular, the timing of the changes of covalency that result in formation of the two diene–dienophile bonds remain to be sharply defined. In the discussion that follows, we shall examine several mechanistic proposals in the light of our experimental results.

The Diradical Mechanism.—One widely discussed mechanism postulates two distinct bond-forming steps, the first being rate determining and leading to a *diradical* intermediate, which quickly cyclizes to product, *e.g.*


Three kinds of evidence have been put forward in favor of this mechanism: (i) The theoretical entropies of activation for the gas phase dimerization of butadiene to vinylcyclohexene can be calculated[15] by statistical mechanical methods for the open-chain diradical and cyclic models of the transition state; the observed value is much closer to that originally calculated[15] on the basis of the open-chain model. (ii) The additions of unsymmetrically substituted dienes to unsymmetrically substituted dienophiles frequently[16] but not invariably[16f,17] give

(6) C. Walling and J. Peisach, J. Am. Chem. Soc., 80, 5819 (1958).

(7) R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959).

(8) M. J. S. Dewar, Tetrahedron Letters, No. 4, 16 (1959).

(9) R. B. Woodward and T. J. Katz, ibid., No. 5, 19 (1959).

(10) P. Yates and P. Eaton, J. Am. Chem. Soc., 82, 4436 (1960), and references therein cited.

(11) G. I. Fray and R. Robinson, ibid., 83, 249 (1961).

(12) A. Wassermann, Trans. Faraday Soc., 34, 138 (1938).

(13) M. Gillois and P. Rumpf, Bull. soc. chim. France, 1823 (1959).

(14) See references cited in ref. 7 for a summary.

(15) G. B. Kistiakowsky and W. W. Ransom, J. Chem. Phys., 7, 725 (1939).

(16) (a) E. C. Coyner and W. S. Hillman, J. Am. Chem. Soc., 71, 324 (1949); (b) W. E. Bachmann and N. C. Deno, ibid., 71, 3062 (1949); (c) C. W. Smith, D. G. Norton and S. A. Ballard, ibid., 73, 5273 (1951); (d) K. Alder and K. Heimbach, Chem. Ber., 86, 1312 (1953); (e) I. N. Nazarov, Y. A. Titov and A. I. Kusnetsova, Proc. Acad. Sci. U.S.S.R., 124, 586 (1959); (f) J. S. Meek, D. R. Wilgus and J. R. Dann, J. Am. Chem. Soc., 82, 2566 (1960); (g) L. E. Miller and D. J. Mann, ibid., 73, 45 (1951); (h) J. S. Meek, B. T. Poon, R. T. Merrow and S. J. Cristol, ibid., 74, 2669 (1952); (i) K. Alder, M. Schumacher and O. Wolff, Ann., 564, 79 (1949).

predominantly the product that would be expected from a diradical intermediate; for example, vinyl-acrylic acid and acrylic acid give[16f] the "*ortho*" (V) rather than the "*meta*" (VI) dibasic acid. This kind of behavior, which is the opposite of that expected on purely polar grounds, is frequently interpreted as
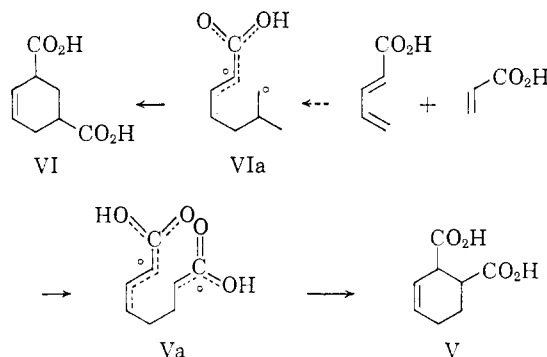
indicating the energetic advantage enjoyed by the more highly delocalized intermediate Va. (iii) The effect of external hydrostatic pressure on the rate of the liquid phase dimerization of isoprene to limonene is interpreted[6] in terms of a molar volume for the transition state that is substantially larger than the molar volume of the final product, a result considered[6] to be inconsistent with the simultaneous formation of both diene–dienophile bonds.

Recent re-evaluations of these three pieces of evidence, however, have indicated that each of them is either ambigous or actually supports a mechanistic conclusion exactly opposite to that originally given: (i) The theoretical entropy of activation for the dimerization of butadiene is strongly dependent on the structural parameters and vibration frequencies chosen for the model of the transition state. Recalculation of the entropy change leads in one case[18b] to differences between the observed and theoretical values that are about the same for a cyclic transition state as for an open-chain one, and in the other[19] to a value for the cyclic model that is in much better agreement with experiment than is that for the open-chain model. (ii) The predominant formation of one type of position-isomer from substituted diene–dienophile pairs does not *require* interpretation in terms of a diradical transition state. As has been pointed out,[20]

(17) (a) J. S. Meek, J. R. Dann and B. T. Poon, J. Am. Chem. Soc., 78, 5413 (1956); (b) R. L. Frank, R. D. Emmick and R. S. Johnson, ibid., 69, 2313 (1947); (c) I. N. Nazarov, A. I. Kuznetsova and N. V. Kuznetsov, J. Gen. Chem. U.S.S.R., 25, 75, 307 (1955); (d) I. N. Nazarov, Y. A. Titov and A. I. Kuznetsova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1270, 1412 (1959).

(18) (a) A. Wassermann, J. Chem. Soc., 828 (1935); (b) 612 (1942).

(19) D. Rowley and H. Steiner, Disc. Faraday Soc., 10, 198 (1951).

(20) M. G. Ettlinger and E. S. Lewis, Abstracts of Papers presented to the Meeting of the American Chemical Society, New York, N. Y., September 11-16, 1960, p. 95 P.

these observations are also accommodated in a four-center transition state, in which both diene–dienophile bonds form simultaneously, provided that due regard is given to its resonance hybrid character. (iii) The pressure-dependence of the rate of dimerization of isoprene is interpretable[21] at least equally well in terms of a molar volume for the transition state that is very close to that of the final product, which is a result expected for a four-center, one-step mechanism but not for a two-step, diradical mechanism.

One further aspect of the diradical mechanism requires examination: Is the alleged diradical transition state a triplet species? It seems clear that at least some of the proponents of the mechanism consider it so. Kistiakowsky and Ransom[15] make a statistical mechanical correction for the change in electronic multiplicity in their calculation of the theoretical entropy, and Walling,[22] while not explicitly stating a preference for a triplet as opposed to singlet transition state, seems to interpret the term "diradical" to mean a species with unpaired electrons.

On the basis of presently available evidence, it seems difficult to support a case for the triplet transition state. Thus, the pre-exponential factors for reactions passing from singlet ground states to triplet transition states are expected[23a] to be abnormally low; yet this parameter for the *retrogressions* of Diels–Alder adducts to addends (the microscopic reverse of the additions) is normal.[2b,12] The rate of addition is, in the one case that has been examined,[2b] unaffected by ferric dipivaloylmethide,
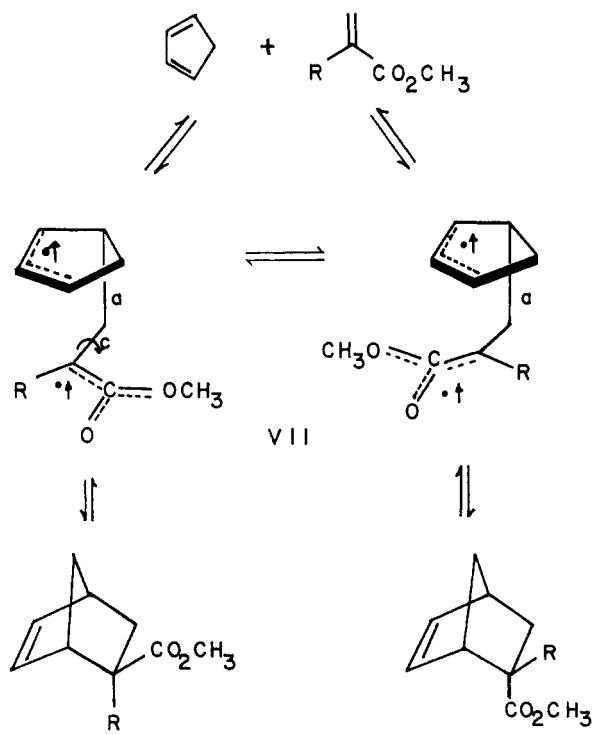
a reagent that catalyzes other[23b] singlet–triplet conversions. Furthermore, a chemical (as distinct from kinetic) consequence that might be expected from the triplet diradical mechanism is not observed. The conversion of a triplet transition state to a singlet product requires that the system reach a stage VII in which one diene–dienophile bond is fully formed and there are two unpaired electrons. Before VII can cyclize to product, there must be a change in multiplicity. This is a process of low quantum mechanical probability, and VII is accordingly expected to have a finite lifetime. If this corresponds roughly to the period of a bond rotational frequency, VII should lose its geometric integrity, and interconversion of the two rotamers shown should occur. Microscopic reversibility ensures that in the retrogression of the adduct, VII will again lie on the reaction path, so that *endo–exo* interconversion of a pair of stereoisomeric adducts should occur with some retention of optical purity.[24] With respect to the forward step of the Diels–Alder reaction, the process would produce a mixture of *cis* and *trans* adducts from either a *cis* or *trans* dienophile. While the wealth of experience[14] with preparative Diels–Alder reactions shows that such phenomena are uncommon and justifies the generalization that the addition is *cis*, it is doubtful if a test as sensitive as the one applied here to the retrogression has been made elsewhere. With the quantities and rotations of material available to us, we could have detected as little as 1% retention of optical purity in the isomerization of the *exo-*cyclopentadiene–methyl methacrylate adduct at 171°. The formation of completely racemic product requires that the free energy of activation for rotation about bond c in the hypothetical VII be at least 4 kcal./mole greater than that for cleavage of bond a (retrogression to addends). Although VII need not represent a potential energy minimum, it must have an energy lower than that of the transition state leading to its formation (which, in the mechanism under discussion, is the transition state for the rate-limiting step of the addition). Therefore, the rotational energy barrier must be even greater than 4 kcal./mole. There are no obvious grounds for expecting the barrier in VII to be so much higher than those in other[25] presumed triplet intermediates, in which loss of rotameric identity is characteristic. The present results and the previous kinetic data[2b,12] provide no basis for postulating a triplet transition state and, in fact, are extremely difficult to reconcile with it.

(24) The occurrence of such a rotation in the reactions of geometric isomers of olefins with triplet species would lead to a mixture of *cis* and *trans* cyclized products. This has been applied as a criterion for detecting the presence of triplet intermediates in addition reactions.[25] (b) It should be noted that VII lies *past* the transition state for the addition (on the adduct side of the energy barrier). Bond a is fully formed, and consequently bond c has no double bond character.

(25) (a) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958); (b) P. S. Skell and J. F. Klebe, Abstracts of Papers, American Chemical Society Meeting, Cleveland, Ohio, April 5–14, 1960, p. 90-O; (c) F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwers, *J. Am. Chem. Soc.*, **82**, 3217 (1960); (d) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); (e) *cf.* also H. M. Frey, *ibid.*, **82**, 5947 (1960); (f) complete loss of geometric integrity would not result if spin inversion were fast enough to allow cyclization to compete with rotation; see K. R. Kopecky, G. S. Hammond and P. Leermakers, *ibid.*, **83**, 2397 (1961).

(21) S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **83**, in press (1961).

(22) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 188–189.

(23) (a) *Cf.* B. G. Gowenlock, *Quart. Revs.*, **14**, 133 (1960); (b) G. S. Hammond, personal communication.

The "Two-stage" Mechanism.—In special cases the pyrolysis of a Diels–Alder adduct produces changes other than simple retrogression to the addends: When the adduct contains the system VIII, the formal structural prerequisites for the Cope rearrangement[26] are satisfied, and a number of such rearrangements have recently been observed

VIIIa   VIIIb
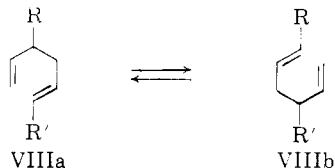
in Diels–Alder systems.[7,27–29]   For example, at 140°, α-1-hydroxydicyclopentadiene (IX) rearranges to *syn*-8-hydroxydicyclopentadiene (X); higher temperatures are required to cause fragmentation into the addends.[7]   The IX → X rearrangement is completely stereospecific,[7] a result that is at least intuitively expected for a Cope rearrangement by analogy to rearrangements[26] of crotyl isopropenyl malonic ester and crotyl 2-(2-butenyl)-cyanoacetic ester, which are intramolecular and occur with specific structural inversion of the crotyl group to α-methylallyl, but is not expected for a complete Diels–Alder retrogression.   In the rearrangement of the (Diels–Alder) dimer of methacrolein,[29] fragmentation competes with isom-

IX   X
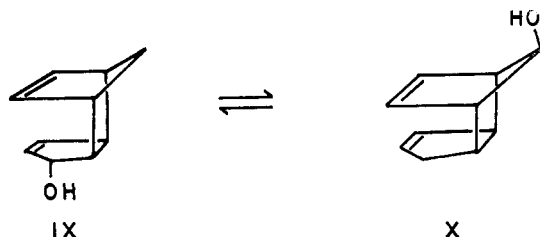
erization, but the non-dissociative part of the isomerization is again structurally and stereochemically specific.   On the *assumption* that the transition state for the IX → X isomerization lies on the same reaction path used by IX in its decomposition to cyclopentadiene and acetoxycyclopentadiene, Woodward and Katz[7] have proposed a "two-stage" mechanism for the Diels–Alder reaction.   The transition state for the forward step of the Diels–Alder addition is assigned structure XI.[7]   (The dashed lines represent partial bonds and the dotted lines represent "secondary attractive forces."[7])

XI   XII
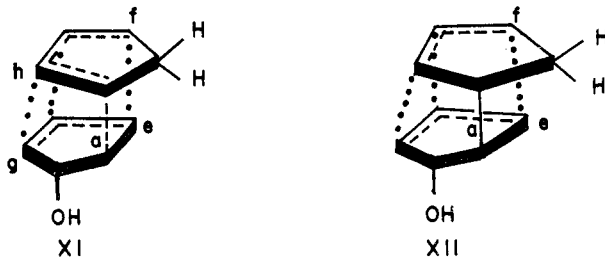
The isomerization proceeds through an ensemble XII (which is not specifically designated a metastable intermediate[7]) in which one of the potential diene–dienophile bonds (a) is fully formed.

The authors[7] extrapolate this interpretation to include all Diels–Alder additions, but explicitly leave open the question of whether the mechanism is one involving a single step or two steps.   Thus, the suggestion is made[7] that the addition has "a two-stage mechanism, in that the formation of the two bonds takes place in separable, even if overlapping, processes, discretely delineated in structural terms and displaced in time."   We note that this concept of simultaneity in the bond-making processes is not derivable directly from the Woodward–Katz[7] interpretation of their system IX as a model of Diels–Alder additions, but is added *ad hoc*.   Bond a in XII is a full covalent bond, but the interaction e–f is a "secondary attractive force," not a partial bond.   Therefore, in the transition state XI for the addition process, there is no partial bond making at e–f either.

We may now distinguish two cases: In the first, it is assumed that an activation energy is required to convert a "secondary attractive force" to a covalent bond.   For the system studied,[7] the Diels–Alder addition is then *two-step*, not "two-stage," and molecules passing from the transition state XI must encounter a metastable intermediate in their progress to IX or X.   The second case is one in which no activation energy is required to convert a "secondary attractive force" to a covalent bond.   This seems to us to be indistinguishable conceptually from a four-center reaction with a transition state in which bond-making at one junction is slightly more advanced than that at the other.   There is in this case no essential distinction in kind between the partial bond at a and those at e–f and g–h in the transition state XI.

We do not share the point of view[7] that "resolution of the extremely subtle problems associated with defining the precise topography of the energy surface for the (addition) reaction after passage of the first barrier is irrelevant," for it is an examination of what is assumed[7] to be this portion of the energy surface which provides the basis for the original mechanistic proposal itself; further, there remains the possibility that the proposal may be experimentally subject to test in that region.[30a]

The "two-stage" and two-step mechanisms, applied to the reactions of cyclopentadiene with acrylic and methacrylic esters, would represent the transition states for formation of the *endo* and *exo* adducts as XIII and XIV.   In the two-step mechanism, *intermediates* XV and XVI, with finite lifetimes, occur between the transition states and products, while in the "two-stage" mechanism, XV and XVI do not represent potential energy minima.   The dotted lines c* and d represent "secondary attractive forces" in the two-step mechanism and partial bonds in the "two-stage" mechanism.

(26) A. C. Cope, C. M. Hofmann and E. M. Hardy, *J. Am. Chem. Soc.*, **63**, 1852 (1941).

(27) R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Letters*, No. **22**, 29 (1960).

(28) P. Yates and P. Eaton, *ibid.*, No. **11**, 5 (1960).

(29) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(30) (a) The postulate that there is only one transition state (the second case above) has the corollary that for a Diels–Alder pair of adducts that are intramolecularly interconvertible by the Woodward–Katz mechanism, the kinetically controlled product ratio in the Diels–Alder *addition* should be unity, provided the transition state theory transmission coefficient ratio is unity.

(b) K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937).

In either mechanism, the atoms that interact along the lines of force d are those not involved in the eventual formation of a bond. These atoms are much closer together in the *endo* transition state XIII than in the *exo* transition state XIV, and to this circumstance is assigned[7] the responsibility for the Alder rule[30b] of "maximum overlap of double bonds." In the two-step mechanism, the interaction d must bear the additional burden of accounting for the known rigidity of the transition state (revealed by the low pre-exponential factors[12] for Diels–Alder additions) and for the cleanly *cis*-stereochemistry of the addition, a quantitative manifestation of which is established in our study of the two optically active adduct systems described above.

If the interaction d were important, one would expect *endo* addition to be strongly preferred. This is not the case. Thus, while the activation energies for the additions of cyclopentadiene to the two dienophiles can hardly be less than about 14 kcal./
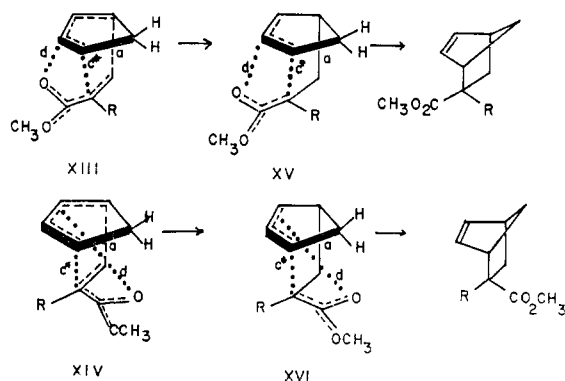
mole (compare cyclopentadiene–acrolein[12]: E_a in benzene = 13.7 kcal./mole, E_a in the gas phase = 15.2 kcal./mole), the activation energies for *endo vs. exo* addition are virtually the same: in decalin, for methyl acrylate, $(E_a^{exo} - E_a^{endo}) = + 0.36$ kcal./mole, and for methyl methacrylate $(E_a^{exo} - E_a^{endo}) = -0.71$ kcal./mole.[5,31] In the case of methyl methacrylate, the *exo*-isomer is actually kinetically favored.[5] Furthermore, the interaction d, whatever its nature, is expected to depend strongly on distance and therefore is expected to be sensitive to the conformational orientation of the unsaturated dienophilic substituent (CO_2CH_3). (For example, the dipole induction energy[18a] falls off as the sixth power of the distance.) Thus, if d is to be strong, a dienophile bearing a more or less freely rotating substituent in the ground state would be expected to suffer a greater loss of entropy in passing to an *endo* transition state than to an

exo transition state because of the restriction to motion required for proper orientation of the CO_2-CH_3 group. No such effect is observed[5]; $\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger}$ in decalin solvent is about +1 e.u. for both methyl acrylate and methyl methacrylate, the effect being very small and opposite in sign to that expected on the above basis. Apparently, the gain in stability provided by d in the *endo* transition state is not enough to pay for the loss in entropy that must be suffered to achieve it.

Regardless of the reasons for the variations in stereoselectivity from case to case, it is hard to see how the interaction d can be of major significance in the energetics of the transition states under discussion. Yet these transition states, like all known Diels–Alder transition states, must be rigid and must require a geometrically highly oriented arrangement of the reactants. An interaction as weak as d would not be expected to make these demands. Furthermore, once the transition state is passed in the two-step mechanism and the system arrives at XV or XVI, it is hard to imagine that the interaction d *in the exo isomer*, in which the relevant centers are remote from each other, could be responsible for the substantial rotational barrier observed.

This leaves the interaction denoted c* to account for the rigidity of the transition state and for the cleanly *cis* addition. The centers involved are the same as those which eventually form a covalent bond in the adduct. We therefore can see no reason for postulating a distinction between c* in XIII or XIV as a "secondary attractive force" and a as a partial bond. In other words, a four-center transition state, with both diene–dienophile bonds partially formed, suffices to explain the facts. Whether the fractional bond orders of these two bonds are identical, or whether the transition state is lopsided, with bond-making at one site in advance of that at the other, are questions that cannot be answered from the data now available. It is conceivable that a graded continuum[7] may be needed to account for the behavior of systems of varying structure, with a completely symmetrical four-center mechanism at one end of the scale and a fully developed two-step mechanism at the other. It will be necessary, however, for an unambiguous connection to be established between the cases of Cope rearrangement (*e.g.*, IX ⇌ X) and the Diels–Alder retrogression before these can be accepted as manifestations of the two-stage or two-step extremes of the mechanistic scale.

Experimental[32]

Thermal Isomerization of the *exo*-Cyclopentadiene–Methyl Acrylate Adduct (IIB–1b).—The ester was prepared from a sample of the corresponding acid[4] of $[\alpha]^{25}D$ +13.6° (95% ethanol) and after distillation had $[\alpha]^{25}D$ +22.0° (95% ethanol). The ratio of the rotations (1.62) was in approximate agreement with that (1.55) determined earlier,[4] but, as is shown below, this ester contained a small amount of optically active impurity. A sample (5.4 g.) of ester was dissolved in 100 ml. of pure decalin and distributed into four short Carius tubes. These were sealed and kept in a preheated bath of boiling phenetole (171°) for 7 hours, where-

(31) (a) Although the methyl methacrylate–cyclopentadiene addition is the first case in which a formal demonstration of a *kinetic* contravention of the Alder rule has been made,[1b,5] for the purpose of the present arguments, the fact that *exo* addition is favored is not the point at issue. What is of primary importance is the small difference in energy between many pairs of *endo–exo* isomeric transition states, which although clearly established from kinetically controlled experiments only in the cases of the methyl acrylate and methyl methacrylate additions to cyclopentadiene, is nevertheless strongly suggested by the qualitative results in a number of other systems[1b] in which mixtures of both possible stereoisomers are formed. (b) For a summary of references, see K. Alder, R. Hartmann and W. Roth, *Ann.*, **613**, 6 (1958); K. Alder and W. Günzl, *Chem. Ber.*, **93**, 809 (1960).

(32) Optical rotations were measured in 95% ethanol solutions in a 4-dcm. jacketed tube cooled with thermostated water. The polarimeter used was a Rudolf model 80 high precision instrument reading directly to 0.001°.

upon they were removed, cooled and opened. The combined contents were extracted with a total of 100 ml. of methanol (7 portions). The methanol extract was distilled to give about 10 ml. of a decalin–ester mixture b.p. 88–96° (26 mm.). This was fractionated through a preparative vapor chromatography column consisting of eight 5/8 × 18 in. brass tubes connected in series through a manifold. The tubes were packed with tetrahydroxyethylethylenediamine[33]-on-Chromosorb (THEED) and the effluent gas was led through a 1/8 in. stainless steel line which led directly from the detector cell of the Perkin–Elmer model 154 C chromatograph to a series of traps through a specially bored exit hole in the cabinet. The trapped fractions, collected from a column held at 127° and a flow rate of 230 cc./min. of helium, were monitored with an analytical column, 1/4 in. × 6½ ft., of THEED or ID (polyethylene glycol 400-on-Chromosorb). Quantitative estimation of the components was achieved from the peak areas, using an empirical correction factor of 1.03 for the area of the endo-ester determined by calibration with known mixtures. The retention times on the analytical columns (exo:endo) in minutes at the flow rates and temperatures used were: THEED, 30:37 min., 56 cc./min., 127°; ID, 23:24,34 cc./min., 106°. The size of the samples used (0.5–0.6 ml.) in the preparative separations did not allow the highest resolution of which the column was capable but was chosen to shorten the procedure. A cut lying between the two esters was usually discarded to improve the separation.

In this manner, three fractions were collected: (1) Decalin and other impurities; this fraction was discarded. (2) Essentially pure exo-ester, which after re-fractionation was homogeneous on the analytical column, $[\alpha]^{25}$D +22.6° (95% ethanol). (3) An endo-enriched fraction which, after bulb-to-bulb distillation, had $[\alpha]$D +9.65° (95% ethanol) and consisted of 54.0% endo-ester and 46.0% exo-ester.

Since the rotation of the exo-ester recovered from the isomerization was slightly higher than that of the starting material and definitely higher than anticipated on the basis of the earlier[4] correlation, an investigation of the difficulty was in order. A sample of the exo-acid, $[\alpha]^{25}$D +13.6° (95% ethanol), was methylated with ethereal diazomethane. After bulb-to-bulb distillation, this material showed a broad contaminant peak of area about 5% of that of the main ester peak. Two successive fractionations on the preparative column gave material of constant rotation, $[\alpha]^{25}$D +22.8° (95% ethanol), homogeneous on the analytical column.

Isomerization of the endo-Ester (IA–1b).—Esterification with ethereal diazomethane of a sample of the corresponding acid Ia–1a, $[\alpha]^{25}$D −20.7°, gave material that contained about 1% of a contaminant. This was readily removed by solution chromatography on acid-washed alumina in 1:9 ether–pentane. A sample of 69.2 ml. of a 0.395 M solution of the ester was heated at 171° as above for 7 hours. The decalin solution was extracted with methanol and the methanol extract was distilled through a short Vigreux column. The distillate contained (by vapor chromatographic analysis), besides decalin, the peak from which was cleanly separated on the chromatogram, a mixture of esters consisting of 92.5 ± 1% endo-ester and 7.5 ± 1% exo-ester. Vapor chromatographically homogeneous endo-ester, $[\alpha]^{25}$D −16.8°, was recovered by preparative vapor chromatography as above. A control experiment[34] showed that the ester mixture could be extracted from decalin with methanol without fractionation of the mixture, material recovered from the methanol extract having a composition identical with that of the starting sample.

Thermal Isomerization of the exo-Cyclopentadiene–Methyl Methacrylate Adduct (IIB–2b).—The corresponding acid (IIB–2a), $[\alpha]^{25}$D +62.5°, gave with ethereal diazomethane a methyl ester, $[\alpha]^{25}$D +60.4°, which was vapor chromatographically homogeneous on a 1/4 in. × 6½ ft. tri-β-cyanoethoxypropane-on-Chromosorb (TCEP) column. Thirty grams of this ester in 400 ml. of pure decalin were sealed in 14 Carius tubes and heated at 171° for 3.5 hours. The reaction mixtures were worked up by methanol extraction, as in the previous cases, and the ester mixture, together with accompanying decalin, collected by distillation at 81–

83° (25 mm.). Vapor chromatographic analysis was carried out with the TCEP column at 90° and a flow rate of 34 cc./min. of helium. Under these conditions, the exo-ester emerged after 59 min. followed by the endo-ester after 71 min. The ester mixture was cleanly separated on the chromatogram from decalin and had the composition 94.4 ± 1% exo and 5.6 ± 1% endo. The distillate was added to 250 ml. of a 4:1 methanol–water solution that was 1 N in potassium hydroxide and boiled with stirring for 20 hours. Most of the methanol was distilled off, and during the distillation 150 ml. of water was added. The resulting solution was extracted several times with ether to remove neutral impurities, acidified with 10% sulfuric acid, and extracted with ether. The ethereal solution was dried over magnesium sulfate, evaporated, and distilled in a bulb-to-bulb apparatus to give 8.0 g. (29%) of recovered acids. Iodolactone separation[35] gave 3.2 g. of pure exo-acid, $[\alpha]^{25}$D +58.1°, from the acid fraction. The neutral fraction contained 1.25 g. of crude iodolactone which on reduction with zinc and acetic acid[4] gave endo-acid, $[\alpha]^{26}$D +1.59°, m.p. 78–98°.

The low over-all yield of mixed acids suggested that not all of the ester had been extracted from the original decalin solution. Accordingly, it was mixed with 200 ml. of water, 800 ml. of methanol and 28 g. of potassium hydroxide and boiled for 42 hours. The methanol was removed by distillation and the aqueous layer was separated from decalin. After several washings with ether, the aqueous solution was acidified with 10% sulfuric acid and extracted with ether. Evaporation of the ether and distillation of the residue gave 9.5 g. (34.5%) of mixed acids. Iodolactone separation gave 1.0 g. of crude iodolactone, which on zinc reduction gave acid, $[\alpha]^{25}$D +10.8°, m.p. 55–89.° This quantity of iodolactone corresponds to 0.55 g. of endo-acid. When corrected for the 18.5% contamination by exo-acid found below, this corresponds to 0.45 g. or 4.7% of endo-acid in the 9.5-g. sample. This figure is in rough agreement with the value of 5.6 ± 1% found in the original methanol extract and indicates the absence of fractionation in the analytical scheme. This was confirmed by a separate experiment[34] like the one applied to the acrylic ester adducts.

The differing rotations of the two samples of endo-acid suggested the presence of an optically active, acidic impurity, probably exo-acid. This was confirmed in the following way: Esterification with diazomethane of a small sample of the acid $[\alpha]^{25}$D +10.8° gave a methyl ester which showed a peak at the position of the vapor chromatogram corresponding to that of authentic exo-ester and amounting to 18.5% of the area of the chromatogram. The remainder of the acid was combined with the previous sample, and re-converted to the iodolactone (m.p. 81–85°) which was chromatographed on acid-washed alumina in 1:1 pentane–ether. A trace of yellow oil emerged first and was discarded; the pure iodolactone was recovered by evaporation of the succeeding eluates. It was obtained as shiny white platelets, m.p. 84–86° (reported[36] m.p. 83–86°). It was optically inactive and gave upon reduction with zinc and acetic acid (no recrystallizations) optically inactive endo-acid, m.p. 104–109.5°. Our best sample[3] of the synthetic racemic acid had m.p. 108–110° after recrystallization and sublimation, reported m.p. 94–95°,[36] 109°.[37] The m.p. is very sensitive to traces of impurity, and the value observed indicates the absence of substantial quantities of contaminants. Esterification of the recovered sample (m.p. 104–109.5°) with diazomethane gave vapor chromatographically homogeneous endo-methyl ester.

In an attempt to prepare the neutral contaminant that must have been present in the crude iodolactone, 5-g. samples of pure exo-acid in buffered aqueous media (pH 4.85 and 7.10) were treated with iodine–potassium iodide solution. After having been stirred at room temperature for 17 hours, each of the solutions was worked up for neutral material by extraction with ether, washing with bicarbonate solution, drying over magnesium sulfate and evaporation. Each afforded a few tenths of a gram of yellow oil which showed carbonyl peaks in the infrared at 5.45, 5.60 and 5.90 μ. The spectral solutions (carbon disulfide) developed a pink color upon standing. No further characterization was attempted.

(33) The analytical separation of these esters on this packing has been reported by A. C. Cope, E. Ciganek and N. A. LeBel, J. Am. Chem. Soc., 81, 2799 (1959). We are indebted to Professor Cope for the personal communication of additional details.

(34) We are indebted to Dr. William A. Mueller for this datum.

(35) Cf. C. S. Rondestvedt, Jr., and C. D. ver Nooy, J. Am. Chem. Soc., 77, 3583, 4878 (1955).

(36) J. S. Meek and W. B. Trapp, ibid., 79, 3909 (1957).

(37) S. Beckmann, R. Schaber and R. Bamberger, Chem. Ber., 97, 997 (1954).

In a control experiment to determine the optical stability of the *endo*-ester, pyrolysis of a sample prepared with diazomethane from acid of $[\alpha]^{25}D$ $+58.9°$ under the usual conditions (2.2 g. in 32 ml. of decalin heated at 171° for 4 hours), followed by the customary work-up (saponification, iodolactone formation, chromatography of the iodolactone, which gave material of m.p. 75–76°, and reduction with zinc and acetic acid) gave *endo*-acid, $[\alpha]^{25}D$ $+55.5°$, m.p. 103–110°.

Thermal Isomerization of the *exo*-Cyclopentadiene–Methyl Methacrylate Adduct IIA–2b in Polymethyl Methacrylate.— A solution of 27.4 g. of (—)-IIA-2b (prepared from acid of $[\alpha]^{25}D$ $-48.8°$) in 420 ml. of freshly distilled methyl methacrylate was treated with 1.2 g. of benzoyl peroxide, sealed in two glass tubes, warmed to about 50° for 15 minutes, and allowed to stand overnight at room temperature. The tubes were cracked away from the solid polymer by tapping with a hammer, the polymer was crushed and finally milled to particles about 2 mm. in diameter. This material was distributed into fourteen Carius tubes and heated at 171° for 8.25 hours. The contents, which had partially flowed together, were removed, repulverized, and extracted with 2.5 l.

of boiling acetone in a Soxhlet extractor. About 50% of the polymer dissolved. The acetone solution was filtered to remove insoluble polymer, the filtrate was treated with 2 l. of anhydrous methanol and evaporated to a volume of 500 ml. under a 14-in. Vigreux column. Another 500 ml. of methanol were added and the precipitated polymer was filtered off. Evaporation of the filtrate to a volume of 75 ml. produced more precipitate, which was again filtered off. Further concentration of the filtrate and distillation gave material which, after having been taken up in ether, washed with bicarbonate solution and water, dried over magnesium sulfate and distilled (101–102°/39 mm.), amounted to 5.3 g. (19%) of mixed esters. By vapor chromatography, the composition was 67.9% *exo* and 32.1% *endo*. The mixed esters were saponified and the acids separated by the iodolactone procedure as previously described. The recovered *exo*-acid had $[\alpha]^{25}D$ $-19.4°$. The iodolactone, after chromatography, was racemic and gave upon reduction racemic *endo*-acid, m.p. 107–110°. Esterification with diazomethane gave *endo*-ester which was homogeneous by vapor chromatography.

Kinetics of Reactions in Moderately Concentrated Aqueous Acids. I. Classification of Reactions[1,2]

BY JOSEPH F. BUNNETT

Plots of (log k_ψ + H_0), or appropriate other function for more basic substrates, against log a_{H_2O} are generally linear or approximately so. The slopes define a parameter, called w, which is useful for the classification of reactions. Plots of (log k_ψ — log [HX]) *versus* log a_{H_2O} are also often linear, and their slopes define a complementary parameter. w^*. w- and w^*-values have been reckoned from literature data for a large number of reactions. Most w-values fall between —2 and +7, and they show no particular tendency to cluster about magnitudes corresponding to the "ideal" Zucker–Hammett categories. Classification according to the Zucker–Hammett categories requires arbitrary decisions in some cases and in general obscures subtle and important differences which are revealed by w- and w^*-values. The latter are therefore recommended for use in the precise classification of acid-catalyzed reactions.

The rates of acid-catalyzed reactions depend on the acid concentration. But they do not all depend in the same way. Some reactions accelerate more rapidly than others as the acid concentration is increased, some pass through a rate maximum at a particular acid concentration and some actually go steadily *slower* as the acid concentration is increased above, say, 1 M.

Interpretation of these phenomena is of course a challenge, and has further interest because of the reward of insight into reaction mechanisms. To date, the most widely used interpretation has been the Zucker–Hammett hypothesis.[3,4] This hypothesis stems from Hammett's important observation that, when rate coefficients for a reaction at several mineral acid concentrations above 1 M are available, log k_ψ[5] is sometimes linearly related to $-H_0$ and other times linearly related to log[HX]. Reactions in the former category give curves when log k_ψ is plotted against log[HX], and *vice versa*.

Hammett postulated that when log k_ψ was linear with $-H_0$, transformation of the protonated substrate (SH$^+$) to transition state did not involve reaction with water, and that when log k_ψ was linear with log[HX] transformation of SH$^+$ to transition state required a molecule of water.

These principles seemed to work pretty well,[6] but in time several inconsistencies were noted. Recently the Zucker–Hammett hypothesis has been sharply criticized.[7–11] Indeed, this subject has become so troubled that R. P. Bell said in the preface of a recent book,[12] "I . . . had originally intended to add a chapter on reaction kinetics in these (concentrated) solutions; however, this was finally abandoned in view of the confused state of the subject at present."

One difficulty with the Zucker–Hammett approach is that few reactions fit the two categories perfectly. A perfect fit would be a straight line

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(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 273–277.

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