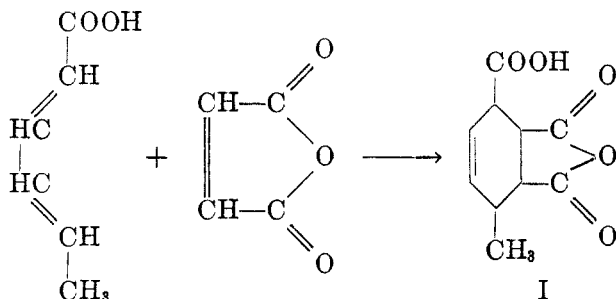


THE DIENE ADDITION OF MALEIC ANHYDRIDE TO SORBIC ACID

ZENO W. WICKS, OLIVE W. DALY, AND HELEN LACK

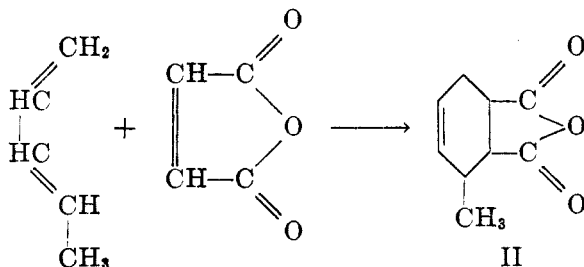
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In attempting to prepare the maleic anhydride adduct of sorbic acid by simple fusion of the reactants as originally described by Diels and Alder (1), difficulty was experienced in obtaining the desired compound, I. The reaction was therefore investigated further in order to determine suitable conditions for the preparation and the cause for the failure of the first attempts.



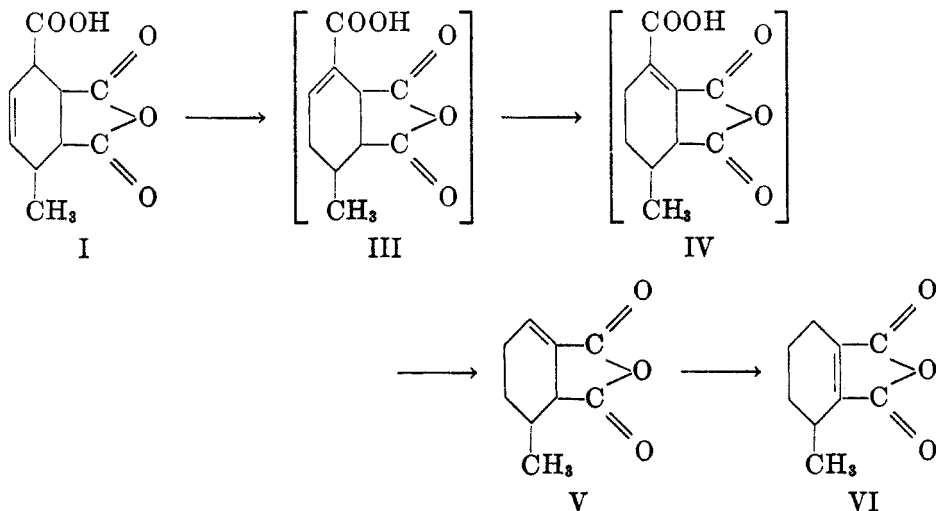
Diels and Alder carried out the reaction on a ten-gram scale, heating the reactants until a vigorous reaction occurred, and obtained a viscous liquid as a product. They isolated the solid tribasic acid derived from I by hydrolysis of this liquid. On a rather larger scale, the present authors found that the reaction could be initiated by warming to 60° when a vigorous reaction ensued and the temperature rose spontaneously to 240–250° with considerable evolution of gas. No solid could be obtained, however, from the liquid product even by hydrolysis. It was found possible to repeat the results of Diels and Alder if the temperature was kept below 130°, for example, by adding the sorbic acid slowly to the molten maleic anhydride. It seems possible that, on the small scale in which Diels and Alder carried out the reaction, the temperature rise was not as great as that encountered in the present work.

The product from the high temperature reaction was subjected to vacuum distillation. The major part of the material was found to be a liquid having the boiling point 117–118° at 2 mm. This is above that of the starting materials but substantially below any anticipated boiling point of the 6-carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride (I). A carbon and hydrogen analysis and



the saponification value of the distillate conformed to a decarboxylation product of I. For purposes of comparison, 3-methyl-1,2,3,6-tetrahydrophthalic anhydride (II), was prepared from piperylene and maleic anhydride (2). This substance had essentially the same boiling point (119° at 2 mm.) as that obtained from the reaction of maleic anhydride with sorbic acid at elevated temperatures, but in contrast to the other it readily solidified. It therefore appeared that the products were isomeric. This isomerism was confirmed by dehydrogenation of the decarboxylated product to give 3-methylphthalic anhydride.

The decarboxylation is unlikely to proceed prior to the addition reaction, since sorbic acid does not lose carbon dioxide when heated to 250° without catalysts. The direct adduct (I), was prepared by the procedure of Farmer and Warren (3), by heating a benzene solution of maleic anhydride and sorbic acid on a steam-bath. When I was heated to 150–160°, it underwent exothermic decarboxylation, yielding a liquid having the same properties as the decarboxylation product obtained directly from sorbic acid and maleic anhydride. Since a compound of structure I would not be expected to undergo decarboxylation easily, it may be postulated that the double bond of I shifts to the 5,6-position (IV).



Compound IV, being a cyclic analog of aconitic acid, would be expected to lose carbon dioxide readily. The product would have structure V, or by further isomerization part or all might be converted to VI. These isomers have conjugated double bonds, in contrast to the piperylene-maleic anhydride adduct (II).

This difference should be apparent in the optical properties of the isomers; therefore, the molecular refractivities and ultraviolet absorptions were compared.¹ For example II (super-cooled) showed no exaltation of molecular refraction ($M_{\text{calc'd}} 40.57$; $M_{\text{obs.}} 40.36$) while the decarboxylation products exhibited

¹ The authors wish to express their appreciation to Daniel Smith and Shirley Erhardt for the optical measurements involved in the determinations of absorption characteristics and exaltations.

exaltation ($M_{\text{calc'd}}$ 40.57; M_{obs} , 41.63). Furthermore, the absorption of ultraviolet light by II was much less than the absorptions of the decarboxylated products, as can be seen in Figure 1. A further distinction between the conjugated

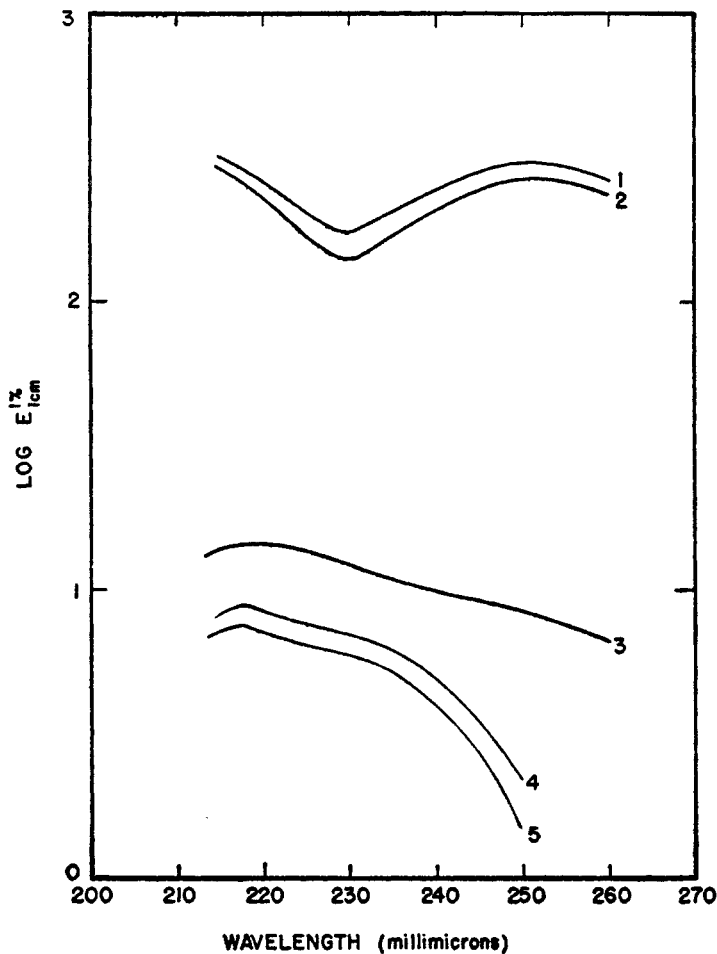


Fig. 1—Ultraviolet absorption spectra of alcoholic solution of:

- (1) product of reaction of sorbic acid and maleic anhydride at elevated temperature.
- (2) decarboxylation product from 6-carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride.
- (3) 6-carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride.
- (4) 3-methyl-1,2,3,6-tetrahydrophthalic anhydride after attempted isomerization by heating.
- (5) 3-methyl-1,2,3,6-tetrahydrophthalic anhydride.

and non-conjugated isomers lay in their different rates of saponification. The first was readily saponified, less than half an hour heating with alcoholic alkali giving theoretical saponification values, while the second was only slowly saponi-

fied, several hours being required to complete saponification. This observation conforms to the previously reported greater reactivity of maleic anhydride as compared with succinic anhydride (4).

The preceding data point to the conclusion that the reaction product of maleic anhydride with sorbic acid at elevated temperatures is a conjugated isomer or isomers of 3-methyltetrahydrophthalic anhydride. On the basis of partial oxidation, Farmer and Warren (3) suggest that the product obtained from the addition of maleic anhydride to sorbic acid in benzene has structure III. In view of its low absorption of ultraviolet light as compared to that of the conjugated decarboxylation products as shown in Figure 1, curve 3, it seems more likely that the adduct has the unisomerized structure I. On the other hand, I must isomerize to III and IV quite readily in view of its easy decarboxylation. That the isomerization occurs before loss of carbon dioxide was shown by the failure of II to undergo conjugation during four hours heating at 230–260°, as compared with the fifteen minutes at 160–190° sufficient to isomerize and decarboxylate I. The ultraviolet absorptions of heated and unheated II are shown by curves 4 and 5 of Fig. 1. An attempt to convert the non-conjugated structure of II to its conjugated isomer by heating with alkali in ethylene glycol at 180–190° was also unsuccessful.

EXPERIMENTAL

Uncontrolled reaction of sorbic acid with maleic anhydride. A mixture of 448 g. of sorbic acid and 392 g. of maleic anhydride was heated slowly to 55° under an atmosphere of carbon dioxide to prevent oxidation. When the maleic anhydride melted, a slight evolution of gas was noted and then a vigorous reaction ensued. Even though the heater was removed, the temperature rose to 240–250° within five minutes and some material was lost through the condenser. The reaction product was allowed to cool and was found to be a somewhat viscous, brownish liquid from which no solid material could be obtained even by hydrolysis of a portion with water (1). The main portion of the product was subjected to vacuum distillation at 4 mm. There was a slight forerun, and then the main portion of the material distilled at 130–132°. There was an appreciable residue of polymeric (?) material from which no pure compound could be isolated. The main fraction was redistilled at 2 mm. pressure through a short Vigreux column; almost all of the material distilled at 117–118°. It has not been possible to make the product crystallize. It has the following properties: n_D^{25} 1.4969; d_4^{25} 1.1669; M_p : (calc'd) 40.57 (found) 41.63; for ultraviolet absorption characteristics see curve 1, Figure 1.

Anal. Calc'd for $C_9H_{10}O_3$: C, 65.05; H, 6.06; Sap. equiv. 83.1.

Found: C, 64.55, H, 6.07; Sap. equiv. 82.6.

The product was dehydrogenated by heating with 5% of a 5% palladium on charcoal at 250° for six hours. After distillation and recrystallization from benzene-petroleum ether, the product melted at 113–115°. Newman and McCleary (2) report the melting point of 3-methylphthalic anhydride as 114–115°.

Controlled reaction of sorbic acid with maleic anhydride. In order to moderate the reaction, 98 g. of maleic anhydride was heated to 100°, and while stirring, 112 g. of sorbic acid was added in small portions such that the temperature did not rise above 130°. The product after cooling was a viscous, resinous liquid. This material was refluxed with an equal weight of water for three hours and cooled. A pale yellow solid was obtained, yield 122 g. or 54%. The melting point was 198–205° with foaming, when heated rapidly; after several recrystallizations from water it was 224–230° with foaming. The neutral equivalent, 73.1,

conforms to 6-carboxy-3-methyltetrahydrophthalic acid. Diels and Alder (1) report the melting point as 198° (decomp.).

6-Carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride, I. The preparation was carried out according to the directions of Farmer and Warren (3). The product was obtained in 64% yield and had the melting point 178°. For ultraviolet absorption characteristics see curve 3 of Fig. 1.

3-Methyl-1,2,3,6-tetrahydrophthalic anhydride II. In order to avoid the necessity for a long reaction time at low temperature (2), 102 g. of distilled piperylene and 197 g. of maleic anhydride, with a trace of Age-Rite Resin D² as a polymerization inhibitor, were heated in a hydrogenation bomb at 100° for two hours. The product was purified by distillation through a short column at 1.5 mm. pressure, and was obtained as a low-melting solid boiling at 116–118°. After further purification by redistillation, b.p. 119° at 2 mm., yield, 79%, the following properties were determined on the supercooled liquid: n_D^{25} 1.4932; d_4^{25} 1.1966, M_p : (calc'd) 40.57, (found) 40.36; for ultraviolet absorption characteristics see curve 5 of Figure 1.

Decarboxylation of 6-carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride. Twenty g. of the adduct (I) was heated under reflux to 160°; when this temperature was reached evolution of gas began. Without additional external heat the temperature rose to 190°. The gas evolved was shown to be carbon dioxide by testing with barium hydroxide solution. The product distilled at 121–122° at 2.5 mm., n_D^{25} 1.4968; d_4^{25} 1.1666; M_p : (calc'd) 40.57, (found) 41.66. These properties are essentially identical with those of the product from the reaction of maleic anhydride with sorbic acid at elevated temperatures. The ultraviolet absorption characteristics of the two materials are also very similar as can be seen in curves 1 and 2 of Figure 1.

SUMMARY

Preparation of the direct adduct of sorbic acid and maleic anhydride by simple fusion of the reactants is successful only if the temperature is kept below 150°. 6-Carboxy-3-methyl-1,2,3,6-tetrahydrophthalic anhydride is most readily prepared by carrying out the reaction of sorbic acid and maleic anhydride in benzene solution (3). If the temperature of the fusion reaction is allowed to rise over 150° or if the isolated adduct is heated to over 150°, rapid decarboxylation occurs leading to the formation of a conjugated isomer or isomers of 3-methyltetrahydrophthalic anhydride.

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² Age-Rite Resin D can be obtained from R. T. Vanderbilt Co.