

THE STERIC FACTOR IN THE DIENE REACTION: ANTHRACENE
WITH α,β -UNSATURATED α,β -DICARBOXYLIC ACIDS. I

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The investigations of Bachmann and Scott (1) have established the generalization that substitution in maleic and fumaric acids decreases the rate of the Diels-Alder reaction for a given diene. This is most readily explained in terms of a steric effect on the rate constant (k) for the addition reaction, inasmuch as excellent yields of adducts can be obtained, given sufficient time (1).

Since the reversible character of the reaction between anthracene and maleic anhydride has been well established (2), it is reasonable to expect that a steric effect may also influence the position of equilibrium. The findings of Bachmann and Kloetzel (2) suggest the existence of such an effect due to substituents in the aromatic diene, but a systematic study is still lacking. Similarly unavailable is a systematic investigation of the effect of substituents in the dienophile. However, a preliminary study in this laboratory indicates the existence of a comparable effect.

According to the reasonable mechanism discussed in a recent review of this reaction (3) the presence of electron-donating groups ($-I$ effect) such as methyl, adjacent to the double bond of the dienophile, should decrease the rate of addition, while electron-attracting groups ($+I$ effect) should increase this rate. The superiority of maleic anhydride over maleic acid or its esters (1, 3) also illustrates the former point. The planar and thus sterically more favorable anhydride structure also permits a maximum electron withdrawal or increase in dienophilic character not afforded by the non-coplanar acid or ester.

The unfavorable effect of a methyl group in the dienophile on the rate is seen in the relative effectiveness of citraconic *anhydride* and maleic *acid*, the *more* favorable anhydride structure affording less adduct in non-equilibrated, completely identical reactions than does the *less* favorable acid structure. Thus a methyl group decreases the effectiveness of maleic anhydride to an even greater extent than does opening the anhydride ring.

The unfavorable effect of a bromine atom on the reaction rate is to be seen in the effectiveness of bromomaleic anhydride as compared with maleic anhydride itself. Electronic theory predicts that the bromoanhydride should react *more* rapidly, owing to the electron-attracting character of the bromine. Here, however, as with methyl, a steric factor enters. The steric requirements of bromine and methyl are nearly alike, the former being somewhat larger as shown by racemization studies on optically active biphenyls (4). Thus any purely steric

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effects cancel out in a direct comparison of the rates of addition of bromomaleic anhydride and citraconic (methylmaleic) anhydride. The inductive (+I) effect of bromine is accordingly seen to be not quite sufficient to overcome its steric effect, whereas the inductive effect (-I) of the methyl group reinforces its steric effect and produces a comparatively poor dienophile.

Direct comparison of rates of addition of *cis* and *trans* isomers and of the corresponding *cis* anhydrides is also possible from the observations of Bachmann and Scott (1). It was shown that the anhydrides of maleic or citraconic acid were more dienophilic than the corresponding fumaric or mesaconic (methyl-fumaric) acids. The differences in rates, however, are not greater than four-fold for either pair at the temperature, concentration, and reaction time employed.

A striking example of the difference in rate of addition to anthracene of a pair of *cis-trans* isomers was encountered by the present investigators in the course of studying the preparation and reactions of certain hindered $\alpha(\beta)$ -bromo- α,β -dicarboxylic acids (5). The addition of bromocitraconic anhydride and

TABLE I
YIELDS IN ADDITION TO ANTHRACENE

DIENOPHILE	SOLVENT	°C.	HRS ^c	%	PRODUCT
Bromocitraconic Anhydride (6) (I) ^a	Xylene	145	120 ^c	67.5 ^d	III
Bromomesaconic Acid (6) (II) ^b	Propionic acid	145	144 ^c	55.5	III

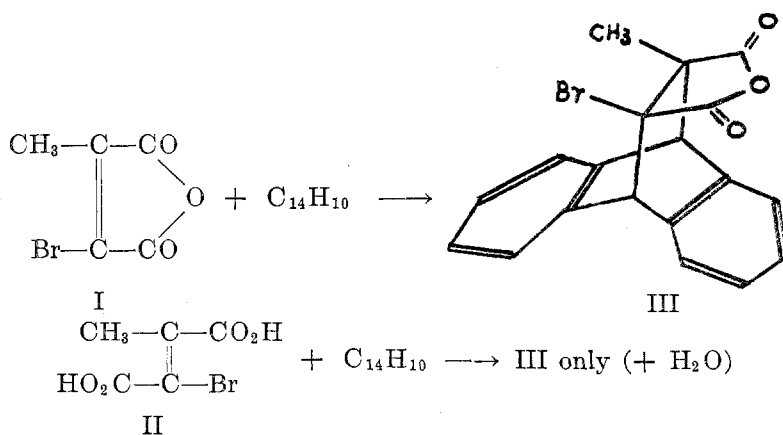
^a Solution contained 0.0817 mole of each addend in 60 ml. sodium-dried xylene.

^b Solution contained 0.00321 mole of each addend in 2.4 ml. of redistilled propionic acid.

^c Time sufficient to establish equilibrium, *cf.* ref. 2.

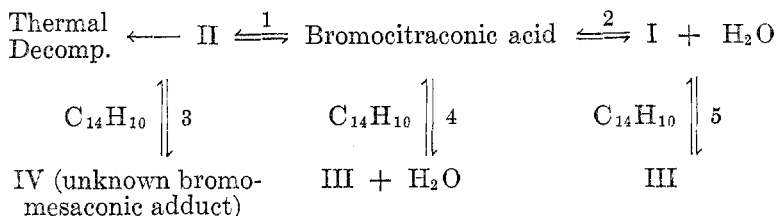
^d *Cf.* ref. 5.

bromomesaconic acid to anthracene was studied. The reactions were carried out at the reflux temperature of the solvent used and with the reactants in a 1:1 molar ratio. The results are summarized in Table I.



Normally the *trans* form of an isomeric pair of acids is considered the more stable. Thus bromomesaconic acid (m.p. 222.5–223.0°) (6) is considered more stable than bromocitraconic acid, which, however, is not known as the free acid, inasmuch as all attempts to prepare it have afforded only the anhydride (m.p. 101°) (7). The interconversion of *cis-trans* pairs of acids is acid-catalyzed (8), and thus one might expect the refluxing of bromomesaconic acid in propionic acid to produce the equilibrium concentration of the stable bromocitraconic anhydride. Unexpectedly bromomesaconic acid affords no detectable quantity of bromocitraconic anhydride but instead suffers extensive thermal decomposition, only 51% being recovered after refluxing for three days in propionic acid. Since the anhydride is readily isolable and is stable under identical conditions (> 90% recovery), one must conclude that bromomesaconic acid affords an indeterminably small quantity of bromocitraconic acid (or anhydride) in refluxing propionic acid, comparable perhaps with that in equilibrium with the anhydride.

With this information at hand, the significance of the isolation of 55.5% of III from the reaction between anthracene and bromomesaconic acid becomes apparent. The yield of III is comparable with that when the dienophile is bromocitraconic anhydride, and it is reasonable to assume that failure to observe complete correspondence in yields at equilibrium is due to the above-mentioned thermal decomposition of bromomesaconic acid. Accordingly the following reaction scheme may be set up:



Thus, where K is an equilibrium constant, K_4 or K_5 must be greater than K_1 . Inasmuch as no IV was ever isolated, nothing can be said of K_3 , although there is nothing to indicate that it should be markedly smaller than K_4 or K_5 , since good yields of *trans* adducts are reported (1).

Inability to isolate any bromocitraconic acid from the anhydride or other potential sources (7) indicates the great magnitude of both K_2 and k_2 (rate constant). Since k_5 is probably larger than k_4 because of the maleic acid-maleic anhydride analogy, it is reasonable to suppose that I is formed and adds to anthracene. Thus the over-all reaction follows the stepwise course 1, 2, 5, even though no demonstrable quantity of I can be isolated in the absence of anthracene.

Consideration of the expressions for the rates (V_3 and V_5) of reactions 3 and 5 in which the concentration of anthracene and of II are finite and equal (A), leads to the conclusion that k_3 must be very small, since the right side of equation (1) is inconsiderable, V_3 being unobservably small.

$$1. (\text{C}_{14}\text{H}_{10})(\text{II}) k_3 = V_3 \text{ or } k_3 = V_3/A^2.$$

By the same argument k_5 must be very large, since the right side of equation 2, which contains the extremely small term, concentration of I, is very large.

$$2. (C_{14}H_{10})(I) k_5 = V_5 \text{ or } k_5 = V_5/A(I)$$

Consequently $k_5 \gg k_3$.

It may accordingly be concluded that, whereas measurable differences in rates exist between *cis* and *trans* dienophiles such as maleic and fumaric acids and whereas these differences are accentuated when the sterically and electrically more favorable anhydride replaces the *cis* isomer, when a group with only moderate steric requirements (e.g., methyl) is present, its effect will be to accentuate the difference in rates of addition to the diene. It may also be concluded that the presence of two groups with similar steric requirements will further accentuate the difference in rates of addition of such isomeric pairs, and where conditions favor isomerization, the thermodynamically less stable *cis* isomer will add, to the complete exclusion of the more stable *trans* isomer. The steric requirements of bromine, while slightly greater than those of methyl, are nearly completely cancelled by its inductive effect, but when it is present with methyl it still contributes sufficiently to the steric requirements of the dienophile so that the additional accentuation of the difference in dienophilic character of the *cis* and *trans* configurations is observed.

EXPERIMENTAL

Anthracene plus bromomesaconic acid. A solution of 0.572 g. (0.00321 mole) of anthracene and 0.671 g. (0.00321 mole) of bromomesaconic acid (6) in 2.4 ml. of propionic acid was refluxed for six days. The black crystalline mass which formed on cooling was dissolved in acetone, and the filtered solution evaporated to dryness: 1.128 g. Evaporation of an ethereal extract of this crude product gave 0.515 g. of material from which 0.050 g. (7.5%) of water-soluble bromomesaconic acid, 0.059 g. of III and small amounts of anthracene were separated. No attempt was made to separate all of the anthracene present. The residue left after the ether extraction was extracted with acetonitrile, and the 0.599 g. of product obtained on evaporation of this solution was crystallized from benzene, giving 0.487 g. of III; m.p. 226.5–227°. The total yield of III (*cis*-9,10-dihydroanthracene-9,10-*endo*- α -bromo- β -methylsuccinic anhydride) obtained was 55.5%. Recrystallization from anhydrous ethyl acetate afforded material which alone and on mixture with authentic III melted at 231.8–232.4° corr.

Bromomesaconic acid plus propionic acid. A solution of 0.200 g. of bromomesaconic acid in 0.7 ml. of ordinary propionic acid was refluxed for three days, cooled and made alkaline with 10% aqueous sodium bicarbonate. The aqueous solution was extracted with 20 ml. of ether in three portions, and the dried ethereal extract evaporated to a glass (0.005 g.) which did not become crystalline when it was triturated with carbon disulfide. The alkaline solution was acidified with 10% sulfuric acid, extracted with ether, and the ethereal extract was dried over anhydrous calcium sulfate and evaporated to give 0.102 g. of starting material; m.p. 212–221° decomp. Under identical conditions 0.20 g. of bromocitraconic anhydride afforded 0.18 and 0.19 g. recovery (90–95%), m.p. 100–101°.

SUMMARY

1. The addition of bromomesaconic acid to anthracene had been attempted, but the only reaction product isolable was the adduct of bromocitraconic anhydride and anthracene.

2. Extensive refluxing of bromomesaconic acid in propionic acid affords no measurable quantity of bromocitraconic anhydride.

3. Therefore the rate of addition of bromocitraconic anhydride to anthracene is extremely rapid compared with the corresponding addition of bromomesaconic acid to anthracene.

4. Both steric and electrical factors influence the reactions studied. The steric effect of bromine is almost exactly cancelled by its electrical effect when bromine alone is present in the dienophile.

5. When bromine is present with methyl, the steric effect appears to be accentuated.

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