

The Steric Factor in the Diels-Alder Reaction. II. Anthracene with Alkylmaleic Anhydrides and Alkylfumaric acids

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Eleven substituted maleic anhydrides, ten substituted fumaric acids and the two parent compounds have been subjected to the Diels-Alder reaction with anthracene at 142–143° in refluxing propionic acid. Twelve new diene addition products have been prepared by these reactions and characterized. Except in the case of branched fumaric acids, the expected adducts have been isolated. A method employing spectrophotometric techniques has been employed for determination of the concentration of anthracene present in the crude reaction mixture, and equilibrium and rate constants have been calculated from the spectrophotometric data. Replacement of the five-membered anhydride ring of the maleic anhydrides by the two *trans* carboxyl groups of the fumaric acids results in large decreases in both forward rate and equilibrium constants. Branching at the α -position is effective in decreasing forward rate and equilibrium constants for both series of compounds.

Branching at the β -position is effective in decreasing forward rate constants in the case of the substituted fumaric acids, but has little effect upon the forward rate constants in the case of the substituted maleic anhydrides. Branching at this position decreases the reverse rate constants for the maleic anhydrides and hence the equilibrium constants. Branching at the γ -position is less effective than at either of the two other positions.

A general theory has been developed to account for the observed results.

Examination of two of the reactions at lower temperatures permits calculation of ΔH and ΔS values and reveals a significant dependence of the free energy value on the entropy change, thus substantiating the steric character of the differences observed between dienophiles.

In 1938, Bachmann and Kloetzel³ found it necessary to postulate an equilibrium between maleic anhydride, diene and adduct.

Recently Brown⁴ has employed Bachmann's data in a theoretical treatment of equilibrium in the Diels-Alder reaction. For these closely related compounds, he assumes that the entropy of the reaction is independent of the hydrocarbon involved and that the differences in the free energy of reaction are due to differences in the heat of reaction. The differences in heat of reaction are represented in differences in the "para-localization" energy, *i.e.*, localization of two of the π -electrons of the conjugated hydrocarbon to form the two new carbon-carbon bonds.⁵ This concept is equivalent to a description of the system in terms of changes in resonance energy.

The importance of steric factors in the dienophile has not been studied systematically. Bachmann and Scott⁶ attributed the differences in rates of reaction of maleic and fumaric acids and their derivatives toward anthracene to a combination of steric and electronic factors. More recently one of us has studied the reactions of bromomesaconic acid and bromocitraconic anhydride with anthracene.⁷ In both cases it was possible to isolate only the

adduct of bromocitraconic anhydride and anthracene. This phenomenon has been attributed to a combination of steric and electronic effects suggesting that the steric effect of the bromine is accentuated when it is present with a methyl group in the dienophile.

The present study was undertaken to provide information relative to the rate and equilibrium constants for a typical Diels-Alder reaction, in order to gain some insight into the operation of purely steric factors in the dienophile. The choice of a diene involved the selection of a compound which when placed in contact with appropriate dienophiles under the proper reaction conditions would undergo the Diels-Alder reaction exclusively with the production of a single product. Moreover, a diene whose concentration could be readily ascertained seemed desirable. Accordingly, anthracene was selected.

The study necessitated the selection of a family of compounds in which the steric factor could be systematically varied. It seemed desirable to choose as the first member of the series a planar molecule which could readily be altered by substitution of appropriate groups to form dienophiles of varying steric requirements. A series of substituted maleic anhydrides was selected. It was also of interest to compare the effect of substituents in the corresponding *trans* diacids, the first member of which is not so rigidly planar as is maleic anhydride. In this case, the steric requirements of the carboxyl groups might be expected to enhance the steric requirements of the molecule as a whole; but the total steric factor in this series should not be expected to parallel that of the other series since steric factors are not necessarily additive.

The complete list of dienophiles appears in Table

(1) Abstracted from a portion of the Ph.D. dissertation of Kathryn G. Spackman, University of Michigan, 1954.

(2) University Fellow 1952–1953, Horace H. Rackham Predoctoral Fellow 1953–1954.

(3) W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 481 (1938).

(4) R. D. Brown, *J. Chem. Soc.*, 1612 (1951).





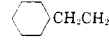
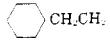

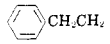
(5) R. D. Brown, *J. Chem. Soc.*, 691 (1950).

(6) W. E. Bachmann and L. B. Scott, *J. Am. Chem. Soc.*, **70**, 1458 (1948).

(7) W. R. Vaughan and K. M. Milton, *J. Org. Chem.*, **16**, 1748 (1951).

I. In most cases the fumaric acid corresponding to the maleic anhydride was also prepared. In the case of bromo-, phenyl-, and β -phenylethyl- substituents, which were introduced primarily to study electronic effects, only one member of each pair was synthesized.

TABLE I
DIENOPHILES

Substituted Maleic Anhydrides		Substituted Fumaric Acids	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{C} \\ \parallel \quad \diagup \\ \text{H}-\text{C}-\text{C} \\ \parallel \quad \diagdown \\ \text{O} \end{array}$		$\begin{array}{c} \text{R}-\text{C}-\text{CO}_2\text{H} \\ \parallel \\ \text{HO}_2\text{C}-\text{C}-\text{H} \end{array}$	
Compound Index	R	Compound Index	R
I _M	H	I _F	H
II _M	CH ₃	II _F	CH ₃
III _M	CH ₃ CH ₂	III _F	CH ₃ CH ₂
IV _M	CH ₃ CH ₂ CH ₂	IV _F	CH ₃ CH ₂ CH ₂
V _M	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \end{array}$	V _F	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \end{array}$
VI _M	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \end{array}$	VI _F	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \end{array}$
VII _M	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CHCH}_2 \end{array}$	VII _F	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CHCH}_2 \end{array}$
VIII _M		VIII _F	
IX _M		IX _F	
X _M		X _F	
XII _M		XI _F	
XIII _M	Br		

Five distinct groups were chosen, four designed to evaluate aspects of the steric factor and one to ascertain the relative importance of the electronic factor. The groups have been summarized below.

A. Increase of chain length from zero to five carbon atoms. Compounds: I, II, III, IV, and VI.

B. Replacement of α -hydrogens by methyl or methylene groups. Compounds: II, III, V, and VIII.

C. Replacement of β -hydrogens by methyl or methylene groups. Compounds: III, IV, VII, and IX.

D. Replacement of the γ -hydrogens by methyl or methylene groups. Compounds: IV, VI, and X.

E. Evaluation of the importance of electronic effects: Comparison of compounds: XIII and II; XI and X. Discussion of XII.

It was desirable to choose conditions which would assure attainment of equilibrium within a reasonable length of time with the production of a detectable quantity of adduct even in cases least favorable to adduct formation. Since the *trans* diacids

react very slowly and anthracene decomposes both photochemically and thermally (as shown by exploratory work), a solvent was chosen which would permit equilibrium to be attained as rapidly as possible. Propionic acid was selected as the solvent having the most desirable characteristics. It will dissolve at least 0.2 mole of anthracene per liter at reflux temperatures and 0.02 mole per liter at room temperature; the initial concentration of reactants was therefore chosen as 0.2 *molar* in each species. A 10-fold dilution of the hot solution prevents precipitation of anthracene from the cooled solution if the reaction proceeded to only a small degree. Since anthracene concentrations of *ca.* 5–50 mg./l. are most readily measured using a Cary ultraviolet spectrophotometer, one or two additional 10-fold dilutions were required.

The fumaric acids reacted *ca.* ten times more slowly than the maleic anhydrides, therefore, relative rates (apparent rate constants) were measured after periods of time differing by about the same factor in order to place results on a comparable scale.

A number of the dienophiles required for this study were new compounds and their preparation has been reported elsewhere.⁸ The remaining dienophiles were prepared by known procedures.

The new adducts were isolated and characterized. Due to the appearance of anomalous products in the case of several of the more complex fumaric acids, the preparative reactions were carried out under the conditions used in the determination of the equilibrium constants. Some of the fumaric acid adducts were prepared in boiling toluene to minimize decomposition. Table II lists the possible adducts. In the cases of isobutyl- and cyclohexylmethyl-fumaric acids, no adduct could be isolated due to very unfavorable equilibrium concentrations. In the cases of isopropyl-, cyclopentyl, β -cyclohexylethyl-, and β -phenylethyl-fumaric acids only the *cis* anhydride adducts were isolable. Since the conditions for adduct formation were considerably less drastic than those required to prepare the dienophilic anhydrides from the corresponding fumaric acids (*e.g.*, distillation from phosphorus pentoxide or prolonged heating with acetyl chloride > 100°; *cf.* ref. 8), it may be assumed that in these reactions normal addition first occurred and was followed by acid-catalyzed isomerization.^{8b}






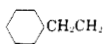
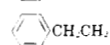
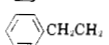

EVALUATION OF THE METHOD

Random errors. Two sources of random errors were considered: uncertainties in measured concentrations and errors in the final results. The former is greatest for reactions which have proceeded least

(8) W. R. Vaughan and K. S. Andersen, *J. Am. Chem. Soc.*, **77**, 6702 (1955).

(8b) W. R. Vaughan, R. L. Craven, R. Q. Little, and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **77**, 1594 (1955).

TABLE II
POSSIBLE ADDUCTS

cis-Anhydrides		trans-Diacids	
Compound Index	R	Compound Index	R
I _C ^a	H	I _T ^a	H
II _C ^a	CH ₃	II _T ^a	CH ₃
III _C ^a	CH ₂ CH ₂	III _T ^a	CH ₂ CH ₂
IV _C ^a	CH ₂ CH ₂ CH ₂	IV _T ^a	CH ₂ CH ₂ CH ₂
V _C ^a	CH ₃ > CH	V _T ^b	CH ₃ > CH
VI _C ^a	CH ₃ CH ₂ CH ₂ CH ₂	VI _T ^a	CH ₃ CH ₂ CH ₂ CH ₂
VII _C ^a	CH ₃ > CHCH ₂	VII _T ^b	CH ₃ > CHCH ₂
VIII _C ^a		VIII _T ^b	
IX _C ^a		IX _T ^b	
X _C ^a		X _T ^b	
XI _C ^a		XI _T ^b	
XII _C ^a			
XIII _C ^a	Br		

^a Isolated in this study or previously. ^b Desired, but not isolated.

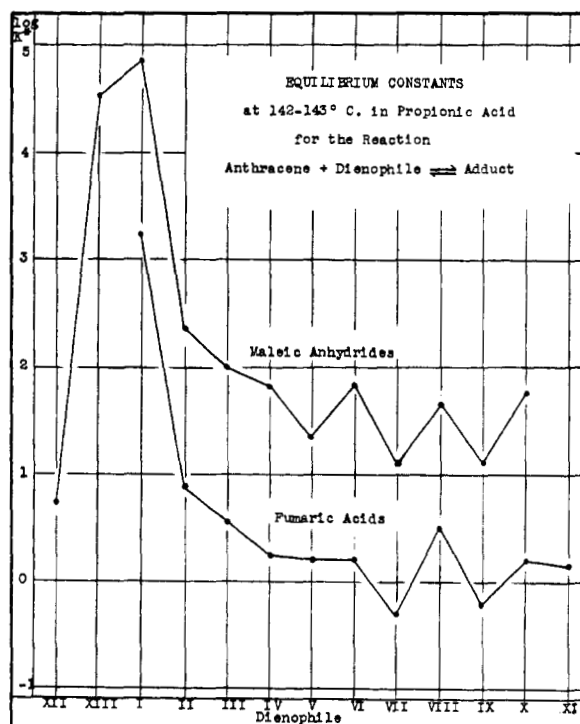
far. In addition the necessity of using a "blank" curve for thermal decomposition of anthracene leads to greatest uncertainty for reactions which have proceeded least far and have been heated for the longest periods. The errors in the final results are relatively large either when the forward reaction has proceeded essentially to completion or when the production of adduct is essentially negligible. Best equilibrium data, therefore, are available for reactions in which the concentrations of the product and of the adducts are about the same. This statement also applies to rate constants, and under optimal conditions it is possible to evaluate either rate or equilibrium constants which are associated with a random error of 2-5% by the method used (cf. ref. 1).

Systematic errors. A systematic error arises from the use of a "blank", which is defined as the difference between the theoretical concentration of anthracene if no thermal decomposition occurs and the actual measured concentration of anthracene for any given heating period. Better internal agreement was obtained by using the "blank" in calculation or measurement of all concentrations (i.e., anthracene, dienophile and adduct). The systematic error inherent in this procedure is certainly as large as, if not larger than, the random error. A detailed study

of the *n*-propylmaleic anhydride-anthracene reaction (cf. ref. 1) indicates that the procedure affords consistent results. The "blank" may encompass the mode of decomposition of species other than anthracene as well as of anthracene, or the agreement may be purely fortuitous.

RESULTS

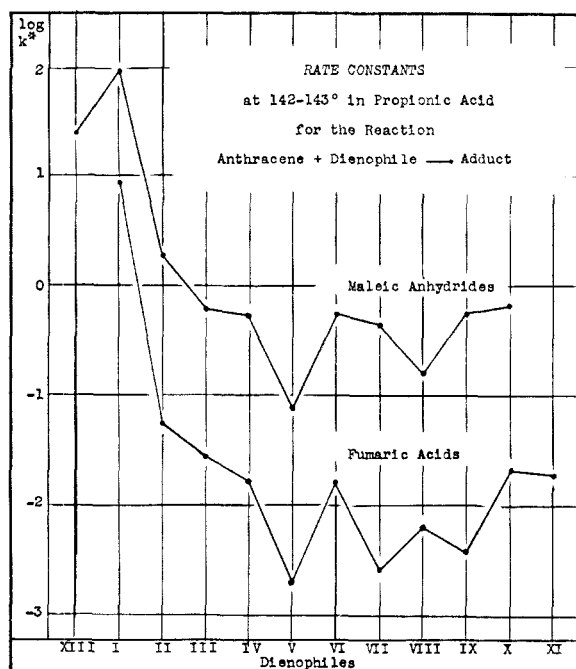
The equilibrium and rate constants are shown in Tables III, IV, and V. In addition, the data in Tables III and IV are presented graphically in Figures 1 and 2. The logarithms of the constants have been plotted for convenience. An examination of Figures 1 and 2 reveals that either set of constants differs by a factor of ten or more for the two families of compounds under consideration. Since the constants for the families are of different orders of magnitude, this discussion deals with the relative differences within each family and not with absolute differences.



* K in l. mole⁻¹

FIGURE 1

Both sets of constants show that adduct formation is more favorable for the (substituted) maleic anhydrides. Inspection of the equilibrium data (Figure 1, Table III) reveals three fundamental differences between the two families of compounds. If the trend for the substituted maleic anhydrides is taken as a standard, it can be said that the equilibrium constants for the isopropyl-, cyclopentyl-, and β-cyclohexylmethyl-fumaric acids are somewhat larger than might be expected. In each of these cases, only an adduct having the *cis*-an-



* k in $l. \text{ mole}^{-1} \text{ hr.}^{-1}$

FIGURE 2

TABLE III

EQUILIBRIUM CONSTANTS AT 142–143°

R	Maleic Anhydrides K (l./mole)	Fumaric Acids K (l./mole)	K_F/K_M $\times 10^2$
H	70000 \pm 9000	1720 \pm 60	2.4
CH ₃	229 \pm 7 ^a	7.27 \pm 0.12	3.2
C ₂ H ₅	96.0 \pm 2.4	2.55 \pm 0.05	2.7
<i>n</i> -C ₃ H ₇	64.5 \pm 1.2 ^b	1.72 \pm 0.04	2.7
<i>i</i> -C ₃ H ₇	22.0 \pm 0.4	1.61 \pm 0.04 ^c	7.3
<i>n</i> -C ₄ H ₉	66.8 \pm 1.6	1.61 \pm 0.05	2.4
<i>i</i> -C ₄ H ₉	12.3 \pm 0.2	0.38 \pm 0.03 ^c	3.1
cyclo-C ₅ H ₉	42.2 \pm 1.3	3.08 \pm 0.09 ^c	7.3
cyclo-C ₆ H ₁₁ CH ₂	12.6 \pm 0.2	0.61 \pm 0.03 ^c	4.8
cyclo-C ₆ H ₁₁ C ₂ H ₄	56.7 \pm 1.0	1.53 \pm 0.04 ^c	2.7
C ₆ H ₅	5.43 \pm 0.08		
Br	34000 \pm 5000		
C ₆ H ₅ C ₂ H ₄		1.43 \pm 0.04 ^c	

^a 788 at 131.5° \pm 0.5°. ^b 322 at 131.5° \pm 0.5°. ^c Apparent equilibrium constants. In these cases the expected product was not isolated.

hydride structure could be isolated from the reaction mixture (*vide supra*). In the case of the forward rate constants (Figure 2, Table IV), again choosing the substituted maleic anhydride trend as a standard, the most apparent differences between the two families are the decreased rate constants for isobutyl- and cyclohexylmethyl-fumaric acids, in which reactions no adduct of any kind could be isolated.

DISCUSSION AND CONCLUSIONS

Results of the investigation designed to evaluate the influence of the steric factors upon the magnitude of the forward rate constant, the reverse rate

TABLE IV

APPARENT RATE CONSTANTS FOR THE FORWARD REACTION AT 142–143° IN REFLUXING PROPIONIC ACID

R	Maleic Anhydrides k (l. mole ⁻¹ hr. ⁻¹)	Fumaric Acids k (l. mole ⁻¹ hr. ⁻¹)	k_F/k_M $\times 100$
H	92.6 \pm 4.9	8.49 \pm 0.13	9.2
CH ₃	1.09 \pm 0.02	0.0561 \pm 0.0018	5.2
C ₂ H ₅	0.615 \pm 0.018	0.0275 \pm 0.0017	4.5
<i>n</i> -C ₃ H ₇	0.542 \pm 0.017	0.0166 \pm 0.0015	3.1
<i>i</i> -C ₃ H ₇	0.076 \pm 0.013	0.0020 \pm 0.0011 ^a	2.6
<i>n</i> -C ₄ H ₉	0.562 \pm 0.017	0.0170 \pm 0.0015	3.0
<i>i</i> -C ₄ H ₉	0.453 \pm 0.017	0.0026 \pm 0.0010 ^a	0.57
cyclo-C ₅ H ₉	0.168 \pm 0.014	0.0065 \pm 0.0010 ^a	3.9
cyclo-C ₆ H ₁₁ CH ₂	0.588 \pm 0.019	0.0037 \pm 0.0010 ^a	0.63
cyclo-C ₆ H ₁₁ C ₂ H ₄	0.667 \pm 0.019	0.0208 \pm 0.0011 ^a	3.1
Br	25.8 \pm 0.6		
C ₆ H ₅ C ₂ H ₄		0.0188 \pm 0.0011 ^a	

^a Rate constant calculated from the simple bimolecular rate expression,

$$k = \frac{MA_t}{Dt(D - A_t)}$$

TABLE V

APPARENT RATE CONSTANTS FOR THE REVERSE REACTION AT 142–143° IN REFLUXING PROPIONIC ACID

R	Maleic Anhydride Adducts k_{-1} (hr. ⁻¹)	Fumaric Acid Adducts k_{-1} (hr. ⁻¹)
H	0.0013 \pm 0.0002	0.0049 \pm 0.0002
CH ₃	0.0048 \pm 0.0002	0.0077 \pm 0.0003
C ₂ H ₅	0.0064 \pm 0.0002	0.0108 \pm 0.0007
<i>n</i> -C ₃ H ₇	0.0084 \pm 0.0003	0.0097 \pm 0.0009
<i>i</i> -C ₃ H ₇	0.0035 \pm 0.0006	
<i>n</i> -C ₄ H ₉	0.0084 \pm 0.0003	0.0106 \pm 0.0010
<i>i</i> -C ₄ H ₉	0.0368 \pm 0.0014	
cyclo-C ₅ H ₉	0.0040 \pm 0.0003	
cyclo-C ₆ H ₁₁ CH ₂	0.0467 \pm 0.0017	
cyclo-C ₆ H ₁₁ C ₂ H ₄	0.0118 \pm 0.0004	
Br	0.00076 \pm 0.00011	

constant, and the equilibrium constant may be summarized in several general statements: 1. Replacement of the five-membered anhydride ring by two *trans* carboxyl groups results in a large decrease in both forward rate constants and equilibrium constants. 2. Replacement of the unsubstituted dienophile by the methyl substituted dienophile gives rise to a larger decrease in forward rate and equilibrium constants than replacement of the methyl group by any alkyl groups under investigation. This effect must be considered to be partially electronic in character. 3. Rate constants for the forward reaction are most affected by the presence of α -substituents in the case of the substituted maleic anhydrides. In the case of the substituted fumaric acids, β -substituents appear to be almost as effective as α -substituents in decreasing the magnitude of the forward rate constant. 4. In the case of substituted maleic anhydrides the reverse rate constant is most affected by the presence of alkyl substituents

in the β -position. The nature of the γ -substituents appears to influence the magnitude of the reverse rate constant also, but it is unaffected by the nature of α -substituents.

A general theory may be developed to account for the observed results. The theory rests on the following hypotheses: 1. The reaction is assumed to proceed by the mechanism proposed by Woodward,^{9a} which assigns rate control to the transformation of an intermediate dipolar-biradical complex into the adduct. 2. The dienophile must assume a conformation such that the molecule is essentially flat on one side before the addition to the diene can occur. 3. In this conformation the oxygens (three in the case of the anhydrides, four in the case of the acids) and two olefinic carbons are coplanar (this plane will hereafter be referred to as "the plane") so that hybridization involving the π -electrons in these groups can occur in the intermediate complex. In other words, the position which these nuclei assume just prior to addition is retained in the intermediate and is such that maximum hybridization of the dienophilic portion of the intermediate is possible. 4. Factors which decrease the possibilities for the above-described conformation, will decrease the forward rate constant. In terms of the Arrhenius theory, the frequency factor will be decreased, and in terms of the absolute reaction rate theory, the equilibrium constant involving the reactants and intermediate complex will be decreased. 5. Factors which increase the possibilities for loss of the above-described conformation in the loosely associated intermediate will increase the reverse rate constant, if rate control in the reverse reaction is in complex dissociation. 6. Fisher-Hirschfelder models may be used adequately to describe the steric factors under consideration.

In considering steric effects in the Diels-Alder reaction, there are two obvious ways in which the size of the equilibrium constant can be reduced. The first embodies primarily orientation *prior* to complex formation, since a large steric factor should tend to work against the required precise orientation. This should be reflected in the entropy term. Since it is assumed that the rate-controlling step is the transition from intermediate complex to adduct,^{9a} a large steric factor should affect the rate through minimizing the concentration of complex.^{9b} In effect, this could lead to passage of rate control from the usual step^{9a} to formation of the complex. The second mode of steric influence is found in the factors which would lead to more facile transition from complex to adduct, *e.g.*, internal repulsions favoring formation of the adduct from the complex (a type of B-strain). For example,

there is more room for the substituent to rotate in the folded-back adduct than in the "sandwich" biplanar complex. This should be reflected in the enthalpy term and should result in an increase in the heat of reaction with increasing steric requirements.

In order to test this hypothesis two typical reactions in the present series were examined at a temperature some 11° lower than the standard otherwise employed. The dienophiles were citraconic anhydride and *n*-propylmaleic anhydride, and the foregoing assumptions were found to be correct. With ΔH and ΔS essentially constant over this range, ΔF for each reaction at each temperature was calculated, and from the equation $\Delta F = \Delta H - T(\Delta S)$, ΔH and ΔS were obtained for each reaction. For citraconic anhydride plus anthracene, $\Delta H = -37.5$ kcal./mole and $\Delta S = -69.4$ cal./degree/mole; for *n*-propylmaleic anhydride plus anthracene, $\Delta H = -48.9$ kcal./mole and $\Delta S = -109.3$ cal./degree/mole. Thus, the more significant difference in the character of the two reactions appears to lie in the entropy term, as would be expected if the difference in behavior is attributable essentially to a steric factor. Values for the equilibrium constants at the lower temperature are included in Table III. With these data at hand it now becomes possible to examine the steric effects on the forward and reverse rate constants and on their quotient, the equilibrium constant.

Influence on the forward rate constant. In order for the dienophile to assume the proper conformation just prior to addition, the carboxyl carbons and oxygens and the olefinic carbons must become coplanar, and further, the bulk of any substituent group present must not fall below this plane in the event of attack from below by the diene.

In the case of the maleic anhydrides, the anhydride structure assures formation of the plane. The only factor which need be considered is the ease of formation of the proper conformation with respect to the substituent group. Models indicate that the only hindrance to free rotation of the alkyl substituent about the bond joining it to the olefinic carbon is the presence of the unsubstituted hydrogen attached to the olefinic double bond. In the case of alkyl substituents which are highly branched in the α -position, *e.g.*, isopropyl and cyclopentyl substituents, models reveal that there is only one position which the group may assume such that attack from a given side of the plane is possible. When branching occurs farther out in the chain, models indicate that the number of acceptable conformations for the alkyl group increases many fold. Thus, branching on the α -carbon should be more significant and should affect the rate of the reaction by decreasing the ease of complex formation, *i.e.*, minimization of instantaneous complex concentration.

In the case of the fumaric acids, not only the conformation of the alkyl substituents but also the

(9a) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 3058 (1942).

(9b) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 6284 (1955).

formation of the plane must be considered. Assuming that the acidic hydrogens are not associated with particular oxygens in the carboxyl groups in the ionizing medium in which the reactions were carried out, formation of the plane involves but two possible positions for the carboxyl groups. Models indicate that in the unsubstituted compound rotation of the carboxyl groups is relatively free; however, the mere restriction to two conformations appears to be sufficient to account for the large difference in rate constants observed for the two families of compounds.

Once the plane has been formed, the alkyl substituent must assume the proper conformation with respect to the plane. In this case, models indicate that the prime hindrance to free rotation of the alkyl substituent is the adjacent carboxyl group, although the other carboxyl group is not without effect. In the case of the fumaric acids the presence of the carboxyl groups serves to restrict rigidly the rotation of substituents which are branched in both the α - and β -positions. This accounts for the observed large decrease in rate constant which is apparent for substituents which are branched in the β -position in the fumaric acids and the absence of such an effect in the substituted maleic anhydrides.

Influence on the reverse rate constant. The steric factors which lead to an increase in heat of reaction (the B-strain discussed above) may effect a decrease in the reverse rate constant, if rate control be in the transition from adduct to complex, or should produce an increase if the rate controlling process is dissociation of the complex into addends. Since the present data reveal an *increase* in the reverse rate constant (*cf.* citraconic anhydride and *n*-propylmaleic anhydride reactions) it follows that rate control for the reverse reaction is vested in dissociation of the complex. Accordingly, any increase in steric demands of the dienophilic portion of the adduct should facilitate dissociation of the complex into addends—which is observed. However, two anomalies appear. The isopropyl and cyclopentyl groups are *less* effective in promoting dissociation than the ethyl group; and β - and γ -branching (*cf.* the isobutyl, cyclohexylmethyl, and cyclohexylethyl groups) are far more effective than α -branching in promoting dissociation, with β the most effective of all. These facts support the contention that rate control is in the dissociation step, since otherwise a decrease in the reverse rate constant would be expected owing to greater B-strain in the complex than in the adduct. But it raises another question. Why should β - (or γ -) branching apparently promote dissociation of the complex and yet at the same time promote the forward reaction?

Models indicate that rotation of groups which are highly branched at the α -position is difficult in a substituted maleic anhydride, whereas there is freer rotation in β - and γ -branched maleic anhydrides. Accordingly, relatively little is to be gained energetically by dissociation of a complex wherein

there is an α -branched substituent. However, upon dissociation of a β - (or γ -) branched complex there should be a substantial entropy increase. On the other hand, little entropy is to be lost in passing from a β - (or γ -) branched complex to the adduct whereas considerable strain may be relieved. In other words, the tendency of the complex to dissociate or to pass over to the adduct is governed by a balance between the entropy and energy factors involved. Apparently the dissociation tendency is at a maximum where substantially greater freedom of rotation is to be gained by separation into the adducts; and this maximum occurs where there is β -branching and decreases when the branching recedes from or approaches the incipient double bond. Models tend to give weight to such an hypothesis.

In the fumaric acids, branching even as far out as the γ -position gives rise to restricted rotation of the alkyl substituent and consequently no such increased tendency to dissociate should be observed. Unfortunately, however, data for reverse rate constants are not available for any branched compounds. But the possibility of rotation of the carboxyl groups exists. Such rotation would be more likely to occur in the unsubstituted compound in which restrictions are slight and this may account for the fact that the unsubstituted fumaric acid has a larger reverse rate constant than that observed for the unsubstituted maleic anhydride. Models indicate that even the presence of a methyl group may be sufficient to restrict seriously rotation of one of the carboxyl groups, and this may well account for the relative differences in magnitudes of the reverse rate constants in the two series.

Influence on equilibrium constants. The preceding sections have pointed up the factors influencing the forward and reverse rate constants whose quotient is the equilibrium constant. The arguments therein advanced lead to the following conclusions.

Since in both families (maleic and fumaric dienophiles) of reactions the size of the reverse rate constant is essentially unaffected by α -branching, the equilibrium constants for reactions involving α -branched dienophiles are mainly a reflection of the forward rate constants. For the same reasons the equilibrium constants for reactions of β -branched fumaric acids reflect the forward rate constants, and a similar argument may be made for reactions of γ -branched fumaric acids. Likewise, since the size of reverse rate constants for reactions of β - (and to a lesser extent γ -) branched maleic anhydrides is greatly increased while the related forward rate constants are essentially unaffected, the equilibrium constants for reactions of such dienophiles reflect the reverse reaction rate constants. And finally, smaller equilibrium constants are to be expected where there is α - (or to a lesser extent β -) branching than where branching occurs farther out, or where there is no branching.

In thermodynamic terms these conclusions may

be stated as follows. Where the equilibrium constant is a reflection of the forward rate constant, there is a large entropy factor involved which arises from the requirement of precise orientation prior to complex formation. Where such precise ordering of the system is rendered difficult by steric factors immediately adjacent to the olefinic bond, the entropy term will dominate the enthalpy term and result in a decrease in free energy, even though a more favorable heat of reaction is achieved by the same steric factors. Where steric factors are somewhat more remote from the reactive center of the dienophile the entropy term remains large, owing to a loss in freedom of rotation of the substituent in the adduct as compared with the dienophile, whereas the enthalpy term may actually increase substantially.

It may be inferred in terms of the Arrhenius rate theory that steric control of the forward reaction, as reflected in the frequency factor, reaches a maximum where there is branching on a carbon attached to the double bond of the dienophile. Where bulky groups are more remote the frequency factor decreases, but steric control is exerted through the energy term and must be attributed to simple repulsion (F-strain for the forward reaction, B-strain for the reverse). It is difficult to visualize substantial differences in frequency factors for the reverse reactions, and consequently the more favorable rate constants for β - (and to a less extent γ -) branched dienophile adducts must be attributed to the energy term. Sterically such an effect is imaginable in terms of B-strains which would tend to force apart the reaction centers, thus recreating the more nearly planar portions of the complex.

In conclusion it must be emphasized that the arguments herein advanced are not necessarily applicable to dienes which are less symmetrical than anthracene or which possess symmetrical substituents about the dienic structure less (or more) bulky than the benzenoid rings of anthracene. For example, steric factors in an alkylmaleic anhydride would probably be insignificant, in a reaction with 1,3-butadiene, whereas a 2,6- or 2,3,6,7-symmetrically alkylated anthracene might increase in the dissociation rate for a γ -branched alkylmaleic anhydride over a β -branched one.

Electronic factors. A brief consideration of electronic factors on the basis of the reactions of compounds X_F , XI_F , XII_M , and $XIII_M$ is in order. It is of interest to compare bromomaleic anhydride ($XIII_M$) and citraconic (methylmaleic) anhydride (II_M). The 23-fold increase in rate constant and the more than 100-fold increase in equilibrium constant found in replacing the methyl group by a bromine indicate the very great importance of electronic factors in the vicinity of the olefinic double bond. Differences of such a magnitude are also encountered in comparison of the unsubstituted with the methyl substituted compound.

The question has been raised whether halogens exert a favorable or unfavorable electronic effect on

the Diels-Alder reaction.^{9b} If their effect be unfavorable, it must be by virtue of the +M effect alone, since by its nature the reaction cannot call into play the +E effect. If it is favorable, it must be by virtue of *net* electron withdrawal, a -I effect overshadowing the +M effect. It is only reasonable to suppose that this is so, since even in electrophilic aromatic substitution, where the +E effect reinforces the +M effect, net ring deactivation is observed. Consequently any unfavorable effect on rate and position of equilibrium in the Diels-Alder reaction due to halogen must be steric, and the electronic effect must on the whole be favorable.

The +I effect of an alkyl group is relatively small, and, therefore, the methyl group should produce a small rate decrease (compared to hydrogen) and a similarly small decrease in equilibrium constant. But large decreases in both rate and equilibrium constants are observed. These, then, must be principally steric effects. One of us has pointed out the similarity of steric requirements of bromine and methyl,⁷ and thus the more favorable constants for bromomaleic anhydride (compared to those of citraconic anhydride) support the argument for bromine's generally favorable electron withdrawing effect.

Since β -cyclohexylethylfumaric acid (X_F) and β -phenylethylfumaric acid (XI_F) possess equal steric requirements, the presence of electronic factors at the β -position exerts no detectable effect whatsoever upon the rate constant. (The equilibrium constants for these reactions cannot be considered, since *cis*-anhydride adducts were isolated in both cases; and isomerization is more probable *after* addition to the diene, as discussed above.) Thus, it is reasonable to consider the rate constants which may be calculated by use of the simple bimolecular expression.

Phenylmaleic anhydride (XII_M) proved different from the other substituted maleic anhydrides in two ways. First, equilibrium was established by the end of two hours of heating whereas the other compounds required one to eight days, *i.e.*, the rate is anomalously great. (The method used was not designed to employ heating periods of less than two hours, consequently no exact rate data are available.) Second, the equilibrium is singularly unfavorable for a maleic anhydride. The first phenomenon may be attributed to the -M and -E effects of the phenyl group, and in the absence of actual kinetic data, it is tentatively suggested that the unfavorable equilibrium be attributed to a large steric requirement coupled with the electronically unfavorable loss of conjugation in the adduct.

EXPERIMENTAL¹⁰

Fumaric acids. Fumaric acid (I_F), Paragon Testing Laboratories, recrystallized from water to constant m.p.

(10) Melting points are uncorrected.

285.5–286.5° (sealed tube); lit.¹¹ m.p. 286–287° (sealed tube).

Mesaconic acid (II_F), Smith Organic Chemicals (New York), recrystallized from water to constant m.p. 201.5–202.5°; lit.¹² m.p. 202°.

The remaining fumaric acids are listed in Table VI.

acid synthesized according to the procedure of Lapworth and Baker²¹ was transformed to phenylsuccinic anhydride by the action of acetyl chloride.²² Phenylmaleic anhydride, m.p. 119.0–120.0° (lit.²⁰ m.p. 119.0–120°) was prepared from phenylsuccinic anhydride by the action of N-bromosuccinimide in 50.0% yield. When a glass stirring paddle

TABLE VI
ALKYL FUMARIC ACIDS PREPARED FOR THIS STUDY

	$\begin{array}{c} \text{R}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{HO}_2\text{C}-\text{CH} \\ \\ \text{R} \end{array}$	M.P., °C.	Reported M.P., °C.	Ref.	Yield, %
III _F	C ₂ H ₅	195.0–196.0	193.0	13	32.2
IV _F	<i>n</i> -C ₃ H ₇	173.0–174.0	173.0	13	31.6
V _F	<i>i</i> -C ₃ H ₇	185.0–186.0	186.0–187.0	13	33.4
VI _F	<i>n</i> -C ₄ H ₉	169.0–170.0	170.0	14	27.8
VII _F	<i>i</i> -C ₄ H ₉	184.5–185.5	185.0	13	25.6
VIII _F	cyclo-C ₅ H ₉	230.5–231.5	new	8	36.9
IX _F	cyclo-C ₆ H ₁₁ CH ₂	204.5–206.0	new	8	28.7
X _F	cyclo-C ₆ H ₁₁ C ₂ H ₄	224.0–224.5	new	8	27.7
XI _F	C ₆ H ₅ C ₂ H ₄	198.5–200.0	new	8	13.7

Maleic Anhydrides. *Maleic Anhydride* (I_M), Eastman Kodak, distilled at reduced pressure, m.p. 202.5° sublimed; lit.¹⁵ m.p. 202.0°.

The alkylmaleic anhydrides were prepared from the corresponding fumaric acids by the method of Tanatar¹⁶ by distillation from phosphorus pentoxide, as described in ref. 8. They are listed in Table VII.

was substituted for a nichrome Herschberg stirrer during the course of the reaction with N-bromosuccinimide, a bromine-free product could not be obtained.

Bromomaleic anhydride was prepared by the following series of reactions. α,β -Dibromosuccinic acid prepared by aqueous bromination of fumaric acid at 100°²³ was distilled three times from phosphorus pentoxide according to Mil-

TABLE VII
ALKYLMALEIC ANHYDRIDES PREPARED FOR THIS STUDY

$\begin{array}{c} \text{R}-\text{C} \\ \\ \text{H}-\text{C} \end{array} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$	Observed		Reported		Ref.	Yield, %	n_D^{25}
	B.P., °C.	Mm.	B.P., °C.	Mm.			
CH ₃	109	30	122	43	17	76.0	1.4692
C ₂ H ₅	119	28	104	15	18	66.6	1.4670
<i>n</i> -C ₃ H ₇	124	30	152–153	68	19	42.9	1.4658
<i>i</i> -C ₃ H ₇	121	30	138	61	19	76.0	1.4631
<i>n</i> -C ₄ H ₉	135	30	new		8	77.9	1.4654
<i>i</i> -C ₄ H ₉	134	30	new		8	45.5	1.4642
cyclo-C ₅ H ₉	95	0.7	new		8	84.3	1.5002
cyclo-C ₆ H ₁₁ CH ₂	127	1.7	new		8	41.2	1.4980
cyclo-C ₆ H ₁₁ C ₂ H ₄	139	1.6	new		8	29.0	1.4647

Phenylmaleic anhydride was prepared according to Miller, et al.²⁰ by the following series of reactions. Phenylsuccinic

ton's²⁴ adaptation of Walden's²⁵ method. The pale yellow liquid boiled at 211.0–212.0° (lit.²⁴ m.p. 212.0–213.0°) after three distillations from phosphorus pentoxide.

Characterization of adducts. In preparing the adducts, no attempt was made to record yields. The adducts were syn-

- (11) A. Michael, *Ber.*, **28**, 1629 (1895).
 (12) T. Morawski, *J. prakt. Chem.*, [2] **11**, 430 (1875).
 (13) E. Demarcay, *Ann. de chim.*, **20**, 433 (1880).
 (14) R. Fittig and F. Fichter, *Ann.*, **304**, 241 (1899).
 (15) R. Anschütz, *Ber.*, **12**, 2280 (1879).
 (16) S. Tanatar, *Ann.*, **273**, 31 (1893).
 (17) R. Anschütz, *Ber.*, **13**, 1541 (1880).
 (18) R. Anschütz, *Ann.*, **461**, 155 (1928).
 (19) W. Ssamenow, *Zhur. Obshch. Khim.*, **23**, 430 (1891); *Zhur. Obshch. Khim.*, **30**, 1003 (1898).
 (20) L. E. Miller, H. B. Staley, and D. J. Mann, *J. Am. Chem. Soc.*, **71**, 374 (1949).

- (21) A. Lapworth and W. Baker, *Org. Syntheses*, Coll. Vol. I, 2nd Ed., 181, 451 (1941).

- (22) P. E. Verkade and H. Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

- (23) H. Rhinesmith, *Org. Syntheses*, Coll. Vol. II, 177 (1943).

- (24) K. Milton, *Dissertation*, University of Michigan, 1951, p. 60.

- (25) P. Walden, *Ber.*, **30**, 2886 (1897).

thesized in order to determine the nature of the product (*cis*-anhydride or *trans*-diacid), and to report the melting point and percentage composition.

Substituted maleic anhydride—anthracene adducts. The adducts were prepared by heating 0.01 mole (1.78 g.) of anthracene and 0.01 mole of the substituted maleic anhydride in 10 ml. of propionic acid at reflux temperature for 3 to 8 days. The solvent was removed on the steam-bath under water pump pressure. To the brown solid residue was added 4 ml. of a 45% potassium hydroxide solution and the mixture was heated on the steam-bath for 5 minutes with occasional stirring. After adding 45 ml. of water, heating and crushing of the residue was continued until no more solid appeared to dissolve (*ca.* 30 minutes). The hot mixture was extracted with hot toluene in 25-ml. portions until all solid material had dissolved (two to four extractions) and one additional time with cold toluene.²⁶ The aqueous solution was cooled and extracted with two 25-ml. portions of ether. The alkaline solution was heated on the steam-bath to expel any ether, filtered, cooled, and poured into 12 ml. of concentrated hydrochloric acid with vigorous stirring. The crude product which precipitated was filtered, washed with water and dried in air. Upon four to six recrystallizations from acetic anhydride, the white powdery material melted at constant temperature. The melting points and analytical data for these compounds appear in Table VIII.

mechanically for 1 hour at room temperature and allowed to stand for 4 hours. The basic solution was heated on the steam-bath and filtered while hot to remove unreacted anthracene.²⁷ The cooled filtrate was overacidified with concentrated hydrochloric acid and allowed to stand 5 days. After heating on the steam-bath to dissolve unreacted dienophile, the crude product was filtered from the hot solution.

2-Ethyl-dibenzo[2.2.2]bicyclooctadiene-2,3-trans-dicarboxylic Acid (III_T).²⁸ The ethyl compound, recrystallized five times from glacial acetic acid and once from aqueous ethanol, melted with sharp decomposition at 224.5°. An analysis of the compound was low in carbon percentage, indicating the presence of unreacted dienophile. The first acetic acid filtrate was concentrated to a small volume, and the second crop of crystals obtained melted at 243.0–243.4° with sharp decomposition, after two recrystallizations from glacial acetic acid. The analysis checked the calculated values (*cf.* Table IX).

2-*n*-Propyl- (IV_T) and 2-*n*-butyl-dibenzo[2.2.2]bicyclooctadiene-2,3-trans-dicarboxylic acids (VI_T). The *n*-propyl and *n*-butyl compounds recrystallized as above from glacial acetic acid and from aqueous ethanol melted with sharp decomposition at 226.8° and 229.0°, respectively. These compounds also analyzed low in carbon. The original acetic acid filtrates were concentrated to yield additional crops. The seventh crop obtained from the *n*-propyl compound

TABLE VIII

CHARACTERIZATION OF SUBSTITUTED MALEIC ANHYDRIDE-ANTHRACENE ADDUCTS

R	M.P. (°C.)	Calc'd		Found ²⁹		Ref.
		C	H	C	H	
H	263.8–264.4		lit. m.p. 264.0–264.5°			6
CH ₃ ^a	185.1–185.5					6
C ₂ H ₅	188.7–189.5	78.93	5.30	79.05	5.60	
<i>n</i> -C ₃ H ₇	137.0–137.5	79.22	5.70	79.02	5.71	
<i>i</i> -C ₃ H ₇	192.7–193.5	79.22	5.70	79.00	5.69	
<i>n</i> -C ₄ H ₉	144.5–145.0	79.49	6.06	79.31	6.16	
<i>i</i> -C ₄ H ₉	119.0–119.5	79.49	6.06	79.27	6.10	
cyclo-C ₃ H ₉	171.5–172.0	80.21	5.85	79.93	5.88	
cyclo-C ₆ H ₁₁ CH ₂	223.2–224.0	80.62	6.50	80.70	6.74	
cyclo-C ₆ H ₁₁ C ₂ H ₄	144.8–145.7	80.80	6.78	80.97	6.95	
C ₆ H ₅ ^a	166.0–168.0					20
Br	171.8–172.9		lit. m.p. 171.5–172.9°			6

^a Known compound not specifically prepared and characterized although melting point is included for completeness.

Substituted fumaric acid—anthracene adducts. The crude adducts of the ethyl, *n*-propyl, and *n*-butyl compounds were prepared by heating 0.01 mole of the substituted fumaric acid and 0.01 mole (1.78 g.) of anthracene in 10 ml. of toluene at reflux temperature for 15 days. The toluene was removed on the steam-bath with a current of air and 30 ml. of a saturated sodium bicarbonate solution was added to the cooled residue. The mixture was stirred

decomposed sharply at 231.5–232.0° but also analyzed too low in carbon. The fourth crop obtained from the *n*-butyl compound decomposed sharply at 233.8–234.5° and analyzed too low in carbon. Upon drying *in vacuo* at 180° for 2 hours these compounds analyzed satisfactorily. Then *n*-propyl compound decomposed at 240.0–240.5°, the *n*-butyl at 237.8–238.3° (*cf.* Table IX).

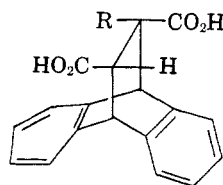
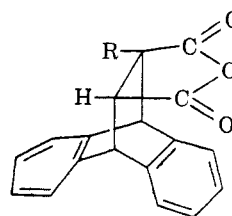
(26) In the case of the β -cyclohexylethyl compound, the solid could not be dissolved after seven toluene extractions or by the addition of 200 ml. of hot water. This material was filtered off and treated independently. A mixture melting-point determination made with this material and product obtained in the usual fashion showed no depression.

(27) The bicarbonate-insoluble residue was heated with 5 ml. of 45% aqueous potassium hydroxide for 10 minutes on the steam-bath, diluted with 15 ml. of hot water and filtered hot. Upon overacidification of the cooled solution, no precipitation occurred showing that the residue contained no *cis*-anhydride adduct.

(28) This compound was also prepared in propionic acid.

TABLE IX
CHARACTERIZATION OF SUBSTITUTED FUMARIC ACID-ANTHRACENE ADDUCTS

R	M.P. (°C.)	Type of Adduct	Calc'd		Found ²⁹	
			C	H	C	H
H	241.0-242.0 (dec.)	<i>trans</i>		lit. ³⁰ m.p. 241-242°		
CH ₃	232.1-232.4 (dec.)	<i>trans</i>				
C ₂ H ₅	243.0-243.4 (dec.)	<i>trans</i>	74.52	5.63	74.71	5.78
<i>n</i> -C ₃ H ₇	240.0-240.5 (dec.)	<i>trans</i>	74.98	5.99	74.72	6.19
<i>i</i> -C ₃ H ₇	193.3-194.0	<i>cis</i>	79.22	5.70	79.17	5.91
<i>n</i> -C ₄ H ₉	237.8-238.3 (dec.)	<i>trans</i>	75.41	6.33	75.17	6.37
cyclo-C ₅ H ₉	171.4-172.0	<i>cis</i>	80.21	5.85	80.08	5.81
cyclo-C ₆ H ₁₁ C ₂ H ₄	145.5-146.3	<i>cis</i>	80.80	6.78	80.88	6.91
C ₆ H ₅ C ₂ H ₄	215.9-216.4	<i>cis</i>	82.08	5.30	82.07	5.45

*trans*-Diacid*cis*-Anhydride

2-Isopropyl- (V_C), 2-cyclopentyl- (VIII_C), 2-β-cyclohexylethyl- (X_C), and 2-β-phenylethyl-dibenzo[2.2.2]bicyclooctadiene-2,3-*cis*-dicarboxylic anhydrides (XI_C). Crude adducts of the isopropyl, cyclopentyl, β-cyclohexylethyl, and β-phenylethyl compound were prepared by heating 0.01 mole of the substituted fumaric acid and 0.025 mole (4.46 g.) of anthracene in 17 ml. of propionic acid for 12 days at reflux temperature. The solvent was removed on the steam-bath at water-pump pressure, and the crude product was isolated following the exact procedure for the separation of the substituted maleic anhydride adducts (*vide supra*).³¹ After one recrystallization from glacial acetic acid, a rough melting point determination showed the similarity of these melting points to those of the corresponding substituted maleic anhydride adducts.³² Further recrystallizations were made using acetic anhydride (except in the case of the β-phenylethyl compound which seemed to be more effectively recrystallized from glacial acetic acid). After three to six recrystallizations from acetic anhydride, the melting points of the isopropyl, cyclopentyl, and β-cyclohexylethyl compounds were identical to the melting points of corresponding adducts prepared from substituted maleic anhydrides. In each case, mixture melting point determinations showed no depression. An analysis of the β-phenylethyl adduct showed it to be the *cis*-anhydride (*cf.* Table IX).

2-Isobutyl- (VII_T) and 2-cyclohexylmethyl-dibenzo[2.2.2]bicyclooctadiene-2,3-*trans*-dicarboxylic acids (IX_T). Numerous attempts to isolate the isobutyl and cyclohexylmethyl adducts failed. In each case only unreacted dienophile could be obtained from the basic solution upon acidification as determined by the method of mixture melting points and by the quantity of material obtained in the light of the

known equilibrium constants. In the case of the isobutyl compound, no adduct could be isolated when the reaction was run for 15 days in toluene using equimolecular quantities of starting materials or when the reaction was run in propionic acid for 15 days using a 5-fold excess of anthracene.

Attempted interconversions. (a) 2-Isopropyl-dibenzo[2.2.2]bicyclooctadiene-2,3-*cis*-dicarboxylic anhydride (V_C) (0.32 g., 0.001 mole), 0.56 g. (0.01 mole) of potassium hydroxide pellets, and 6 ml. of water were heated on the steam-bath for 16½ hours. The hot solution was filtered, cooled, and overacidified with concentrated hydrochloric acid. The white powder-like crystals were filtered, washed with water, and dried in air. The melting point of this material was identical to that of the starting material (192.0-193.0°) and a mixture melting point of the two showed no depression.³³

(b) 2-Isobutyl-dibenzo[2.2.2]bicyclooctadiene-2,3-*cis*-dicarboxylic anhydride (VII_C) was treated in the above fashion with a heating period of 48 hours. Again, only unreacted starting material could be recovered.³³

PHYSICAL MEASUREMENTS

Purification of materials. Eastman Kodak anthracene was purified to a blue-violet fluorescence by three co-distillations with ethylene glycol. The dienophiles were recrystallized to constant melting point in the case of solids or distilled through a 20-plate column in the case of liquids. Eastman Kodak propionic acid was used without additional purification.

Rate studies. These Diels-Alder reactions were carried out using equimolar quantities of diene and dienophile in refluxing propionic acid, b.p. ca. 142°. Anthracene (178.2 mg., 1.000 millimole) and dienophile (1.000 millimole) were quantitatively transferred to a microdistilling apparatus using 5.00 ml. of propionic acid. The microdistilling tube was well coated with silicone grease and the flask was lowered into an oil-bath maintained at 160-170°, which effected a reaction temperature of 142-143°. Reactions involving maleic anhydride and its derivatives were allowed to proceed for 2.00 ± 0.05 hours, those involving fumaric acid and its derivatives for 24.00 ± 0.05 hours. At least

(29) Micro-Tech Laboratories, Skokie, Illinois.

(30) O. Diels, K. Alder, and S. Beckmann, *Ann.*, **486**, 191 (1931).

(31) In the case of the β-cyclohexylethyl compound, difficultly soluble material was again formed (*cf.* preparation of substituted maleic anhydride adducts). As previously this material was treated independently and proved to be the *cis*-anhydride adduct as ascertained by a mixture melting point determination made with this material and product obtained in the usual fashion.

(32) In general, substituted maleic anhydride adducts melt without decomposition at a temperature lower than that at which the corresponding substituted fumaric acid adducts decompose.

(33) Under essentially these conditions Bachmann and Scott were able to effect substantial isomerization of the maleic and citraconic anhydride adducts to the isomeric *trans* adducts; ref. 6.

two samples of each dienophile were run. In both families of reactions the times employed were sufficiently small fractions of the total reaction time to permit calculation of apparent rate constants using only the initially equal concentrations and the concentrations after the observed intervals.

Equilibrium studies. These Diels-Alder reactions were carried out following the procedure outlined for the rate studies. Reactions involving maleic anhydrides required 1-7 days to attain equilibrium, those involving fumaric acids required 1-21 days. At least two samples were run for heating periods differing by 2 or more days (except the first member of each series and bromomaleic anhydride where equilibrium was approached from both directions.³⁴

Physical measurements. Equilibrium and rate constants were determined by a spectrophotometric analysis of the concentration of anthracene remaining in the reaction mixture after an appropriate heating period. The method used in analyzing for the concentration of anthracene was carefully standardized. Due to the large coefficient of expansion of the solvent in the temperature range of 20-30°, it was found necessary to carry out all dilution and spectrophotometric operations within a temperature range of 1.6°. These operations were undertaken in a constant temperature room maintained at 21.2 ± 0.8°. Only Kimble EXAX glassware was employed.

Calibration of Cary recording spectrophotometer. Standard solutions were made up from a stock solution containing 125.0 mg. of anthracene diluted to 250.00 ml. with propionic acid (0.5000 g./l.). Aliquots of 1.00, 2.00, 3.00, 4.00, and 5.00 ml. were taken and diluted to 50.00 ml. The spectra were recorded using matched quartz cells of ca. 1-cm. thickness, the same cell always containing the sample. Five spectra were recorded for the range 3500-4000 Å for each concentration, the instrument initially being balanced to read zero at 4000 Å in each case. The balance of the instrument was checked with pure solvent in both cells after every third spectrum. An average of the five optical density measurements for the anthracene absorption peaks at 3554 and 3734 Å was plotted vs. concentration for the above samples.³⁵

Preparation of samples. In each case the reaction mixture while still hot was quantitatively transferred to a 50-ml. volumetric flask which was placed in the constant temperature room for at least 3/4 hour before diluting to the mark. The same pipet used in taking aliquots for the calibration measurements was used in all sample dilution operations. Aliquots of 2.50 ml. were diluted to 25 ml. The original reaction mixture was diluted either 100- or 1000-fold depending upon which dilution gave the better optical density reading. For rate studies, samples were prepared 1.0 ± 0.2 hour after the reaction mixtures were removed from the bath and the spectra were recorded immediately.³⁶ No strict

(34) A number of preliminary runs was made in order to ascertain the time required for equilibrium to become established. If the concentrations of anthracene remaining differed by more than ±0.16 g./l. for the maleic anhydrides and ±0.25 g./l. for the fumaric acids for two runs heated for periods differing by at least 2 days, additional samples which had been heated for longer periods were subjected to analysis.

(35) A number of preliminary investigations indicated that propionic acid from different lots did not affect the measured optical density in the indicated region.

(36) Preliminary investigations indicated that the original 10-fold dilution and cooling operations "quenched" the reaction sufficiently so that more strict adherence to timing was not warranted.

time standards were observed in recording the spectra for the equilibrium studies.

Recording of spectra. The spectra were recorded exactly as for the calibration procedure with two minor exceptions; only three recordings were made for each sample and the instrument was balanced to read zero with pure solvent in both cells after every sixth spectrum. For results see Tables III and IV.

Blanks. Samples of 178.2 mg. (1.000 millimole) of anthracene in 5.00 ml. of propionic acid were treated exactly as the Diels-Alder reactions. These samples were heated for different periods ranging from 2 hours to 21 days. The blanks are defined as the difference between the theoretical anthracene concentration (35.64 g./l.) and the measured concentration after a specified heating period. These samples frequently became dark in color after long heating periods and charred material could be noted in the bottom of the reaction vessel. Since the purpose of this study was not an investigation of the thermal decomposition of anthracene, no attempts were made to determine the nature of the decomposition products. It has been assumed that the decomposition is linear with time after the first 1 or 2 days. The concentration of anthracene was taken as the observed concentration plus the blank.

Test of blank. The equilibrium constant for the reaction between anthracene and *n*-propylmaleic anhydride was obtained using the following original concentrations of reactants and heating periods: A. Anthracene, 0.2000 mole/l.; dienophile, 0.1000 mole/l.; reaction time, 3 days. B. Anthracene, 0.2000 mole/l.; dienophile, 0.4000 mole/l.; reaction time, 3 1/2 days.

The equilibrium constants calculated for these two cases agree within experimental error with the equilibrium constant calculated from the reaction of equimolar quantities of diene and dienophile.

Reverse reactions. These reactions were carried out using 1.000 millimole of adduct in 5.00 ml. of propionic acid in the case of dibenzo[2.2.2]bicyclooctadiene-2,3-*cis*-dicarboxylic anhydride, the 2-bromo compound, and dibenzo[2.2.2]bicyclooctadiene-2,3-*trans*-dicarboxylic acid. The anhydrides were heated for 1 day, the acid for 2 days. The samples were prepared and the spectra were recorded exactly as for the forward reactions.

Phenylmaleic anhydride. This compound was found to absorb strongly in the region of the 3554 Å peak of anthracene although the adduct was transparent in this region. In order to obtain a corrected optical density measurement for this peak the following procedure was used. The optical density of the peak at 3734 Å was assumed to be due to anthracene absorption alone. The concentration was determined from this optical density measurement and a solution of phenylmaleic anhydride in propionic acid of the same concentration was prepared. The optical density was measured at 3554 Å and this optical density was subtracted from that determined for the reaction mixture.

The reaction between phenylmaleic anhydride and anthracene was assumed to reach equilibrium within 2 hours. Optical density measurements made on reactions which were heated for 4 and 6 days, were essentially the same as those made after the 2-hour heating period. These measurements were discarded because addition of the appropriate blanks resulted in concentrations of anthracene which were larger than the 2-hour concentrations.