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The Diels–Alder Reaction and the Rearrangement of the Maleic Anhydride Adducts of 6,6-Dimethylfulvene

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For short periods of reaction between room temperature and 80° it was found that 6,6-dimethylfulvene and maleic anhydride react almost completely to form mixtures containing about equal amounts of the previously studied *endo* and *exo* adducts. These rearrange so that during a few hours in concentrated benzene solution at 80°, an equilibrium mixture containing 85 to 88% of the *exo* isomer is obtained. Both adducts undergo retrogression, the *endo* the more readily. Retrogression does not seem necessary for rearrangement. This particular diene synthesis is one in which Alder rule II does not apply, *i.e.*, the reaction is not stereospecific for the reason that an Alder complex is unlikely. An infrared spectrophotometric technique for determining the ratio of *endo* to *exo* adduct in solid mixtures is described.

Retrogression in the Diels–Alder reaction in some instances has been held to account for the rearrangement of an initially formed, though more unstable, isomer. Alder and Trimborn[1,2] postulate that this dissociation–recombination mechanism, first reported on in some detail by Woodward and Baer[3] is a general one. A different view recently has been published for the case of the cyclopentadiene–maleic anhydride adducts,[4] for which evidence was presented to show that the adducts rearranged into each other without intermediate dissociation. This "direct" mechanism involved a non-isolable intermediate and hydrogen migration. The present paper describes the application of a direct mechanism to an *endo–exo* rearrangement in the fulvene series in which a hydrogen shift seems unlikely and in which dissociation is easily recognized.

Alder and Rührmann[5] reported 60 to 70% conversion to mixtures of the *endo* adduct (I) and *exo* adduct (II) when 6,6-dimethylfulvene and maleic anhydride are contacted between 0 and 80° in ether or benzene. They also reported the yield of II to be strongly favored at the expense of I by temperature increase. II was found to dissociate less readily than I.

We have found that the melting points of I and II are somewhat higher than those previously reported and are 118 and 140°, respectively. Also in concentrated solution the reaction appears to be essentially complete during 16 hours at 25° and at least 94% complete during five minutes at 80°. The ratio of II to I was 1.1 at 15° and 1.3 at 80°; however, when the reaction was conducted for a period of three hours at 80° or when the *endo* adduct was refluxed in benzene for this period, an 85% yield of II was secured. When II was heated for five hours at 80° in benzene, infrared spectrophotometric analysis of the product indicated that a 12% conversion to the *endo* adduct had resulted. We infer therefore (a) that the equilibrium mixture contains between 85 and 88% of II and (b) that Alder

and Rührmann's yield of II at 80° is the result of initial *exo* adduct formation combined with rearrangement of initially formed I. This was confirmed when it was found that I during a period of five minutes in benzene at 80° gave 97% of a product containing only about 11% of II, *i.e.*, most of the II isolated from the diene synthesis conducted at 80° for five minutes must have been formed as an initial product. Alder and Rührmann's picture appears confused because of the possibility that their product melting at 112° was not pure and may have contained II. We have found that maleic anhydride does not affect the rearrangement but that it represses dissociation into fulvene and maleic anhydride, both of which were isolated as dissociation products.

It is of interest to attempt the fitting of the behavior of I and II, as well as the unusual structure of the fulvene, into the general background of the diene synthesis, especially that having to do with Alder rule II.[6] One is tempted to consider the adducts to be formed through Alder complexes Ia and IIa. These are the complexes which would result if the fulvene were a normal diene. However, considering the resonance forms of 6,6-dimethylfulvene, a more probable complex would be a hybrid in which IIb would make a major contribution and IIa a minor one. An *endo* type similar to IIb obviously does not need to be considered. Since nearly half of the product is I, this line of reasoning fails and a mechanism not involving an Alder complex is needed to account for the formation of I as well as II.

If charged forms really make great contributions to the hybrid of the fulvene, as is indicated by its high dipole moment,[7] then I and II should be

(1) K. Alder and W. Trimborn, *Ann.*, **566**, 58 (1950).

(2) Compare J. A. Berson and R. Swidler, THIS JOURNAL, **75**, 1721 (1953).

(3) R. B. Woodward and H. Baer, *ibid.*, **66**, 646 (1944).

(4) D. Craig, *ibid.*, **73**, 4889 (1951).

(5) K. Alder and R. Rührmann, *Ann.*, **566**, 1 (1950).

(6) Alder rule III has recently been proposed. It states in effect that the diene always reacts in the *cisoid* configuration (*cf.* K. Alder, *Ann.*, **571**, 157 (1951)). This principle has long been recognized; thus in the case where the *cisoid* configuration is impossible, reaction either fails or takes place with difficulty. Examples are 2,3-dichloro-1,3-butadiene (G. J. Berchet and W. H. Carothers, THIS JOURNAL, **55**, 2006 (1933)), *cis*-1-phenylbutadiene (O. Grummit and F. J. Christoph, *ibid.*, **73**, 3479 (1951)), 2,3-di-*t*-butyl-1,3-butadiene (H. J. Backer, *Rec. trav. chim.*, **58**, 643 (1939)) and *cis*-piperylene (D. Craig, THIS JOURNAL, **65**, 1006 (1943); **72**, 1678 (1950)). Adduct I and II, of course, have structures in accord with rules I and III.

(7) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

formed through charged intermediates IIIa and IIIb, which now appear to be more probable than the Alder complexes. These really constitute two almost equally probable stereochemical pairs of forms. IIIa should lead to I, and IIIb, by rotation around the single bond joining the fulvene and anhydride moieties, should lead to II. The fact that about equal amounts of the adducts appear in the reaction supports this polar mechanism for the major course of the reaction. Complexes IIIa and IIIb seem likely as intermediates for the rearrangement of the adducts. Attack of maleic anhydride on one side of IIIa or IIIb could result in its liberation on the other side with either formation of the same or the isomeric adduct.

The reaction of the fulvene and anhydride is quite different from that of cyclopentadiene or that of *trans*-piperylene with maleic anhydride where the diene synthesis is stereospecific and where it could be non-polar in nature. Since Smith, Norton and Ballard[8] believe from the study of dissimilar ad-

I a   Endo, I, m.p. 118°

II a   II b   Exo, II, m.p. 140°

III a   III b
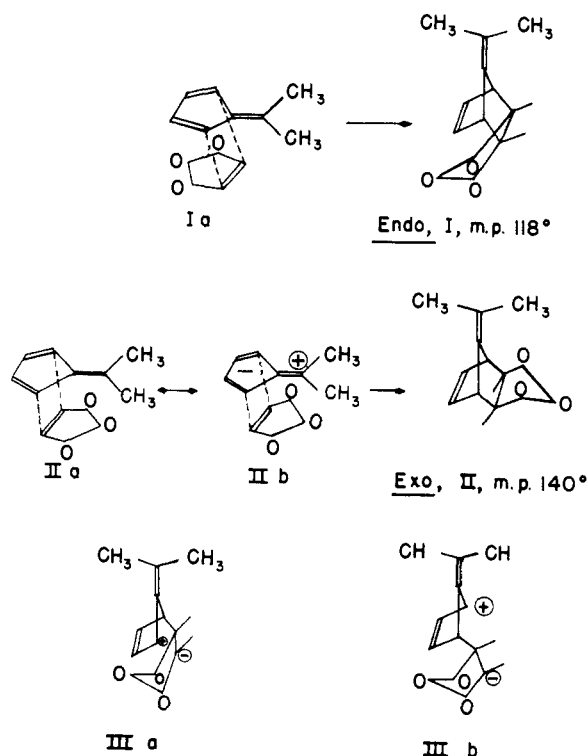
denda in the Diels–Alder reaction that a diradical mechanism best accounts for the direction of addition, we are inclined to accept their mechanism. However, for the simple dienes, as an additional feature, we believe in the formation of two bonds simultaneously by way of an Alder complex to give the single adduct which, though unstable, can be isolated in high yield. Dissociation, except for the liberation of small amounts of maleic anhydride for use in reaction with intermediates such as IIIa and IIIb, may always be a side reaction to direct rearrangement in any diene synthesis. A hydrogen shift, though attractive or even necessary in the case of the cyclopentadiene adducts, may not be

(8) C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, 73, 5276 (1951).

essential in other cases. Hydrogen shifts, presumable by way of non-isolable enolic forms, seem well established for the adducts of open-chain dienes such as piperylene.[6]

Experimental

6,6-Dimethylfulvene was prepared from freshly distilled cyclopentadiene and acetone by the method of Thiele and Balhorn[9] and fractionated through a glass helices packed column at 50 mm. The fraction distilling at 76.8° melted at 1.4°, $n^{25}D$ 1.5441 and d^{25}_{25} 0.8808. The bright orange-yellow color of the hydrocarbon faded noticeably when cooled to −70° in the solid state or when dissolved in xylene. The xylene solution deepened slightly when heated to 135°. The color changes were reversible and it is concluded that the compound is slightly thermochromic. It is believed that our product is nearly but not quite pure since reaction mixtures with excess maleic anhydride have the odor of dicyclopentadiene. The hydrocarbon in isoöctane displayed ultraviolet absorption maxima at 271 and 264 mμ where $E = 165.3$ and 171.5, respectively, at a concentration of 0.000654 g./l.

endo and *exo* Adducts I and II.—These were prepared according to Alder from maleic anhydride and dimethylfulvene. Ether, ethyl acetate or benzene, as described below, were often used as solvents. With ether as the solvent it was possible to filter off most of the II in a nearly pure state. Evaporation of the ether and crystallization of the residue from ethyl acetate with careful seeding gave alternate crops of I and II. This was a laborious process but the I was obtained as large chunky, transparent plates melting at 117–118°. The *exo* adduct II came down from ether as needles, m.p. 139–140°. Usually from ethyl acetate it crystallized as needles, but in one case transparent, chunky crystals were secured which melted at 140°. In one fractionation after most of the I and II had been separated, the ethyl acetate was evaporated and the residue extracted with hot hexane in which the adducts are difficultly soluble. A small amount of maleic acid was isolated from the hexane-insoluble part and from the soluble part a crop of transparent granular crystals came down which melted at 102–104°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.55; H, 5.93. Found: C, 70.62, 70.48; H, 5.95, 6.07.

This new compound melted at 95–98° when mixed with either I or II. On standing several weeks or quickly on heating in benzene solution it changed mostly into II. It is believed to be a double compound of I and II. A melting temperature of 95° is about the lowest found for any mixture of I and II.

Maleic anhydride, 5.00 g. (0.051 mole), was dissolved in 20 ml. of benzene at 80° and 5.30 g. (0.050 mole) of dimethylfulvene added during two minutes while keeping the temperature at 80°. After heating 80° for three minutes longer the mixture was cooled to 25°. A crop of the *exo* adduct crystallized which weighed 2.58 g., m.p. 139–140°. The mother liquor was concentrated and crystallized from ether to give 1.16 g. of crystals which melted at 137–138°. The mother liquor on evaporation at 25° at 15 mm. gave a residue of 6.51 g.; thus the total yield of reaction product is 10.25 g. or 99.5%. Short-path distillation of the residue at 30–35° and 0.5 mm. gave 0.41 g. (0.04 mole) of maleic anhydride and no dimethylfulvene. The conversion of maleic anhydride was thus 0.47 mole or 94%. Based on the infrared spectrum (see procedure below) of the short-path distilled residue (final wt. 6.09 g.), we infer that it contains the adducts in a ratio of about 73% *endo* to 27% *exo* and that other substances are substantially absent. When 1.00 g. of the residue was heated in benzene solution at 80° for 20 hours a 78% yield of the *exo* adduct was isolated. The ratio of *exo* adduct to *endo* in the reaction product including 27% of the residue is 56 to 44 or 1.27. Similar experiments conducted under a variety of conditions are summarized in Table I.

Heating and Distillation of the Adducts.—The short-path distillation of 2.00-g. quantities of I and II at 65–68° at 0.5 mm. pressure gave colorless distillates melting 1 to 2° below the melting points of the pure starting materials. The distillands consisted of the pure starting materials. This behavior reflects a relatively good stability for both isomers in the solid state.

(9) J. Thiele and H. Balhorn, *Ann.*, 348, 5 (1908).

TABLE I

THE REACTION OF 5.00 G. OF MA WITH 5.30 G. OF DMF

Expt. no.	Crude yield	Yield solid exo, g.	Total yield exo, %	Temp., °C.	Reacn. time, min.
1[a]	9.83	3.74	56	80	5
2[a]	10.00	3.06	55	80	6
3[a]	9.92	5.30	76	80	60
4[a]	10.07	5.83	86.5	80	180
5[b]	9.89	3.20	55.5	80	6
6[c]	10.14	3.41	51.5	38	30
7[a]	10.00	3.66	54	30	180
8[a]	10.17	3.42	57.5	30	960
9[d]	10.26	2.85	57.5	25	30
10[a]	9.83	2.65	51	25	30
11[b]	9.94	2.72	57	25	60
12[f]	10.19	4.27	59	25	3600
13[a]	9.83	3.05	51.5	15	120
14[e]	10.14	2.42	53.5	15	120

[a] Twenty ml. of benzene used as solvent. [b] Twenty ml. of benzene used as solvent, 100% excess MA also present. The excess MA was extracted with water without hydrolyzing the adducts. [c] Thirty ml. of diethyl ether used as solvent. [d] Twenty ml. of benzene used as solvent, 0.1 g. of Bu₂NH also present. [e] Fifteen ml. of benzene plus 5 ml. of pyridine used as solvent. [f] Thirty ml. of diethyl ether used as solvent, 0.1 g. of phenyl-β-naphthylamine and 0.01 g. of hydroquinone also present.

Two grams (0.0098 mole) of exo adduct was placed in a Claisen flask connected in turn to an air-cooled receiver, a Dry Ice–acetone-cooled receiver and a vacuum line at 6 mm. pressure. Upon heating carefully with a free flame to effect sublimation of the adduct from one part of the flask to another, yellow distillate appeared in the side-arm and was driven over to the Dry Ice-cooled receiver. Soon no more yellow distillate would appear even though the distilland was sublimed several times during the course of 30 minutes. The yellow distillate amounted to 0.11 g. and melted at +1° alone or mixed with dimethylfulvene. The distilland consisted of 0.85 g. of II which melted at 135–137°. The distillate in the air-cooled receiver weighed 1.00 g.; upon short-path distillation at 50° at 0.5 mm. it gave 0.10 g. of maleic anhydride, m.p. 51–54° alone or mixed with authentic material. The yield of dimethylfulvene (approx. 10%) corresponds approximately to the yield of maleic anhydride. The distilland from which most of the maleic anhydride had been removed was distilled further to remove 0.02 g. of intermediate material. The final distilland weighed 0.87 g. and melted at 90 to 100°. It was a mixture of I and II.

Since decomposition did not go to completion in the previous experiments, another one was conducted to test the effects of maleic anhydride in repressing the dissociation. Two grams of II and 5 g. of maleic anhydride were charged to a 50-ml. modified Claisen flask and distilled at 80 mm. pressure. A distillate of 4.26 g. of maleic anhydride, m.p. 52–54°, came over first. It was free of dimethylfulvene. The pressure was reduced to 20 mm. while collecting 0.90 g. of impure maleic anhydride, which melted at 48–50°. The residue, 1.78 g., was a red resin, presumably formed from equimolar amounts of fulvene and anhydride. Polymer formation largely is repressed if the temperature is kept below about 150° and if excess maleic anhydride is present in the mixture.

Heating 1 g. of I with an equal weight of maleic anhydride in a Claisen flask to 60° for a short time caused no color formation, but at 80° at 80 mm. a deep greenish-yellow color soon formed. The temperature was raised to 97° for 30 minutes and then reduced to 50° and the pressure to 0.5 mm. The temperature was then raised to 75° but no dimethylfulvene distilled. The side-arm of the flask was found to contain 0.06 g. of maleic anhydride, m.p. 52–54°. Crystallization of the distilland from 5 ml. of benzene gave 0.27 g. of exo adduct melting at 135–138°. Evaporation of

the liquor, short-path distillation of the residue to remove 0.91 g. of maleic anhydride (m.p. 51–54°), and crystallization from benzene gave 0.59 g. of exo adduct melting at 133–137°. The total yield of exo adduct was 86%.

Two grams of II and 6 ml. of benzene were refluxed for five hours and the benzene evaporated at 25°, finally at 0.5 mm. in a short-path still at 40°. The residue weighed 1.98 g. and melted at 110–130°. Crystallization from benzene gave 1.54 g. of II, m.p. 138–139°. The liquor, evaporated to dryness, gave 0.44 g. of residue which contained 0.21 g. of II and 0.23 g. of I as inferred from its infrared spectrum. This experiment indicates that the mixture formed in benzene at 80° contains about 88% of II and 12% of I.

The endo isomer I (0.1675 g.) was refluxed for 5 minutes in 0.5 ml. of benzene. A yellow color indicated the formation of the fulvene. Evaporation of the solvent and warming at 0.5 mm. pressure gave 0.161 g. of nearly colorless residue. This melted at 110–113° and according to infrared analysis was composed of the isomers in a ratio of 89% endo to 11% exo. Refluxing for 15 minutes gave a mixture containing 73% endo and 27% exo. In other experiments, an 84% yield of II was obtained in 2.5 hours and an 85% yield in 3 hours.

The greater stability of II over I in dilute solution in isooctane can be followed by ultraviolet absorption. Thus the absorption spectrum of solutions of I and II after standing two months, or longer, are essentially the same, except for intensity, as solutions of 6,6-dimethylfulvene, or of solutions of the fulvene and maleic anhydride.

Infrared Analysis of endo–exo Mixtures.—The spectra, Fig. 1, of the endo and exo isomers were taken from 2 to 25 μ with the B. F. Goodrich infrared spectrophotometer. From 2 to approximately 7.4 μ a sample mulled with Fluorolube was used; from 7.4 to 25 μ a mineral oil mull was scanned.

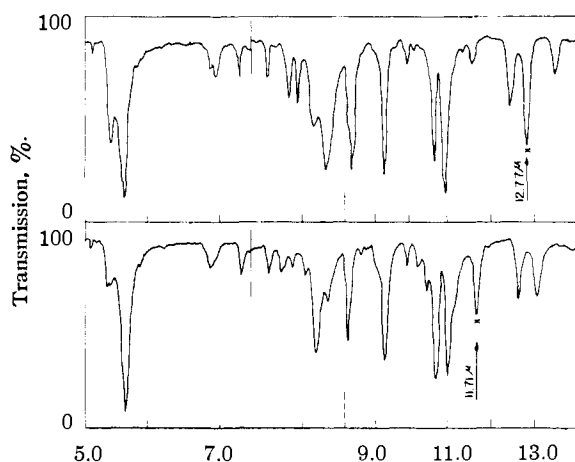

Fig. 1.—Infrared absorption spectra of I and II: top curve, endo; bottom, exo.

The endo isomer has a medium intense peak at 12.77 μ which does not interfere with any peak in the spectrum of the exo isomer. The exo isomer has a similar peak at 11.71 μ. The intensities of these peaks were measured using mulls of approximately equal thickness for several known mixtures of the isomers. The ratio of the optical density at 12.77 μ to that at 11.71 μ was calculated for each mixture and plotted against the percentage of endo isomer present. The resultant curve was then used for the determination of the amounts of endo and exo isomers present in the unknown mixtures. Usually the mixtures were prepared by solution in benzene, ether or ethyl acetate followed by evaporation of the solvent at reduced pressure. When mixtures were prepared by merely grinding weighed amounts of the isomers, the results were entirely misleading. This is believed due to uncontrolled double compound formation during the grinding operation.

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