[Contribution from the Department of Chemistry, University of Michigan]

MECHANISM OF THE REACTION OF MONO-OLEFINS WITH DIENOPHILES. I. ALLYLBENZENE AND ARYLMALEIC ANHYDRIDES

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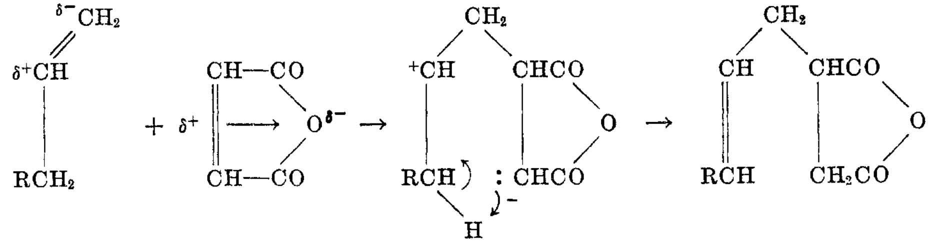
The diene synthesis (Diels-Alder reaction) is a well-established reaction known for 25 years. However, the thermal condensation of *mono*-unsaturated olefins with dienophiles is quite youthful, dating back only to 1943. In his first paper, Alder demonstrated that a variety of olefins would react with maleic anhydride (and with azodicarboxylic ester) to form alkenylsuccinic anhydrides (IV) (and alkenylhydrazinedicarboxylic esters) (1a). He contented himself with broad speculations about the mechanism, but he concluded tentatively that maleic anhydride attacked the *alpha*-position in "substituting addition." When he resumed work after the war, he studied a wider variety of olefins and revised his mechanistic ideas drastically (1b).

We noted that this reaction was formally similar to others which involved addition of an electrophilic reagent to a double bond, followed by elimination of a proton to form a new double bond [*e.g.*, chlorination of isobutylene (2)]. In later papers, we shall consider possible radical or "homolytic" mechanisms. For the present, we consider that both olefin and dienophile are polarized and that the reaction is initiated by attack of the negative end of the olefin upon the relatively positive double bond of maleic anhydride. A similar picture has been given by Arnold (3) and in several patents (4), with emphasis upon precise orientation so that the transition state is a quasi-six-membered ring.



I II III IV

If the reaction does indeed proceed through a polar mechanism such as that pictured, then alteration of the polar and steric nature of the dienophile should cause a predictable change in the course of the reaction (Structures V and VI). We elected to study this reaction using arylmaleic anhydrides, in which the steric effect can be held constant and the polar nature can be varied widely by appropriate choice of the *para*-substituent. The reference olefin was allylbenzene,

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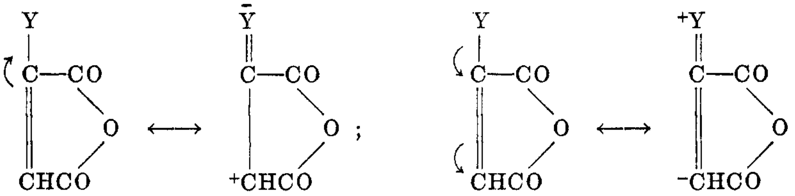
[1] From the dissertation of A. H. Filbey, 1953. Present address, Ethyl Corporation, Detroit, Michigan.

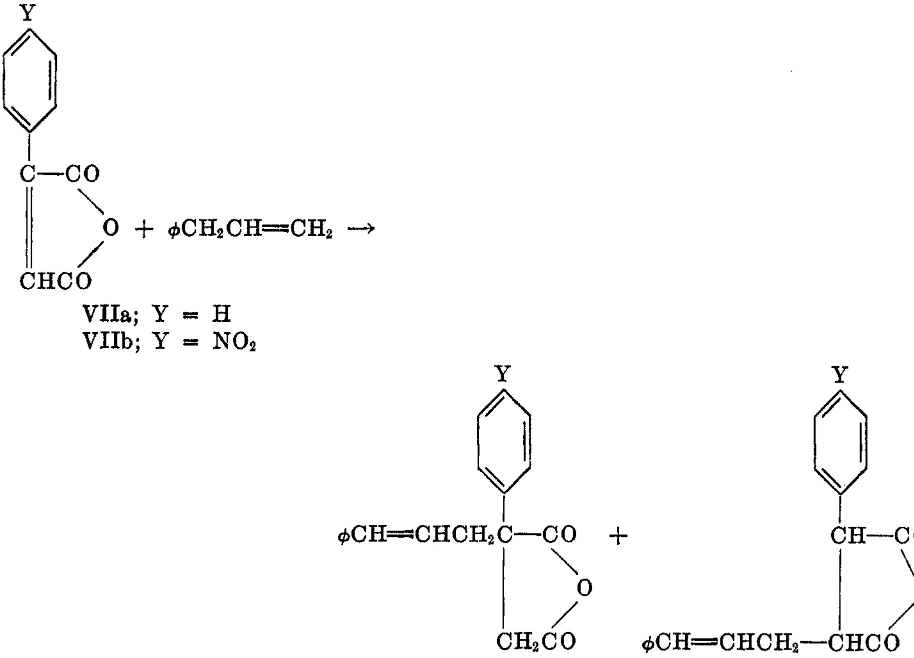
which is readily prepared and purified and has a convenient boiling point; moreover, the expected products are susceptible to independent synthesis.



Va Vb VIa VIb

RESULTS

Equimolar amounts of allylbenzene and phenylmaleic anhydride were heated together in benzene. The best yield of mixed isomeric adducts (43%) was obtained at 250° for 14 hours. Higher temperatures and longer times increased the amount of higher-molecular weight material. On the other hand, the yield was only 17% at 215° for 18 hours, and considerable starting material was recovered. The average yield in several runs at 250° was 33%. *p*-Nitrophenylmaleic anhydride reacted with allylbenzene to form the mixed adducts in only three hours at 230°. The yield averaged 35%.

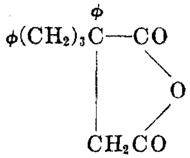


VIIa; Y = H
VIIb; Y = NO_2

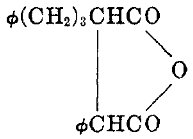
VIIIa; Y = H
VIIIb; Y = NO_2

IXa; Y = H
IXb; Y = NO_2

The location of the side-chain double bond in the mixture of VIIIa and IXa was established by oxidation to benzaldehyde in good yield. Its position in the nitro adducts was assumed by analogy. Since the double bond would interfere in the analytical methods to be used, it was catalytically saturated, and the analyses were performed on the mixed hydrogenated adducts Xa and XIa.



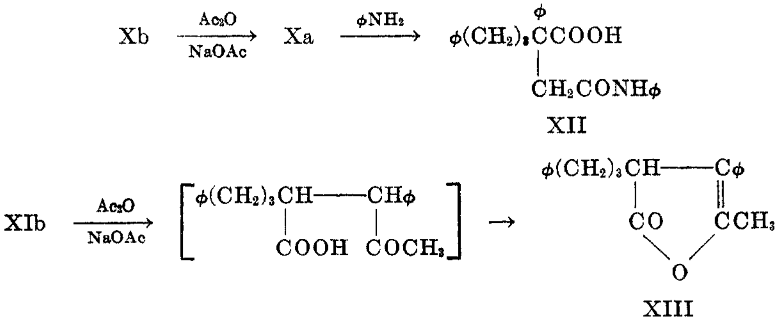
Xa; anhydride
Xb; dibasic acid



XIa; anhydride
XIb; dibasic acid

This offers the further advantage that *cis-trans* isomerism about the double bond cannot complicate matters.

The compound XIa can still exist as two diastereoisomeric racemates, so that the hydrogenated adduct would more correctly be considered a mixture of three distinct compounds. Quantitative separation hardly appeared feasible, so we turned to other methods. In Xa, one carbonyl group is flanked by a methylene group of low steric requirements; in XIa, both carbonyl groups are partially obstructed by the α-substituents. Thus authentic Xa reacts rapidly with aniline to form a monoanilide (XII), while XIa scarcely reacts. The mixture of Xa and XIa from the adduct deposited the Xa as XII when treated with aniline, indicating that the original adduct was about 30% VIIIa and 70% IXa. A second method was based on the observation (5, 6) that an arylacetic acid underwent decarboxylative acetylation with hot acetic anhydride-sodium acetate only when an α-hydrogen was present. Such an α-hydrogen is present in XIb but not in Xb. Thus authentic Xb was reconverted to Xa, while XIb formed the unsaturated lactone XIII (no longer diastereoisomeric) when heated with acetic anhydride and sodium acetate. When the hydrogenated adduct was subjected to this treatment, 58% appeared as XIII and the balance (after reaction with aniline) as XII.



XII

XIII

The most accurate method was based on the fact that the infrared spectrum of Xa (Fig. 1) has bands at 7.04 μ (assigned to the methylene group *alpha* to the carbonyl) and 9.77 μ which are absent from the spectrum of XIa (Fig. 2). The intensities of both bands obeyed Beer's Law in mixtures of authentic Xa and

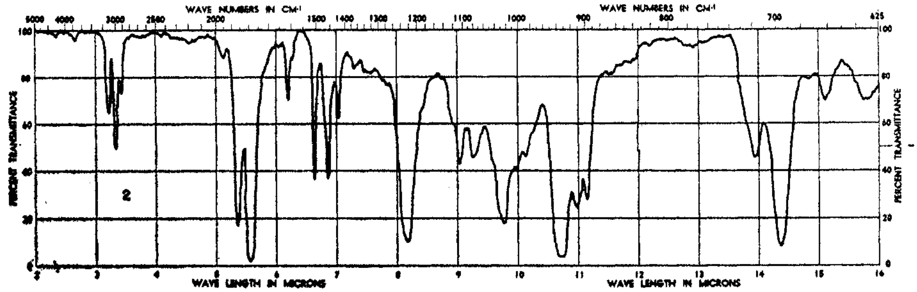


FIG. 1. INFRARED SPECTRUM OF 2,5-DIPHENYLPENTANE-1,2-DICARBOXYLIC ANHYDRIDE (Xa); 5% solution in carbon tetrachloride.

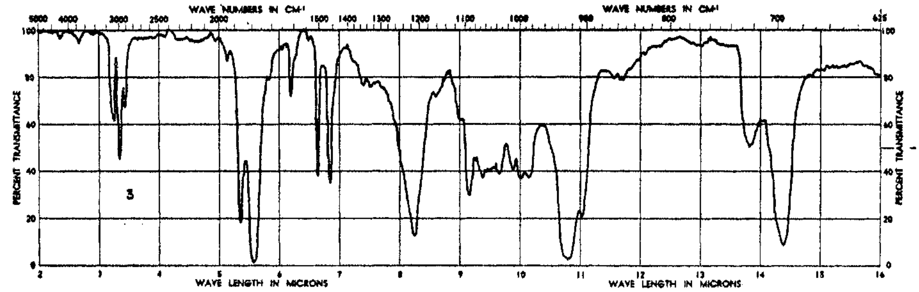


FIG. 2. INFRARED SPECTRUM OF 1,5-DIPHENYLPENTANE-1,2-DICARBOXYLIC ANHYDRIDE (XIa); 5% solution in carbon tetrachloride.

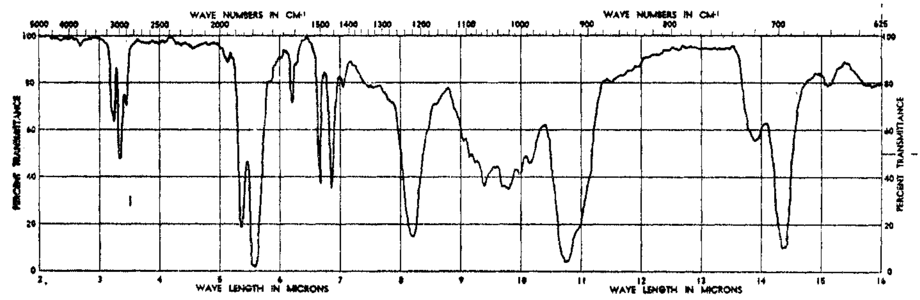


FIG. 3. INFRARED SPECTRUM OF THE HYDROGENATED ADDUCT FROM ALLYLBENZENE AND MALEIC ANHYDRIDE; 5% solution in carbon tetrachloride.

XIa, so that the spectrum of the hydrogenated adduct mixture (Fig. 3) corresponds to the composition 36% of Xa and 64% of XIa.

The adduct mixture from *p*-nitrophenylmaleic anhydride was to be converted to a mixture of Xa and XIa for infrared analysis by saturation of the double bond and removal of the nitro group by reduction and deamination. Unfortunately, catalytic hydrogenation reduced only the double bond, and ammonium sulfide achieved only incomplete reduction of the nitro group. However, comparison of the spectra of the adducts from phenyl- and *p*-nitrophenyl-maleic anhydrides

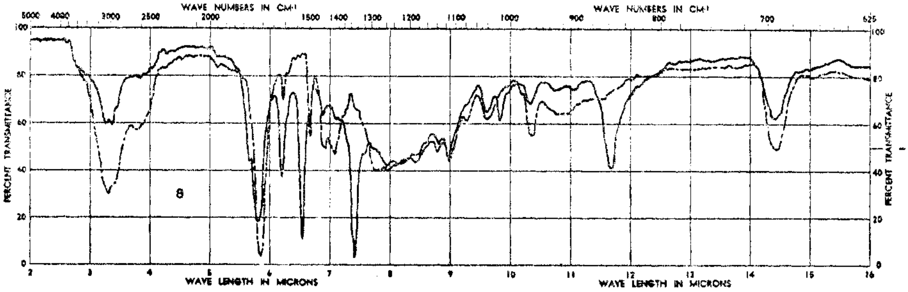
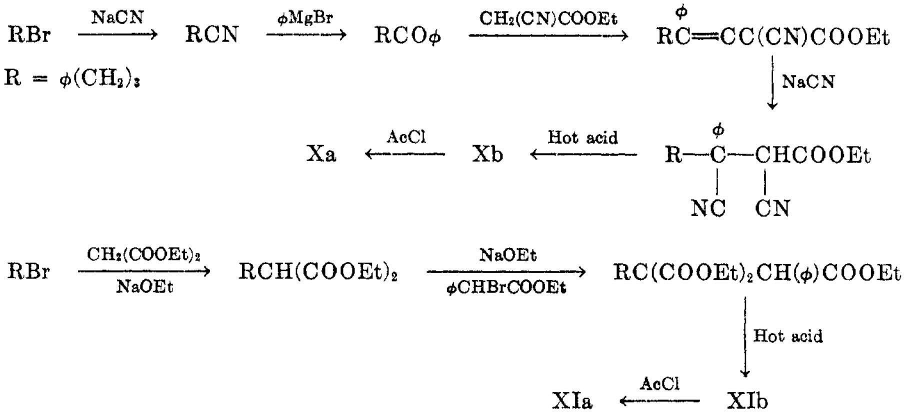


FIG. 4. INFRARED SPECTRA OF THE ADDUCTS (as the acids) FROM ALLYLBENZENE AND PHENYLMALEIC ANHYDRIDE (————) AND FROM *p*-NITROPHENYLMALEIC ANHYDRIDE (—•—•—•—•); 5% solutions in chloroform.

CHART I



with allylbenzene (Fig. 4) leads to the conclusion that the isomer ratio is approximately the same; the two spectra are very similar in the 9.6–9.8 μ region, although the expected peak at 7.06 μ is largely masked by the intense absorption at 7.40 μ due to the nitro group. Further study will be required to make a definite determination of the ratio.

The hydrogenated compounds Xa and XIa required for comparison and study were built up as portrayed on Chart I. One diastereoisomer of XIb was isolated in pure form; the other resisted crystallization and remained as an oil. However, the solid and oily forms were separately converted to XIa, and the two anhydrides were spectroscopically indistinguishable.

The reaction of allylbenzene with esters of maleic and fumaric acids was explored briefly. No adduct was formed until the temperature was raised to 250°.[2] At this temperature an ester of cinnamylsuccinic acid was obtained in 45–55% yield and was identified by hydrolysis to the known acid (8).

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[2] The unreacted maleate ester always appeared as the fumarate. It is likely that isomerization occurs first, followed by reaction with the olefin. The fumarate seems to react more readily.

DISCUSSION

If maleic anhydride reacts with a reference olefin at some standard rate, a substituted maleic anhydride will react at a different rate which will be a function of the steric requirements of the substituent and its electrical characteristics. It is difficult to evaluate the steric factor quantitatively; however, *any* group larger than hydrogen should slow the reaction sterically, and some correlation between size and rate should exist. Different substituents Y of the same effective size should exhibit entirely different effects upon the reaction rate, depending upon their electrical characteristics. An electron-attracting group ought to accelerate the reaction, in opposition to its steric inhibition, by lowering the electron density at the dienophilic double bond, but an electron-releasing substituent should exhibit the reverse effect.

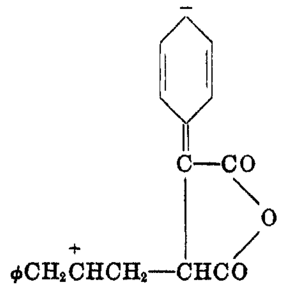
Our earlier work (7) has shown that this is indeed the case. Maleic anhydride reacts readily with allylbenzene at 180° (8), whereas methylmaleic anhydride (citraconic anhydride) shows little inclination to react until the temperature is raised to 250° (7). Chloromaleic anhydride reacts at least as fast as maleic anhydride though the yields are poorer as a result of a side reaction. We predict that fluoromaleic anhydride should react even more readily, since fluorine has a stronger inductive effect and a smaller size than chlorine.

A second consequence of the mechanism is apparent from structures V and VI. Since the symmetry has been destroyed by group Y, two products are now possible, α,α- and α,α'-. Since the negative end of the olefin I attacks the dienophile, it should seek preferentially the more positive carbon in the substituted maleic anhydride. The relative magnitudes and directions of polarization in a series of substituted maleic anhydrides may readily be deduced from the electronic theory. The picture is not quite so simple, however. It is apparent from the literature that the steric effect may be quite important or dominant in determining the isomer ratio. For example, in the addition of anions (such as sodiomalonic ester) to ethyl citraconate, the more positive end of the double bond—the methyl-substituted carbon—should certainly be attacked preferentially. Yet the product of the Michael reaction is tetraethyl 1,1,2,2-butanetetracarboxylate derived by attack at the more negative but unhindered carbon (9). It requires a group of unusually strong electron-releasing power to reverse the orientation dictated by the steric factor. A study of disubstituted maleic anhydrides will provide a clearer picture.

However, the steric factor is of no consequence in deciding whether the reaction is governed by polar forces. The steric effect in phenylmaleic anhydride cannot be estimated, since its chemistry is almost unknown (10). Electrically, it may be regarded as a symmetrically substituted styrene, hence polarized in the sense of structure VIb. *p*-Nitrophenylmaleic anhydride should partake of structure Vb to a greater extent.

Phenylmaleic anhydride (VIIa) reacts with allylbenzene with much more difficulty than does maleic anhydride. This considerable difference must reflect the large steric nature of the phenyl group, diminished somewhat by the ability of the aromatic ring to act as an electron sink. As predicted, *p*-nitrophenylmaleic anhydride (VIIb) reacts much more readily than VIIa. *p*-Methoxyphenylmaleic anhydride, when it becomes available, will probably require temperatures in the neighborhood of 300° for satisfactory reaction.

The isomer ratio observed with VIIa could not have been predicted except by intuition. Polarization as in VIb would favor adduct VIIIa. The steric effect would operate in powerful opposition, however, and resonance stabilization of the transition state leading to IXa by structures such as XIV,



would further increase the amount of the α,α'-isomer. The adduct is actually about two-thirds IXa and one-third VIIIa. This result can be used as a standard for evaluating the contribution of the electrical effect in substituted phenylmaleic anhydrides. At the present time, it is not possible to venture more than a tentative statement, that the electrical effect of even as powerful a group as nitro has little influence upon the isomer ratio, and that therefore the steric effect is orientation-controlling. The results of our continuing work should permit a future, more positive conclusion. However, the reaction *rate* is markedly affected by the electrical features of a group.

EXPERIMENTAL[3]

Materials. Allylbenzene, prepared by coupling phenylmagnesium bromide with allyl bromide, was freed from peroxide by shaking with acidified ferrous sulfate solution, dried, and fractionated under nitrogen. *Phenylmaleic anhydride* and *p-nitrophenylmaleic anhydride* were prepared as previously described (11). *Methyl* and *butyl maleates* were obtained through the courtesy of Commercial Solvents Company, and *methyl fumarate* (m.p. 101.0–101.5°) was formed by the iodine-catalyzed isomerization of methyl maleate.

Allylbenzene and methyl maleate. Dimethyl 5-phenyl-4-pentene-1,2-dicarboxylate. A mixture of 11.8 g. (0.1 mole) of allylbenzene, 14.4 g. (0.1 mole) of methyl maleate, and 0.1 g. of hydroquinone (to inhibit radical polymerization) was heated in a Carius tube at 250–275° for eight hours. Upon distillation, there was recovered 2 g. of allylbenzene and 2.1 g. of methyl *fumarate*[2] boiling below 140°/3 mm. The adduct was obtained as a light green oil, b.p. 140–155°/3 mm., 12.4 g. (47% based on material charged). The polymeric residue weighed 8.5 g. The redistilled adduct boiled at 136–140°/2.5 mm., n_D^{20} 1.5241.

When methyl fumarate was substituted for the maleate, and when the mixture was heated at 250–275° for 15 hours, no unreacted ester was recovered, and the yield of adduct was 55%. Butyl maleate at 250–275° for eight hours gave a 45% yield of butyl ester, b.p. 192–199°/2 mm.

Either the methyl or butyl ester could be hydrolyzed in high yield to the known (8) cinnamylsuccinic acid, m.p. and mixture m.p. 140–142° (from acetonitrile), by standing for two days at room temperature with aqueous alcoholic potassium hydroxide.

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[3] Melting points are uncorrected.

Allylbenzene and phenylmaleic anhydride. A. Formation of the adduct. A mixture of 24.2 g. (0.14 mole) of freshly sublimed phenylmaleic anhydride, 16.4 g. (0.14 mole) of allylbenzene, and 45 ml. of dry benzene was heated in a Carius tube at 245–255° for 14 hours. Upon distillation, benzene and unreacted allylbenzene came over first, followed by 3.1 g. of unreacted phenylmaleic anhydride, b.p. 120–140°/0.3 mm. The crude adduct, 14.5 g. (36% based on material charged), was collected at 203–210°/0.28 mm. The viscous residue (10 g.) boiled above 240°/0.3 mm. Redistillation of the adduct gave 13.0 g. of a light green, viscous oil, b.p. 194–195°/0.17 mm.

Anal. Calc'd for $C_{19}H_{16}O_3$: C, 78.05; H, 5.52.
Found (K):[4] C, 77.67; H, 5.43.

In other experiments, longer reaction times increased the proportion of polymer, and lower temperatures resulted merely in larger recoveries of starting materials. Addition of hydroquinone in some runs did not appear to alter the quantity or quality of product. In one experiment, a small amount of dry hydrogen bromide was added; the yield was slightly decreased, and the adduct contained bromine. Thus hydrogen bromide does not exhibit the hoped-for acid catalysis. Acid catalysis is being investigated further.

B. Oxidation of the adduct. The adduct (1 g., 0.0034 mole) was dissolved in 100 ml. of 5% sodium carbonate solution. Then 60 ml. of 1% aqueous potassium permanganate was added in 20 minutes to the stirred solution, which was maintained at neutrality by passing in carbon dioxide. The mixture was steam-distilled until 100 ml. had been collected. The distillate was extracted with ether; evaporation left 0.3 g. (84%) of crude benzaldehyde, identified as its phenylhydrazone (m.p. and mixture m.p. 155–156°). The other oxidation fragment was a brown gum which was not identified.

C. Hydrogenation of the adduct. A solution of 14 g. (0.048 mole) of crude adduct in 200 ml. of purified dioxane or benzene with 0.1 g. of platinum oxide required about six hours in a Parr hydrogenator to absorb one equivalent of hydrogen. The filtrate, on vacuum-distillation, gave 12.5 g. (89%) of green viscous liquid, b.p. 190–192°/0.2 mm., and a small tarry residue. Redistillation at 180°/0.1 mm. gave a light green oil; infrared spectrum, Fig. 3.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16.
Found (K): C, 77.80; H, 6.05.

D. Monoanilide formation. To a boiling solution of 3.91 g. (0.013 mole) of hydrogenated adduct in 100 ml. of dry benzene, 1.24 g. (0.013 mole) of aniline in 5 ml. of benzene was added (12). The solution was allowed to stand at room temperature overnight. The solid was collected and the filtrate was cooled to 10° to obtain an additional crop; total, 2.19 g. of material, m.p. 153–157°. The solid was dissolved in sodium hydroxide solution and extracted with benzene to remove aniline. Acidification gave 1.5 g. (30%) of a white solid. Two recrystallizations from aqueous alcohol gave white needles; mixture melting point with authentic XII (see below) not depressed.

E. Selective decarboxylative acetylation. A solution of 4 g. (0.014 mole) of hydrogenated adduct and 1.6 g. (0.029 mole) of potassium hydroxide in aqueous methanol was kept at room temperature for 24 hours. The methanol was blown off, then excess water was added and the solution was acidified. The crude acid (4.2 g., 98%) was recovered by extraction with isopropyl ether.

A solution of 4.2 g. (0.014 mole) of the mixed adduct acids and 1 g. (0.012 mole) of anhydrous sodium acetate in 45 ml. of acetic anhydride was refluxed for six hours (5). Addition of 150 ml. of isopropyl ether to the cool solution precipitated the sodium acetate, and the solvents were then removed by vacuum evaporation. Excess benzene was added and sucked off to assure removal of acetic acid and acetic anhydride. Finally, the residue was held at 100°/1 mm. for one hour.

The orange residue (3.95 g.), a mixture of Xa and XIII, was dissolved in 200 ml. of boiling benzene and treated with 1.27 g. of aniline in 25 ml. of benzene. After standing at room temperature for 12 hours, the solution was extracted with aqueous sodium bicarbonate.

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[4] Microanalyses by Goji Kodama (K), and W. J. Byrd (B) of this Laboratory, and by Clark Microanalytical Laboratory (C), Urbana, Illinois.

Acidification gave 1.0 g. (19% based on hydrogenated adduct acid) of XII, m.p. and mixture m.p. 158–159° (from aqueous alcohol).

The benzene layer left after the bicarbonate extraction was extracted with dilute hydrochloric acid to remove aniline. After drying, it was vacuum-distilled. The orange viscous liquid, 2.3 g. (58% based on hydrogenated adduct acid), b.p. 190°/0.08 mm., decolorized aqueous permanganate solution.

The orange lactone XIII was hydrolyzed with alcoholic potassium hydroxide at room temperature overnight. After removing the alcohol in an air stream, the residue was diluted with water. The crude viscous keto acid was isolated in 99% yield by extraction with isopropyl ether. Its anilide was prepared (13), m.p. and mixture m.p. with authentic 3,7-diphenylheptane-2-one-4-carboxanilide, 115°.

Allylbenzene and p-nitrophenylmaleic anhydride. A. Formation of the adduct. A mixture of 3.3 g. (0.015 mole) of *p*-nitrophenylmaleic anhydride, 1.8 g. (0.015 mole) of allylbenzene, and 10 ml. of reagent benzene was heated in a Carius tube at 225–235° for three hours. The contents were hydrolyzed with excess alcoholic potassium hydroxide at room temperature overnight. After diluting with three volumes of water, the precipitated tar (allylbenzene plus polymer) weighed 1.2 g. The acidified aqueous filtrate was extracted rapidly with ether to remove the adduct without extracting the rather water-soluble *p*-nitrophenylmaleic acid. The crude residue from the ether extract weighed 2.0 g. (40%). Two recrystallizations (Norit) from alcohol gave a tan solid with no definite melting point. Infrared spectrum, Fig. 4.

The recrystallized acid was dissolved in standard sodium hydroxide solution, to give a deep purple solution. A gray amorphous solid precipitated when one equivalent of standard acid had been added. This substance did not melt up to 250° and it left an ash when burned on a spatula. It is probably the mono-sodium salt of the acid.

Anal. Calc'd for $C_{19}H_{16}NNaO_6$: C, 60.49; H, 4.28.

Found (K): C, 61.04; H, 4.25.

In other runs, it was found that most of the *p*-nitrophenylmaleic anhydride was recovered at temperatures below 210°. If the reaction were run above 245°, a dark tarry material, insoluble in warm alcoholic potassium hydroxide, was formed.

B. Reduction of the adduct. A solution of 3 g. (0.0085 mole) of recrystallized acid adduct in 50 ml. of purified dioxane was stirred with 0.1 g. of platinum oxide in a hydrogen atmosphere. One mole of hydrogen was taken up fairly rapidly (side-chain double bond), but some of the reduced acid precipitated and coated the catalyst. Several attempts at further low-pressure reduction with platinum or palladium failed. The filtrate was vacuum-evaporated to a dark residue weighing 3.2 g. It was dissolved in 100 ml. of aqueous sodium bicarbonate and reprecipitated with acid. The product, 2.5 g. (83%), was a dark gummy solid with no apparent melting point. Its infrared spectrum indicated that the compound was the saturated nitro adduct.

Reduction of the nitro group with ammonium sulfide was somewhat more successful. A solution of 6 g. (0.017 mole) of acid adduct in 20 ml. of 6 *N* ammonium hydroxide was saturated with hydrogen sulfide (14). After boiling, the solution was filtered and acidified with glacial acetic acid. The brown gum which separated (5.2 g.) was filtered with extreme difficulty. Its infrared spectrum showed that an N—H frequency was present, but there was still strong nitro absorption. Separation of the amino acid from the nitro acid by extraction with hydrochloric acid was unsuccessful. Recrystallization from various solvents gave dark gummy material. Reprecipitation from alkaline solution likewise did not increase the purity of the product.

Two attempts were made to deaminate the above reduction mixture. Diazotization in hydrochloric acid, followed by treatment either with hypophosphorous acid or absolute ethanol gave no gas evolution on warming; neither did an attempted diazotization in hypophosphorous acid. It is apparent that very little, if any amine was produced by the reduction.

Synthesis of Xa. α-Phenylbutyronitrile was prepared by refluxing γ-phenylpropyl bromide

(Matheson) with excess sodium cyanide in aqueous alcohol for 24 hours. The yield was 81%, b.p. 142–145°/16 mm. (15). *1,4-Diphenyl-1-butanone* was prepared by addition of phenylmagnesium bromide to the nitrile; the ketimine hydrochloride, an oily gum, was hydrolyzed by dilute hydrochloric acid on the steam-bath for 30 minutes. The yield was 80 %, b.p. 167–172°/3 mm., m.p. 55–56° (from aqueous alcohol), *dinitrophenylhydrazone* m.p. 144.5–145.0° (from ethyl acetate) (16).

Ethyl 2,5-diphenyl-1-cyano-1-pentene-1-carboxylate. A solution of 24.0 g. (0.11 mole) of 1,4-diphenyl-1-butanone, 24.0 g. (0.21 mole) of ethyl cyanoacetate, 8.4 g. (0.14 mole) of glacial acetic acid, and 0.6 g. of ammonium acetate in 40 ml. of benzene was refluxed under a continuous water separator. Ammonium acetate (0.6 g.) was added at four-hour intervals for 20 hours (17). The cooled solution was washed with water, dried over sodium sulfate, and distilled. At a temperature of 190–195°/0.1–0.2 mm., 28 g. (82%) of a viscous yellow liquid was collected and used without further purification in the next step.

Ethyl 2,5-diphenyl-1,2-dicyanopentane-1-carboxylate. A solution of 28.0 g. (0.088 mole) of ethyl 2,5-diphenyl-1-cyano-1-pentene-1-carboxylate in 37 ml. of absolute alcohol was added to 12.1 g. (0.186 mole) of potassium cyanide in 37 ml. of water, and the resultant mixture was heated with stirring for 15 minutes on the steam bath (17). The cooled solution was poured into 50 ml. of water and acidified with hydrochloric acid. Extraction with benzene and removal of the solvent on the water-pump left 27 g. (90%) of a yellow oil. Attempts to obtain a solid product from the crude oil were unsuccessful.

2,5-Diphenylpentane-1,2-dicarboxylic anhydride (Xa). A solution of 27 g. (0.078 mole) of ethyl 2,5-diphenyl-1,2-dicyanopentane-1-carboxylate, 106 g. of concentrated sulfuric acid, 110 g. of glacial acetic acid, and 21 ml. of water was refluxed for 16 hours. After pouring on 320 g. of ice, extraction with benzene and removal of the solvent left a dark residue which was refluxed with 20% aqueous potassium hydroxide for three days (17). After treatment with Norit and acidification, the solution was extracted with benzene. Upon solvent removal, the dibasic acid remained as an oil and failed to crystallize.

Refluxing the oil with acetyl chloride, followed by distillation, gave 11.9 g. (55%) of a viscous green liquid, b.p. 187–188°/0.15 mm. With cooling and scratching, the liquid slowly began to crystallize. Recrystallization from benzene-petroleum ether (60–75°) gave small needles, m.p. 62.5–63.0°.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16; Sapon. equiv., 147.

Found (C): C, 77.32, H, 6.19; Sapon. equiv., 147.

The *monoanilide* (12) formed needles, m.p. 158–160°.

Anal. Calc'd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; Neut. equiv., 387.

Found (B): C, 76.90; H, 6.53; Neut. equiv., 381.

Synthesis of XIa. γ-Phenylpropylmalonic ester was prepared in 74% yield, b.p. 125–130°/0.15 mm. (18). A solution of 84 g. (0.33 mole) of the diester in 150 ml. of dry ethyl carbonate was added with stirring to solid sodium ethoxide (from 6.9 g., 0.33 g.-atom of sodium). The ethanol formed was removed by fractionation (19). Then 86 g. (0.35 mole) of ethyl α-bromophenylacetate (20) was added slowly to the stirred solution. The separation of sodium bromide began immediately. After 18 hours on the steam-bath, the cooled solution was washed with 240 ml. of water. The organic layer was distilled, yielding 108 g. (82%), b.p. 190–200°/0.1 mm., of *triethyl 1,5-diphenylpentane-1,2,2-tricarboxylate.*

1,5-Diphenylpentane-1,2-dicarboxylic acid (XIb) was prepared by boiling (130°) a solution of 95 g. (0.22 mole) of triester, 250 ml. of glacial acetic acid, and 250 ml. of 50% sulfuric acid for 17 hours (5). The cooled solution was poured onto 1 kg. of ice, and the mixture was extracted with isopropyl ether. The organic layer, after washing with water, was extracted with aqueous sodium bicarbonate. (Evaporation of the ether from the organic layer left 36 g. of unhydrolyzed triester.) Acidification of the aqueous alkaline layer gave a gummy solid (a mixture of stereoisomers). The crude material was dissolved in ethyl alcohol, treated with decolorizing charcoal, and recrystallized from aqueous alcohol. Filtration gave 20 g. of an oily solid, but manipulation of the filtrate produced only an oil.

After washing the oily solid three times with 10-ml. portions of benzene, 12 g. of a pure solid stereoisomer, m.p. 186.5–187.5°, was obtained by recrystallization from dilute alcohol.

Anal..Calc'd for $C_{19}H_{20}O_4$: C, 73.05; H, 6.45; Neut. equiv., 147.
Found (C): C, 73.39; H, 6.69; Neut. equiv., 149.

The alcoholic filtrate, from which a second crop of solid could not be obtained, was concentrated and extracted with isopropyl ether. The organic layer and the benzene washings from the solid stereoisomer were combined and evaporated. The 22 g. of residue, a mixture of a solid and a viscous oil, was converted directly to the anhydride. Total yield, based on unrecovered ester, 34 g. (81%).

1,5-Diphenylpentane-1,2-dicarboxylic anhydride (XIa). (a) A solution of 8.0 g. (0.026 mole) of solid XIb in excess acetyl chloride was refluxed for 45 minutes. Vacuum distillation gave 6.9 g. (92%) of a viscous liquid, b.p. 191–200°/0.13 mm. Redistillation at 185–186°/0.11 mm. gave a water-white viscous liquid (XIa). Attempts to obtain a solid product were unsuccessful.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16.
Found (C): C, 77.22; H, 6.11.

(b) A solution of 22.0 g. (0.07 mole) of 1,2-diphenylpentane-1,2-dicarboxylic acid (solid-oil mixture above) in excess acetyl chloride was refluxed 45 minutes. Vacuum distillation gave 16.7 g. (81%) of a liquid, b.p. 189–195°/0.2 mm. Redistillation at 189–191°/0.18 mm. gave a green viscous liquid (XIa) which did not solidify.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16; Sapon. equiv., 147.
Found (C): C, 76.71; H, 6.47; Sapon. equiv., 148.

3,7-Diphenylheptane-2-one-4-carboxylic acid. A mixture of 4 g. (0.013 mole) of XIa and 1 g. (0.012 mole) of anhydrous sodium acetate in 50 ml. of acetic anhydride was refluxed for six hours (5). Addition of excess isopropyl ether and filtration of the precipitated sodium acetate, followed by concentration of the filtrate, gave 3.6 g. (96%) of the lactone.

This residue was taken up in 50 ml. of alcohol and mixed with 25 ml. of 10% alcoholic potassium hydroxide. After standing overnight, the alcoholic solution was diluted with water and acidified. Extraction with isopropyl ether and solvent removal gave 3.4 g. (89%) of viscous oil. Its anilide (13) (3,7-diphenylheptane-2-one-4-carboxanilide) melted at 116–117°.

Anal. Calc'd for $C_{26}H_{27}NO_2$: C, 80.99; H, 7.06.
Found (K): C, 81.13; H, 6.27.

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SUMMARY

1. Phenylmaleic anhydride reacts with allylbenzene at 250° to form a mixture of α-phenyl-α-cinnamylsuccinic anhydride and α-phenyl-α'-cinnamylsuccinic anhydride in a ratio of approximately 1:2.

2. *p*-Nitrophenylmaleic anhydride reacts more readily with allylbenzene. The adduct appears to be a mixture of α,α- and α,α'-*p*-nitrophenylcinnamylsuccinic anhydrides in about the same ratio, 1:2.

3. The results are discussed in terms of a polar mechanism which can be influenced by both electrical and steric effects.

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