[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

The Rearrangement of *endo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride

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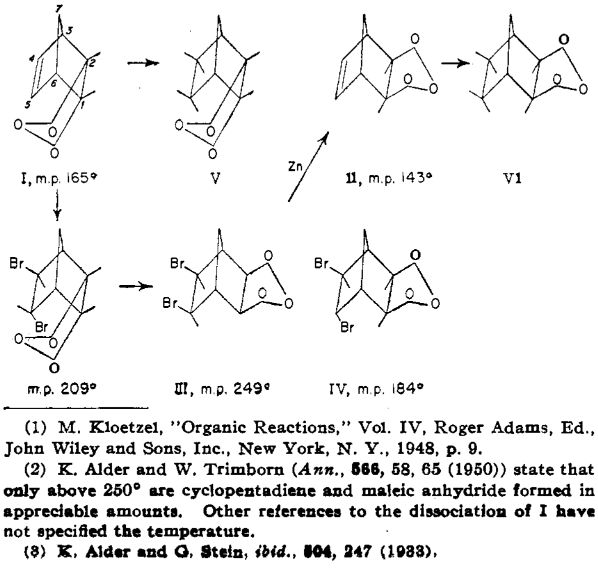
The often studied 1,3-cyclopentadiene maleic anhydride adduct, m.p. 165°, which has the *endo* configuration, has been found to rearrange to the *exo* isomer, m.p. 143°. A mechanism proposed to account for this change involves a hydrogen shift on one side of the molecule subsequent to the breaking of a C to C bond on the other side. The rearrangement which can be followed by melting point is catalyzed neither by tertiary amines nor by acids and is not repressed by the presence of maleic anhydride, at least in the early stages. The *exo* adduct is not formed initially in the diene synthesis.

In connection with another problem in this Laboratory, the heating of *endo*-3,6-methylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride (I) failed to produce cyclopentadiene. Since the belief[1] is currently held that I decomposes reversibly into cyclopentadiene and maleic anhydride when warmed, a study was initiated, the results of which are reported in the present paper.

When I, m.p. 165°, is heated above its melting point[2] an isomer (II) is formed but cyclopentadiene is not evolved in more than traces up to at least 210°. The isomerization, though not quantitative, appears to be reversible. Mixtures containing both isomers are produced from the heating of either I or II.

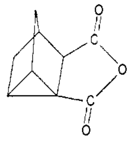
Isomer II which melts at 143° proved to be the *exo*-3,6-methylene-1,2,3,6-tetrahydro-*cis*-phthalic anhydride which was previously prepared by Alder and Stein[3] by a roundabout method. These workers brominated I to form a dibromide, m.p. 209°, which with careful treatment to avoid lactone formation hydrolyzed to a dibromo acid. This acid having the *endo* configuration decomposed and rearranged when heated to form a dibromide anhydride (III), m.p. 249°. The III when warmed with zinc and acetic acid formed II for which the *exo* configuration was definitely proved. Therefore, III must have the *exo* configuration. It can now be reported that III is not formed by the bromination of II. Instead a new dibromide anhydride (IV) melting at 184° is formed. IV cannot be converted directly to III but the debromination of IV as with III leads to II. Therefore IV must be an *exo*-derivative and the configuration of the bromine bearing carbon atoms evidently must account for the difference between III and IV. Since the bromine atoms in IV presumably are *trans* to each other, those in III are *cis* but there is no evidence to reveal if they are *exo* or *endo* to the methylene group.



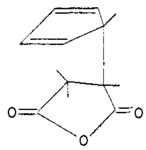
I, m.p. 165° V II, m.p. 143° VI

m.p. 209° III, m.p. 249° IV, m.p. 184°

The conversion of I to II, *a priori*, could result from five possibilities. These are: (1) the alkali-catalyzed inversion of carbon atoms one and two; (2) an acid-catalyzed Alder and Stein mechanism similar to that applied by Bartlett and Schneider[4] to the rearrangement of *endo*-dicyclopentadiene to the *exo*-dimer; (3) the dissociation of I followed by a diene synthesis contrary to Alder[5] rule II; (4) a hydrogen shift to form either a nortricyclyl[6] derivative VII or cyclopentadienylsuccinic anhydride VIII; and finally, (5) rearrangement with the formation of no isolatable intermediate.



VII



VIII

The rate at which I and II rearrange at 190° was followed by a melting point technique. The values in Fig. 1 when compared with the melting point diagram, Fig. 2, show that the rate for I is not affected by the presence of 1% of di-*n*-butylaniline. Other similar measurements show it to be unaffected by the presence of 1% of benzenesulfonic acid monohydrate. The negative results with the epimerizing reagents seem to show that possibilities (1) and (2) above cannot account for the change of I to II.

In order to test further the possibility of epimerizing carbons one and two the saturated anhydrides V and VI, previously reported by Alder and Stein,[3] were heated both in the presence and absence of di-*n*-butylaniline. They were found to be stable and thus to differ in this respect not only from I and II, but also from the two piperylene–maleic anhydride adducts and their dihydro derivatives. The rearrangement of the piperylene derived com-

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[1] M. Kloetzel, "Organic Reactions," Vol. IV, Roger Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 9.

[2] K. Alder and W. Trimborn (*Ann.*, **566**, 58, 65 (1950)) state that only above 250° are cyclopentadiene and maleic anhydride formed in appreciable amounts. Other references to the dissociation of I have not specified the temperature.

[3] K. Alder and G. Stein, *ibid.*, **504**, 247 (1933).

[4] P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

[5] The reaction of cyclopentadiene with maleic anhydride occurs at room temperature in complete accordance with Alder Rule II to form I. *Cf.* Reference 1.

[6] J. D. Roberts and others, THIS JOURNAL, **72**, 3116 (1950); *ibid.*, **72**, 3329 (1950).

pounds, unlike the rearrangement of I and II, is catalyzed by tertiary amines,[7] presumably by way of intermediate enolic forms.

The stability of V and VI can be ascribed to the non-planar rigid bridged structure of these cyclic anhydrides which no doubt prevents the hydrogen shift needed to form an intermediate enol. Now the unsaturated anhydrides I and II on a similar basis should also resist enolization. *Hence the reversible change with them must be due to the presence of the* Δ^4*-double bond* though not as noted above by an acid-catalyzed mechanism. Of interest, too, is the fact that the saturated dibromide anhydrides III and IV are relatively stable toward heat.

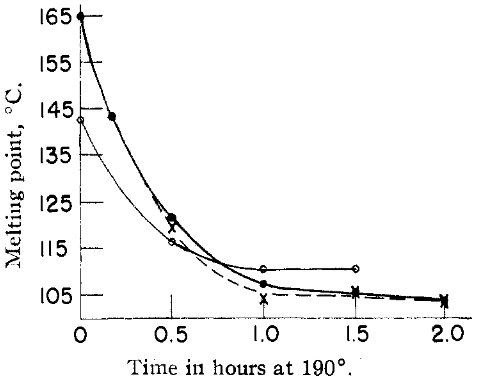


Fig. 1.—The effect of heat on the melting point of *endo*- and *exo*-3,6-methylene-1,2,3,6-tetrahydrophthalic anhydride: -●-, the *endo*-isomer; --×-, the *endo*-isomer + 1% di-*n*-butylaniline; -O-, the *exo*-isomer.

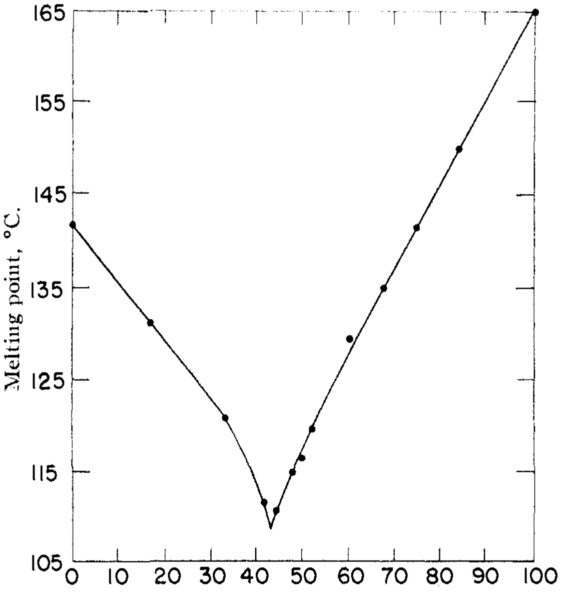
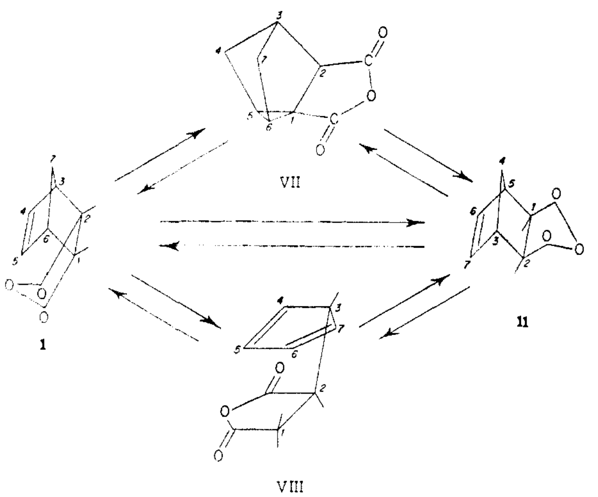


Fig. 2.—The melting point diagram for mixtures of *endo*- and *exo*-3,6-methylene-1,2,3,6-tetrahydropthalic anhydride.

A comparison of the melting point diagram (Fig. 2) with Fig. 1 shows that mixtures prepared by heating I may be several degrees lower in melting point than the eutectic of I and II. This fact, less evident with the heating of II, which appears to form an equilibrium mixture containing 57% of II, indicates the presence of at least one other substance. The following formulation pertaining to such a substance and to possibility (4) is intended to show how either VII or VIII could serve as tautomeric intermediates for the *endo–exo* rearrangement of I to II. Evidence against the presence of VIII is the almost complete lack of ultraviolet absorption of I, II and of the rearrangement mixtures and also that there has been no indication of an adduct of VIII when I is heated with maleic anhydride. With respect to VII, such conclusive evidence is not available, although the mixture secured by heating I for one hour at 190° absorbed exactly one molar equivalent of hydrogen. By heating I, with periodic removal of II, it has been possible in one experiment to isolate a 77% yield of II. A residue remained which melted at about 90°, amounted to 20% of the I started with, and apparently consisted in the main of I and II. The presence of one or more byproducts in small amount is thus confirmed and VII if present must have nothing to do with the change of I to II.



Since it was not possible to isolate or detect an intermediate such as VII or VIII, the direct conversion of I to II, possibility (5), by way of a non-isolatable intermediate IX becomes attractive. The mechanism suggested for this change involves a scission of the bond between carbons 1 and 6 in accord with the Schmidt rule to form IX with the subsequent hydrogen shift from position 7 to position 4. Finally a bond between carbons 1 and 5 is established to form II. The hydrogen shift[8] can occur on one side of the molecule while the carbon to carbon shift occurs on the other. This shift is quite similar to that proposed by Ross, Gebhart and Gerecht[9] for the "substitution" addition and is applicable also to the rearrangement of II.

The choice between possibilities (3) and (5) is of obvious interest to the chemistry of the diene

[7] D. Craig, THIS JOURNAL, **72**, 1678 (1950).

[8] A similar shift was found to occur in the reaction of a 1,4-dihydropyridine with maleic anhydride (D. Craig, THIS JOURNAL, **72**, 5236 (1950)).

[9] J. Ross, A. J. Gebhart and J. F. Gerecht, *ibid.*, **68**, 1373 (1946); compare K. Alder, H. Soll and H. Soll, *Ann.*, **565**, 84 (1949).

synthesis. The former, which is the Alder mechanism,[2] postulates dissociation into diene and dienophile[10] as the intermediate step. Arguments that might be raised against this interpretation are (a) that cyclopentadiene and maleic anhydride could not be detected at 190° and (b) the fact that neither VIII nor a reaction product of maleic anhydride with VIII is produced as an intermediate. Compound VIII is the hypothetical "substitution" product of the reaction of cyclopentadiene and maleic anhydride. Though not expected at low temperatures, it should be formed irreversibly at temperatures above 150°. However, for very small concentrations of diene and dienophile the amount of VIII formed will be inappreciable. Hence, argument (b) is actually pointless.

Likewise, argument (a) does not rule out possibility (3) since only a very small quantity of the dissociation products are required. This clearly and in a way unfortunately follows directly from the Alder[2] mechanism in which the ratio of the concentration of I to that of II, $C_{\mathrm{I}}/C_{\mathrm{II}}$, equals K the overall equilibrium constant. This is equal to $k_1/k_2 \times k_4/k_3$ where k_1, k_2, k_3 and k_4 are the rate constants in the following formulation. Also shown is an alternate route to I by way of the Alder complex X. A similar route is not open for the formation of II; hence, if X is sufficiently stable, I should be the sole initial product. The formation of I by way of X should display a "ceiling temperature" above which the formation[11] of II and also I might occur without benefit of a complex such as X. When cyclopentadiene was added to maleic anhydride at about 190° during 10 minutes there was produced a mixture containing about 82% of I. This by reference to Figs. 1 and 2 shows that very little II could be formed initially and that 190° is below any ceiling temperature for the formation of I by way of X. The direct formation of II from the diene and dienophile seems to fall in the class of the synthesis from dienes which cannot form an Alder complex readily such as *cis*-piperylene. Hence, it would appear that the rearrangement by way of the dissociation mechanism of Alder is unlikely since a plausible alternate path through IX is available. This path involves the breaking of only one C to C bond while the Alder path involves two.

$$\begin{tikzcd}
 & \mathrm{X} \arrow[dl] \arrow[d, shift left] & \\
\mathrm{I} \arrow[r, shift right, "k_2"'] \arrow[dr, shift left] & C_5H_6 + C_4H_2O_3 \arrow[l, shift right, "k_1"'] \arrow[u, shift left] \arrow[r, shift right, "k_3"'] \arrow[d, shift left] & \mathrm{II} \arrow[l, shift right, "k_4"'] \arrow[dl, shift left] \\
 & \mathrm{IX} \arrow[ul, shift left] \arrow[u, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

As a final point in the study, it was found that I at about 200° underwent diene interchange with 2,3-dimethylbutadiene to form cyclopentadiene and 4,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride. Likewise, fumaric acid reacted with I to form maleic anhydride and 3,6-methylene-1,2,3,6-tetrahydro-*trans*-phthalic acid. These reactions, the *endo–exo* rearrangement of dicyclopentadiene, and its dissociation into cyclopentadiene all appear to follow a mechanism similar to that proposed for the change of I to II.

Experimental

Alder and co-workers' preparations of I, II, III, V and VI were repeated and in most cases verified. However, some additions and revisions should be made especially with respect to their observations concerning the acids of these anhydrides. Thus *endo-3,6-methylene-1,2,3,6-tetrahydro-cis-phthalic acid* after crystallizing from water melted at 193–194° with decomposition. (*Anal.* Calcd. for $C_9H_{10}O_4$: C, 59.30; H, 5.56. Found: C, 59.19; H, 5.55.) Alder and Stein[3] reported 177–178° with decomposition and also stated that the exact value varied with the manner of heating. The "melting point" also is strongly dependent on purity.

***exo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Acid.**—The reported melting point of 148° could not be observed for samples of this acid prepared according to Alder and Stein[3] and Bartlett and Schneider.[4] Moreover, a monohydrate crystallized from water. It melted at 153–154° with decomposition alone or mixed with the acid prepared by the hydrolysis of the anhydride, m.p. 142–143°, which was isolated from the rearrangement of the *endo*-anhydride I. The latter acid was analyzed.

Anal. Calcd. for $C_9H_{10}O_4 \cdot H_2O$: C, 53.98; H, 6.05. Found: C, 53.87; H, 6.13.

When the hydrate was heated for 30 minutes at 0.5 mm. pressure on the steam-bath, one mole of water was evolved and the acid remaining then melted at 161–162° with decomposition.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.30; H, 5.55. Found: C, 59.45; H, 5.56.

The acid reacted with an excess of acetic anhydride at 100° to quantitatively reform the *exo*-anhydride II, m.p. 139–142°, alone or mixed with an authentic specimen.[3]

***trans*-4,5-Dibromo-*exo*-3,6-methylenehexahydro-*cis*-phthalic Anhydride (IV).**—The method used was the one Bartlett and Schneider[4] reported for brominating the *endo*-anhydride. Two grams of the *exo*-anhydride II gave 2.6 g. (68%) of crystals m.p. 180–182°. Recrystallization from ethyl acetate yielded 2.0 g. of pure dibromoanhydride, m.p. 183–184°.

Anal. Calcd. for $C_9H_8Br_2O_3$: C, 33.32; H, 2.49. Found: C, 33.45; H, 2.58.

The anhydride suffered no change in melting point while being heated at 250° for two minutes. Debromination[4] with zinc and acetic acid gave the *exo* unsaturated acid in 66% yield. It reacted slowly but completely with two equivalents of hot one normal sodium hydroxide. Acidification then precipitated an acid monohydrate which was dried at 50° and 0.5 mm. pressure. It melted at 160–161° with decomposition.

Anal. Calcd. for $C_9H_{10}Br_2O_4 \cdot H_2O$: C, 29.99; H, 3.36. Found: C, 30.18; H, 3.35.

***exo*-3,6-Methylenehexahydro-*cis*-phthalic Acid.**—Four and fifteen-hundredths grams (0.025 mole) of the *exo*-anhydride II, m.p. 140–142°, absorbed exactly 0.025 mole of hydrogen during two minutes over PtO_2 in ethyl acetate solution. The catalyst was filtered off and the solvent was almost completely evaporated. The addition of cyclohexane to the residue then caused 3.65 g. (87% yield) of poorly defined crystals to form which melted at 83–84°. Bartlett and Schneider[4] reported 77.5–78.5°. The anhydride was boiled for five minutes with 15 ml. of water and the resulting clear solution cooled. A yield of 3.06 g. of colorless crystals, m.p. 155–156° with decomposition, was obtained. After several days at room temperature the melting point with decomposition was 158–159°.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.66; H, 6.57. Found: C, 58.76; H, 6.73.

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(10) The Alder mechanism cannot be eliminated by the failure of maleic anhydride to repress the rearrangement as was pointed out independently by two referees of this paper, to whom the author is grateful.

(11) See, for example, F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950).

This acid evidently shows less tendency to form a hydrate than do the other *exo*-acids reported on here. It was also isolated as a by-product in the debromination of the dibromide anhydride III according to the method of Alder and Stein.[3]

The Rearrangement of *endo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride (I).—Fifteen grams of I was heated in an open flask immersed in an oil-bath. The temperature was held at 190 ± 2° as measured by a thermometer in the reacting liquid. There was no loss in weight during 1.5 hours. The product (m.p. 105°) was crystallized twice from benzene. A yield of 5.3 g. of the *exo*-anhydride II, m.p. 140–142, was secured. The benzene mother liquors were united and the solvent was evaporated. The residue was heated at 190° for one-half hour and the product crystallized from benzene as before to provide 2.8 g. of II. The cycle was repeated three times to give 1.64-g., 1.14-g. and 0.63-g. portions of II amounting to a total yield of 77%. The final residue melted at 80–90° and weighed 3.1 g. (20.5%). This residue when vacuum distilled yielded a distillate containing I and II and a small non-distillable residue. Maleic anhydride was looked for but was not detected. Proof that I was present in the distillate was readily secured by boiling it with water. The crystals which formed on cooling melted at 191–193° with decomposition alone or mixed with an authentic specimen of the *endo*-acid. Recrystallization of the 140–142° melting product from benzene gave a colorless crop of crystals, m.p. 142–143° alone or mixed with the *exo*-anhydride prepared according to Alder and Stein.[3]

The data for Fig. 1 were obtained on 5.00-g. samples of I. The melting points (clear points) after zero, one-half, one, 1.5 and two hours were, respectively, 165°, 122°, 107°, 106° and 104°. The values in the presence of 1% of either *n*-butylaniline or benzenesulfonic acid monohydrate were not substantially different from these. The mixture produced by heating 3.28 g. (0.02 mole) of I with 1.96 g. (0.02 mole) of maleic anhydride for one hour at 190° and then distilling off the unreacted maleic anhydride at 0.5 mm. melted at 108° and weighed 2.87 g.; crystallization twice from benzene gave 0.56 g. of the *exo*-anhydride, m.p. 139–141° alone or mixed with an authentic specimen.

The Rearrangement of the *exo*-Anhydride II.—This was conducted as for I using 5.00 g. of II. The melting points of the mixture produced after zero, one-half, one, and 1.5 hours at 190° were, respectively, 142.5° 116°, 109° 108°. The data show (Figs. 1 and 2) that there is less by-product formation on heating II than on heating I. It would appear that the equilibrium mixture produced at 190° has nearly the eutectic composition. The presence of I in the mixture was proved by first crystallizing from benzene to remove II (yield 1.45 g.) and then boiling the mother liquor with water to remove benzene and to hydrolyze the anhydrides present to acids. A clear solution which resulted was cooled. A crop of crystals formed; yield 0.78 g., m.p. 181–183° with decomposition. Recrystallization from water gave a pure product, m.p. 193–194°, with decomposition alone or mixed with authentic specimens of the *endo*-acid prepared directly from maleic acid and cyclopentadiene or by the hydrolysis of I.

The Melting Points of Mixtures of I and II.—Five-gram samples of the desired mixtures were weighed into test-tubes and the melting points (actually clear points) were taken while stirring with a thermometer. The values given in Figs. 1 and 2 seemed reproducible to within about 1°. The mixtures used for the data of Fig. 1 were obtained by heating 5-g. samples in an oil-bath for the desired periods of time.

Attempted Rearrangement of *endo*-3,6-Methylene Hexahydro-*cis*-phthalic Anhydride.—A 1.80-g. sample initially melting at 167° was heated at 255° for two minutes. The melting point was found to be unchanged. 0.030 g. of di-*n*-butylaniline was then added. The melting point of the mixture was found to be 163.5° before and after heating for two minutes at 275–280°. There was no change in weight during the heating. The anhydride used in this experiment was prepared by hydrogenating I over PtO_2 in ethyl acetate solution. Exactly one equimolar amount of hydrogen was absorbed during two minutes. The acid prepared from the hexahydro anhydride melted at 173–174° when crystallized from water. Alder and Stein[3] gave 161°.

Similarly the *exo*-dibromide, m.p. 183–184° when heated to 250° for two minutes, underwent no change in melting point and the *exo*-acid monohydrate dehydrated smoothly merely by heating to 250° to form the anhydride, m.p. 183–184°.

Diene Interchange Experiments.—One-hundredth mole (1.64 g.) of I, 0.016 mole (1.33 g.) of 2,3-dimethylbutadiene and 0.005 g. of hydroquinone were heated in a sealed tube at 200° for 20 minutes. The contents of the tube were distilled through a short column to give a distillate, b.p. 50–65°, weighing 0.50 g. and a residue of 2.28 g. The distillate reacted vigorously with maleic anhydride to form a crystalline product which after two crystallizations from benzene melted at 163–164° alone or at 164–165° mixed with authentic I. Thus the presence of cyclopentadiene was established in the distillate. The residue had a b.p. of 275°. It was crystallized from a mixture of benzene and cyclohexane to give 0.15 g. of crystals, m.p. 73–76°, alone or at 75–77° mixed with authentic 4,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride.

A mixture of 0.05 mole (8.2 g.) of I and 0.05 mole of fumaric acid was heated at 200° for 15 minutes at 100 mm. pressure in a distilling flask. Distillation was then effected by steadily reducing the pressure and finally raising the temperature to 230°. The distillate and residue weighed 4.1 g. and 9.6 g., respectively. The residue was boiled with water and filtered hot to remove 1.05 g. of fumaric acid, m.p. 295–298° with decomposition. The filtrate on cooling first gave 1.7 g. of impure fumaric acid, m.p. 265–270°. A further crop (0.20 g.) of crystals then formed which melted at 180–183° alone or at 183–188° mixed with authentic 3,6-methylene-1,2,3,6-tetrahydro-*trans*-phthalic acid, m.p. 190°, prepared by the reaction of aqueous fumaric acid and cyclopentadiene. Maleic anhydride, 1.8 g., m.p. 54° alone or mixed with authentic material, was secured by redistillation of the distillate. The residue (2.0 g.) from this distillation was recrystallized from benzene to give 0.25 g. of the *exo*-anhydride, m.p. 137–139° alone or 139–141° mixed an authentic specimen of II.

Diene Synthesis at 190°.—A 200-ml., 3-necked flask was equipped with reflux condenser, dropping funnel, magnetic stirrer and a thermometer that could be adjusted to any desired level in the flask. Two tenths moles (19.6 g.) of maleic anhydride was added and heated to 180°. Then during ten minutes 7.4 g. of cyclopentadiene was added from the dropping funnel. Reaction occurred rapidly even in the vapor phase where the temperature was about 200° while the liquid was kept at 180–190°. The flask was cooled and the excess maleic anhydride (10.8 g.) distilled off at 6 mm. The reaction product melted at 148° which according to Fig. 2 indicates it contains 82% of I. The average time of heating at about 190° during the reaction was five minutes. This period and 148° correspond fairly well to the data of Fig. 1.

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RECEIVED JANUARY 29, 1951