

The four Willgerodt reactions described above in detail may be considered as representative and typical of all those carried out. Therefore the remaining experiments are presented in tabular form, Table II consisting of the data on the various and diverse substances discussed in the text of this paper, and Table III consisting of the data on the series of simple mercaptans therein mentioned.

Summary

A series of interrelated experiments has shown

that not only aliphatic ketones, but also the corresponding alcohols, thiols and olefins undergo the Willgerodt reaction to produce carboxylic acid amides. The results of these experiments have further elucidated the course of the reaction and offer additional support for the mechanism previously proposed.

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[CONTRIBUTION FROM COLGATE-PALMOLIVE-PEET CO.]

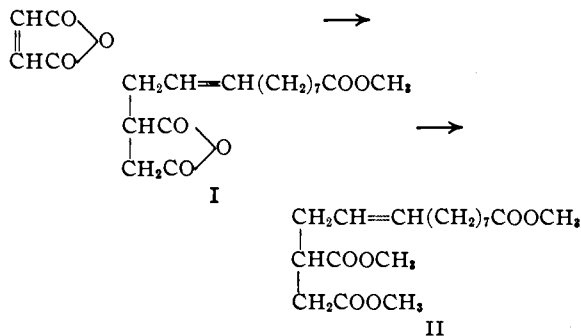
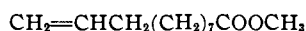
The Addition of Olefinic Esters to Maleic Anhydride

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

There have been several reports in the patent and technical literature¹ where it is claimed that maleic anhydride reacts with mono-olefinic and non-conjugated poly-olefinic acids or esters at temperatures of 200–250° to give addition compounds. The structure of the products obtained and the nature of addition reaction involved have not been established. We have examined the conditions under which maleic anhydride will unite with long chain mono-olefinic acids and esters and have determined the constitution of the major addition products of undecylenic and oleic esters.

Mono-olefinic esters and maleic anhydride react at temperatures of about 200–250° to give good yields of the simple addition compound of one molecule of ester with one molecule of maleic anhydride and under these conditions only negligible amounts of higher molecular weight or polymeric material is formed.

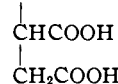
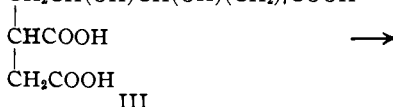
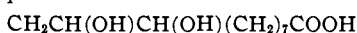
With undecylenic ester, maleic anhydride gives a product which consists mainly of stereomeric forms of structure I. The crude condensation



product was converted to the trimethyl ester II which was distilled. The acids corresponding to this ester were separated into two fractions by crystallization of the potassium salts, from which

(1) E. A. Bevan, *Oil and Colour Chem. Assoc.*, **34**, 1939 (1940); *C. A.*, **34**, 5960 (1940); E. T. Clocker, U. S. Patent 218,882–90 (1940); *C. A.*, **34**, 3845 (1940); W. G. Bickford, P. Krauczunas and D. H. Wheeler, *Oil and Soap*, **19**, 23 (1942).

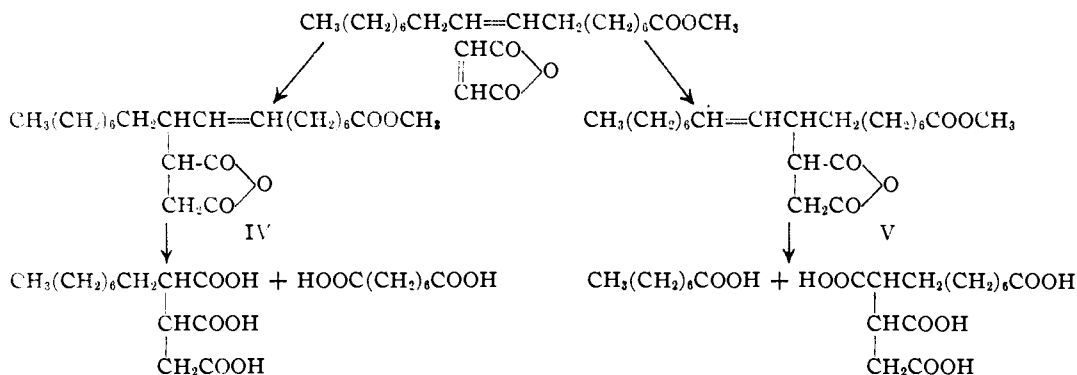
were obtained a solid acid m. p. 98.5° and a liquid acid fraction. Di-hydroxylation of the solid acid from the less soluble potassium salt gave a mixture of isomeric lactones of 4,5-dihydroxy-dodecane 1,2,12-tricarboxylic acid III. The lactone form of III could not be oxidized with periodic acid in acid media.



However, periodate oxidation of an alkaline solution of this lactone *i. e.*, a solution of the trisodium salt of the dihydroxy tricarboxylic acid III, proceeded quantitatively and by oxidation of the resulting aldehydes there was obtained azelaic and tricarballylic acids which demonstrated the structure of the addition product. The solid acid m. p. 98.5° which was thus shown to correspond to the ester II, upon hydrogenation took up two atoms of hydrogen to give dodecane 1,2,12-tricarboxylic acid.

The liquid tricarboxylic acid fraction remaining after removal of the less soluble potassium salt gave no dodecane 1,2,12-tricarboxylic acid after reduction and consequently could not have this skeletal structure. This material therefore could not be the geometrical stereomer of the solid acid m. p. 98.5° although it had the same approximate analysis. It is therefore concluded that this fraction is probably an impure mixture of position isomers of the solid acid and was not further examined.

With methyl oleate at a temperature of 200° maleic anhydride gives rise to an isomeric mixture of addition products formed by attachment of the maleic residue to C₉ or C₁₀ and the remaining double bond shifting to the C₁₀–C₁₁ or C₉–C₈ positions, respectively, of the octadecenoic acid chain.



The trimethyl esters prepared from the reaction product were distilled but the mixture of isomers could not be separated into pure individuals. This was also true of the free tricarboxylic acids and of the mixture of lactones obtained from these by dihydroxylation. However, the oxidation residues upon treatment of the alkaline solution of the trisodium dihydroxytricarboxylates with periodic acid followed by oxidation of the resulting aldehydes were separable. There was isolated and recognized *n*-octanoic acid, suberic acid and 1,2,3-undecanetricarboxylic acid which demonstrated the structures and the mode of addition to give the products IV and V.

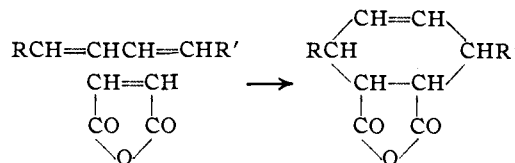
From the above examples of undecylenic and oleic esters it is apparent that such esters will add readily to maleic anhydride whether the ethylenic linkage is terminal or toward the center of the hydrocarbon chain. The choice as to which carbon atom of the ethylenic group the maleic residue will become attached is apparently influenced by position relationships of that carbon atom within the molecule and it would be expected that other substituents would have a directive influence. A terminal double bond as in undecylenic ester gives largely terminal addition; in oleic ester addition occurs at both carbon atoms of the original double bond in approximately equal proportions.

Concomitant with attachment of the maleic anhydride, hydrogen is added to the other unsaturated carbon atom of the maleic residue and the double bond of the olefinic ester moves to the β,γ -position, the carbon atom where addition occurs being designated α . This net result is paralleled by the manner of addition or first stage polymerization of olefinic esters described recently² where two molecules of undecylenic ester added to one another at the terminal carbon atom to give 8-eicosene 1,20-dicarboxylic ester.

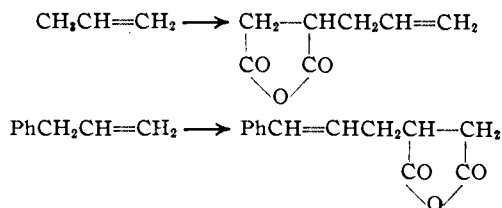
The essential similarity in the reactions of maleic anhydride with mono-olefins and conjugated dienes is worthy of note. One molecule of maleic anhydride combines with one molecule of olefin and also with one molecule of conjugated diene to give a substituted succinic anhydride.

(2) J. Ross, A. I. Gebhart and J. F. Gerech, *THIS JOURNAL*, **67**, 1275 (1945).

However, the reaction with the conjugated diene occurs below 100° while the mono-olefin requires a temperature of about 200°. Addition of the conjugated diene occurs at both terminal carbon atoms of the conjugated system with movement of the residual double bond from the carbon atoms where addition occurs to give the familiar cyclohexene structure



Alder, Pascher and Schmitz³ examined the action of maleic anhydride with certain olefinic hydrocarbons at elevated temperatures under pressure and found that propene gave allyl succinic anhydride, isobutene gave 2-methylallylsuccinic anhydride, a mixture of 1 and 2 *n*-butene gave crotylsuccinic anhydride. They concluded that addition occurred at the methyl group as a form of "substitution addition." However, allylbenzene gave 3-phenylallylsuccinic anhydride which result they considered surprising, having expected substitution on the methylene group between the phenyl and vinyl groups.



The view of substitution on the methylene or methyl groups is only apparent in the cases where two interpretations are possible. The reaction with allylbenzene does not have this ambiguity and this reaction is entirely parallel to the results we have obtained with undecylenic and oleic esters. In all these examples addition or attachment of the maleic residue can be considered as occurring on the original olefinic carbon atoms and the final result of the reaction shows that the

(3) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76B**, 27 (1943); *C. A.*, **37**, 4700 (1943).

double bond migrates to the adjacent carbon atoms while one hydrogen atom moves to saturate the maleic group to complete the addition of the olefin to the maleic anhydride.

Experimental

Addition of Methyl Undecylenate to Maleic Anhydride.—Preliminary examination showed that methyl undecylenate and maleic anhydride in boiling xylene (140°) gave 46% addition in twenty-three hours. Omitting the solvent and going to higher temperatures the following procedure was adopted.

Methyl undecylenate (100 g.) was mixed with maleic anhydride (30 g.) and heated in an atmosphere of nitrogen under reflux to 215–230°, liquid temperature for two hours. Agitation was obtained by bubbling the nitrogen through the liquid mixture. At the end of this time the partly cooled product was taken up in three volumes of methanol and 4 g. of concentrated sulfuric added as esterification catalyst. The methyl esters, recovered in the usual manner, were fractionally distilled from a Claisen flask at 1 mm. pressure. Some unchanged methyl undecylenate and methyl maleate were separated as a low boiling fraction and 99.7 g. of addition product obtained b. p. 185–190° (1 mm.) as a clear liquid ester. This ester was a mono-olefinic tricarboxylic ester corresponding to the addition of one molecule of maleic anhydride to one molecule of undecylenic ester as shown by analysis.

Anal. Calcd. for $C_{18}H_{30}O_6$: mol. wt., 342; sap. equiv., 114; I. V., 74.7. Found: mol. wt. by H_2 addn., 346; sap. equiv., 121; I. V., 74.7.

Upon saponification of this ester (145 g.) with caustic potash in methanol, a solid tripotassium salt was obtained which was filtered off and washed with methanol. The dry solid was taken up in water and carefully acidified. Between pH 6.6–5.7 a crystalline monopotassium salt separated which was filtered off (72 g.). On further acidification of the mother liquor an oily liquid acid was obtained and recovered by ether extraction (37 g.). From the alcoholic filtrate from the tripotassium salt 45 g. of liquid acids were recovered by acidifying. These liquid acids were combined.

4-Dodecene-1,2,12-tricarboxylic Acid (Solid Form).—The above sparingly soluble monopotassium salt which represented about half of the material from the ester of the addition product, was recrystallized from hot water and the free acid prepared by acidifying the hot aqueous solution. It was taken up in ether and crystallized from acetone-benzene mixture and had m. p. 98.5°.

Anal. Calcd. for $C_{18}H_{30}O_6$: C, 59.96; H, 8.06; mol. wt., 300.2. Found: C, 60.09; H, 8.36; neut. equiv., 100.5.

Dihydroxylation of 4 Dodecene-1,2,12-tricarboxylic Acid, m. p. 98.5°.—A sample of this acid (14 g.) was treated with 12 ml. of hydrogen peroxide in 35 ml. of acetic acid⁴ at 95° for fifteen minutes and allowed to stand twelve hours at 35°. The reaction mixture was poured into water, saturated with sodium chloride and shaken out with ether. The hydroxy acid was treated with 12 g. of caustic soda in 100 cc. of water by warming on the steam-bath and standing for twelve hours at 40° to complete saponification.

Periodate Oxidation.—The pH of the above solution was adjusted to 7.5. A solution of 8.0 g. of periodic acid was added to this solution of the sodium salt of the dihydroxy acid. After fifteen minutes at 30° a few grains of potassium iodide was added, the solution acidified with hydrochloric acid and the liberated iodine rapidly destroyed with strong thiosulfate solution. The solution was made acid to congo red, saturated with sodium chloride and thoroughly shaken out with ether. The aqueous liquor was then continuously extracted with ether for twelve hours. Both of these aldehydic extracts were separately oxidized to carboxylic acid with peracetic acid

in the usual manner. From the material shaken out with ether there was obtained 6.0 g. of solid acid which was recrystallized from ethylene dichloride and had m. p. 106–107° (neut. equiv. 94.5). This was identified as azelaic acid by direct comparison and mixed melting point with a known sample of azelaic acid. From the material removed by continuous extraction there was obtained through the lead salt an acid, m. p. 158°, which upon purification by recrystallization from a mixture of acetone "Skellysolve A" gave fine prisms (neutral equiv. 59.5) and this was recognized as tricarballic acid by direct comparison and mixed melting point with a known sample of tricarballic acid m. p. 161°.

Lactone of 4,5-Dihydroxydodecane-1,2,12-tricarboxylic Acid.—A portion of 4-dodecene-1,2,12-tricarboxylic acid (m. p. 98.5°) (10 g.) was treated with peracetic acid (8 ml. of 30% hydrogen peroxide in 24 ml. of glacial acetic acid) by heating for fifteen minutes at 90–105° and then allowing to stand overnight. The product was diluted with water and ether added. An insoluble crystalline material (4.0 g.) was filtered off and washed with water and ether. The ether extract weighed 6.0 g. The material insoluble in ether was recrystallized from 65 cc. of water and had m. p. 148.5°. This compound is a diacid lactone as is apparent from the analysis. *Anal.* Calcd. for $C_{15}H_{24}O_7$: mol. wt., 316.2. Found: sap. equiv., 103.5; neut. equiv., 161.5.

Upon acidifying the saponified material there was recovered the original lactone m. p. 148.5°. The material soluble in ether was saponified by heating on the steam-bath three hours with aqueous potassium hydroxide. The mixture solidified and crystals which separated were filtered and recrystallized from water, giving a solid of m. p. 106–111° which was not further examined. It was apparent that dihydroxylation of 4-dodecene-1,2,12-tricarboxylic acid gives a mixture of stereomeric lactones.

Dodecane-1,2,12-tricarboxylic Acid.—The unsaturated acid (15 g.) m. p. 98.5° in 100 cc. methanol was treated with hydrogen in the presence of 15 mg. of PtO_2 (Adams catalyst). 1092 cc. of hydrogen were absorbed at S. T. P. The product was crystallized from acetone-benzene mixture and had m. p. 99–100° after removal of acetone of crystallization (2 moles). The material crystallized from benzene or ethylene dichloride had m. p. 99–100°.

Anal. Calcd. for $C_{15}H_{26}O_6$: C, 59.57; H, 8.67. Found: C, 59.47; H, 8.66.

Dodecene-tricarboxylic Acid (Liquid Fraction).—The combined acids from the filtrates of the tri- and monopotassium salts from the original ester addition product was a sirupy liquid. This was not a simple material and probably consists of isomeric forms of dodecenetricarboxylic acid. Upon catalytic reduction with hydrogen we could not isolate dodecane-1,2,12-tricarboxylic acid m. p. 99–100° but obtained a liquid saturated acid. This indicates the absence of acids of the skeletal structure of dodecane 1,2,12-tricarboxylic acid. The fraction was not examined further.

Addition of Methyl Oleate to Maleic Anhydride

Methyl oleate (120 g.) purified by low temperature crystallization⁵ was heated at 215–235° with an equimolar quantity of maleic anhydride for one and one-half hours in a nitrogen atmosphere. Upon cooling, the product was converted to the methyl esters and these fractionally distilled from a Claisen flask. There was obtained a 40% yield of simple addition product b. p. 212–215° (1 mm.) as a colorless mobile liquid. There was less than 5% of higher boiling residue.

Anal. Calcd. for $C_{26}H_{44}O_6$ monoolefinic: I. V., 57.8. Found: I. V., 58.2.

Hydrogenation of Ester Addition Product.—A 5.26-g. sample of above ester in 25 ml. of methanol was shaken with hydrogen in presence of 20 mg. of PtO_2 (Adams catalyst). A total of 263 ml. of hydrogen was absorbed;

(5) D. Swern, H. B. Knight and T. W. Findley, *Oil and Soap*, **21**, 133 (1944).

(4) Scallan and Swern, *This Journal*, **62**, 2305 (1940).

calculated for one olefinic linkage required 268 ml. at S. T. P. The hydrogenated ester was a liquid at 0°.

Hydroxylation of Ester Addition Product.—A 25-g. sample of the methyl ester was treated with peracetic acid in the usual manner. The hydroxylated material recovered by water dilution of the reaction mixture and shaking out with ether followed by deacetylation with methanol containing 2% sulfuric acid was a colorless liquid; calcd. saponification equivalent, 158; found, 160.

The corresponding hydroxylated acid recovered after saponification and acidifying was a very viscous liquid.

Anal. Calcd. for lactone: neut. equiv., 207; sap. equiv., 138. Found: neut. equiv., 206; sap. equiv., 140.

Periodate Oxidation of Hydroxylated Product.—An attempt to oxidize the hydroxylated ester in ethanol with periodic acid showed this material to be unoxidizable under these conditions. The sodium salt, however, when treated with sodium periodate was 88% oxidized. The hydroxylated acids in alcohol solution when treated with periodic acid showed 16.5% oxidation which indicated that the lactone structure is unoxidizable under these conditions. Accordingly 35 g. of the hydroxylated acids was heated on the steam-bath with an excess of aqueous caustic soda and then the solution made up to 500 ml. and the pH adjusted to 7.3 with dilute hydrochloric acid. A solution of 19.5 g. of periodic acid ($\text{HIO}_4 \cdot 2\text{H}_2\text{O}$) in 200 ml. of water was neutralized with 6% caustic soda to pH 6.3 using one equivalent of alkali. The solutions of sodium periodate and the sodium salts of the hydroxylated acids were mixed at room temperature and stood for twenty minutes. During this time the pH was maintained at about 8 by addition of dilute hydrochloric acid as required.

The above alkaline oxidation mixture was then extracted with ether to remove aldehyde. A total of 4.2 g. of an oil was obtained which was oxidized to the fatty acid which was distilled, b. p. 104–106° (3 mm.). This acid (neut. equiv. 145) was recognized as *n*-octanoic acid and identified by the *p*-bromophenacyl ester, m. p. 65.5°. A mixed melting point with the *p*-bromophenacyl ester of known *n*-octanoic acid gave no depression.

After removal of the octyl aldehyde the aqueous solution was made acid to congo red with hydrochloric acid and the liberated iodine rapidly destroyed by addition of sulfur dioxide. The solution was saturated with sodium chloride and thoroughly shaken with ether. After removal of the solvent ether the residual carboxylic aldehydes were oxidized with peracetic acid. The carboxylic acids were recovered by dilution with water and evaporation on the steam-bath so as to remove acetic acid and water. A total of 30.9 g. of viscous liquid was obtained. Extraction of this with petroleum ether removed 2.4 g. of oily material and the residue which partially solidified was extracted with hot water and the water soluble acids fractionally crystallized successively from ethylene dichloride, water

and finally acetone. The following acids were recognized and identified.

Suberic acid, m. p. 139–140°, neutral equivalent, 87.0: This was identified by comparison and mixed melting point with a known sample of suberic acid and of the di-*p*-bromophenacyl ester m. p. 144°.

1,2,3-Undecanetricarboxylic acid, m. p. 141°; neutral equivalent, 101: This was identified by analysis, comparison and mixed melting point with a sample synthesized as described below, since it has not previously been described in the literature.

Preparation of 1,2,3-Undecanetricarboxylic Acid.—Twelve grams of α -carboxysuccinic ester was added to a solution of 1.2 g. of sodium in 12 ml. of methanol and to this was added 12.6 g. of α -bromodecanoic ester.⁶ The reaction mixture was left to stand overnight and then warmed for several hours on the steam-bath, after which it was acidified with acetic acid, poured into water and the ester extracted with ether, washed, dried and distilled. There was thus obtained 10 g. of 1,2,2,3 undecanetetracarboxylic ester, b. p. 200° at 5 mm. This ester was saponified with alcoholic potash and the recovered acid boiled three hours with 1:2 aqueous hydrochloric acid. The resulting tricarboxylic acid was extracted with ether and crystallized from acetone and finally from water. It had m. p. 141–142°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_6$: C, 58.31; H, 8.39; mol. wt., 288.26. Found: C, 58.20; H, 8.42; neut. equiv., 97.0.

Summary

1. The conditions for addition of undecylenic and oleic esters to maleic anhydride have been examined and the structures of the major addition products have been determined.

2. It has been shown that in this addition reaction the maleic residue becomes attached to one of the original unsaturated carbon atoms of the olefinic ester, the double bond moves to the adjacent β, γ -position with respect to the carbon atom where attachment occurs concomitant with the movement of one hydrogen atom to saturate the maleic group to form a substituted succinic anhydride.

3. The relationship of this type of addition of ethylenic compounds with the addition of conjugated dienes to maleic anhydride is discussed.

JERSEY CITY, N. J.

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(6) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 108.