A sample of polymer III reduced in the above manner (0.0091 g.) was dissolved in 7 ml. of wet dioxane in a weighing flask; 1.75 ml. of 0.1 *N* sodium hydroxide was added and the solution warmed to 65° for 1.5 hours. It was then cooled and back-titrated potentiometrically with 0.1 *N* HCl; neut. equiv. calcd. 86.0, found 84.6.

Copolymerization of *l*-α-Methylbenzyl Methacrylate and Maleic Anhydride.—*l*-α-Methylbenzyl methacrylate ($[\alpha]^{25}\text{D}$ -41.48, 0.349 g., 1.83×10^{-3} mole), maleic anhydride (0.535 g., 5.46×10^{-3} mole) and α,α'-azobisisobutyronitrile (0.020 g., 0.12×10^{-3} mole) were dissolved in 3 ml. of dioxane, processed as before and irradiated for 80 hours at 30–35°. The resulting viscous solution was precipitated four times in petroleum ether to remove unreacted maleic anhydride, freeze-dried from dioxane for 24–48 hours and dried to constant weight in a 60° vacuum oven; 0.2126 g. of copolymer was obtained. The copolymer showed characteristic peaks of absorption at 252, 258 and 263 mμ (Fig. 2); $[\alpha]^{25}\text{D}$ $-50.2°$ (*c* 2.1 in dioxane, *l* 0.5) and [M] $-128°$. A dioxane solution cast film showed no evidence of crystallinity by X-ray diffraction.

Anal. Calcd. for $(CH_2C(CH_3)COOCH(CH_3)C_6H_5)_{1.5n}$-$(C_4H_2O_3)_n$: C, 69.0; H, 6.01. Found: C, 68.94; H, 6.13.

Reaction of α-Methylbenzyl Methacrylate–Maleic Anhydride Copolymer (V)–(VI) with Phosphonium Iodide.—Poly-*l*-α-methylbenzyl methacrylate–maleic anhydride copolymer (V) (0.150 g., $[\alpha]^{25}\text{D}$ $-50.2°$) was dissolved in 10 ml. of glacial acetic acid and allowed to react in the manner described above with 0.450 g. of phosphonium iodide. The solution was cooled to room temperature, the reduced copolymer precipitated in a curdy flocculent form in absolute ether and left to settle for 24 hr. It was then centrifuged off, redissolved in dioxane and reprecipitated in absolute ether four to six times to remove traces of iodine, freeze-dried from dioxane for 24–48 hours and dried to constant weight in a 60° vacuum oven; 0.060 g. of reduced copolymer (VI) was obtained in 67.5% yield. The ultraviolet absorption spectrum of VI (Fig. 2) showed no characteristic peaks for the α-methylbenzyl group.

Anal. Calcd. for $(CH_2C(CH_3)(COOH))_{1.5n}(C_4H_2O_3)$: C, 52.9; H, 6.1. Found: C, 52.9; H, 4.9.

A 2% solution in dioxane was examined for optical activity (*l* 0.5 dec.). It showed an angular rotation of $\alpha = +0.22 \pm 0.05°$, specific rotation $[\alpha]^{25}\text{D}$ $+23°$ and molecular rotation [M] $+34.8°$. A film cast from dioxane showed no evidence of crystallinity by the X-ray diffraction method.

SYRACUSE 10, N. Y.

[CONTRIBUTION FROM THE POLYMER RESEARCH DEPARTMENT, RESEARCH DIVISION, STAMFORD LABORATORIES, AMERICAN CYANAMID CO.]

The Dimers of Ring Substituted α-Methylstyrenes[1]

BY JOHN C. PETROPOULOS AND JAMES J. FISHER

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The course of the acid-catalyzed dimerization of α-methylstyrenes containing the following ring substituents is described: *p*-CH_3, *p*-COOH, *p*-NH_2 and *m*-CH_3. Depending on conditions, two types of dimers are formed. These are open chain unsaturated dimers (IV and V) and cyclic substituted phenylindanes (VI). The former are converted readily into the latter by more vigorous acid treatment. The basis for assignment of structures to these various dimers is presented.

The acid-catalyzed dimerization of both styrene and α-methylstyrene has been known for many years.[2-6] Recent kinetic data indicate that the course of the styrene dimerization follows the scheme shown in Fig. 1.[5] Essentially, the reaction proceeds *via* the protonation of styrene monomer to form the styrylcarbonium ion IIa which adds a molecule of monomer to yield the dimer carbonium ion IIIa. The latter can (1) add additional monomer units to form polymer, (2) eject a proton to yield the unsaturated dimer IVa or (3) undergo an intramolecular alkylation to afford the cyclic dimer VIa. By regulating the acidic strength of the catalyst, excellent yields of either dimer may be obtained.[5]

The dimerization of α-methylstyrene (Ib) and α,p-dimethylstyrene (Ic) has not been investigated as thoroughly as the dimerization of styrene. Nevertheless, it is more than likely that these two monomers dimerize in a fashion analogous to styrene since they both afford after acid treatment the corresponding unsaturated and cyclic dimers (see Fig. 1). Furthermore, in both cases the unsaturated dimers are converted readily to the saturated cyclic forms VIb and VIc by more vigorous acid treatment.[3,7]

Unlike styrene, the α-methylstyrenes can form two unsaturated dimers (IV and V) depending upon which carbon atom in intermediate III loses the proton. In the case of α,p-dimethylstyrene both unsaturated dimers IVc and Vc have been identified by degradation experiments.[7] Similarly, with α-methylstyrene it is more than likely that a mixture of IVb and Vb is formed in spite of the fact that only IVb has been established by degradation studies.[3]

The present work expands the scope of the dimerization reaction to include other ring substituted α-methylstyrenes.

It was reported in 1883 that dilute hydrochloric acid readily dehydrated *p*-(1-hydroxy-1-methylethyl)-benzoic acid to yield *p*-isopropenylbenzoic acid (Id, m.p. 161°), while concentrated hydrochloric acid at elevated temperatures produced an "isomer" of m.p. 255–260°.[8] This work was repeated and it was found that the higher melting acid melted over a wide range (245–265°), and that the melting point did not change appreciably after repeated recrystallizations. The infrared spectrum of this higher melting acid suggested the presence of olefinic unsaturation including terminal olefinic unsaturation. Moreover, a more rigorous acid treatment converted it to the cyclic isomer

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[1] Presented at the 131st Meeting of the A.C.S., Miami, Fla., April 7-12, 1957.

[2] R. Stoermer and H. Kootz, *Ber.*, **61**, 2330 (1928).

[3] E. Bergmann, H. Taubadel and H. Weiss, *ibid.*, **64**, 1493 (1931).

[4] J. Risi and D. Gauvin, *Can. J. Research*, **B14**, 255 (1936).

[5] M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

[6] M. J. Rosen, *ibid.*, **19**, 17 (1954).

[7] J. Hukki, *Acta Chem. Scand.*, **3**, 279 (1949).

[8] R. Meyer, *Ann.*, **219**, 270 (1883).

VId.[9] The possibility that the higher melting acid was a mixture of Id and VId was excluded on the basis that VId depressed the melting point of the higher melting acid on mixed melting. In view of these facts, it is now believed that the higher melting acid was a mixture of the unsaturated acids IVd and Vd.

Some time ago it was reported that *p*-isopropenylaniline (Ie) will dimerize slowly into an unsaturated dimer of undetermined structure having a m.p. of 173°.[10] Our work showed that mild acid conditions will catalyze this dimerization and that the product (m.p. 171–173°) had the structure represented by IVe. The structure was established by converting it to the known cyclic dimer VIc with strong acid. (Structure proof of VIe will be discussed later.) Infrared analysis demonstrated the absence of a terminal double bond, thus eliminating structure Ve as the other possibility. Apparently, only one unsaturated dimer is formed from *p*-isopropenylaniline, in contrast to the other ring substituted α-methylstyrenes.

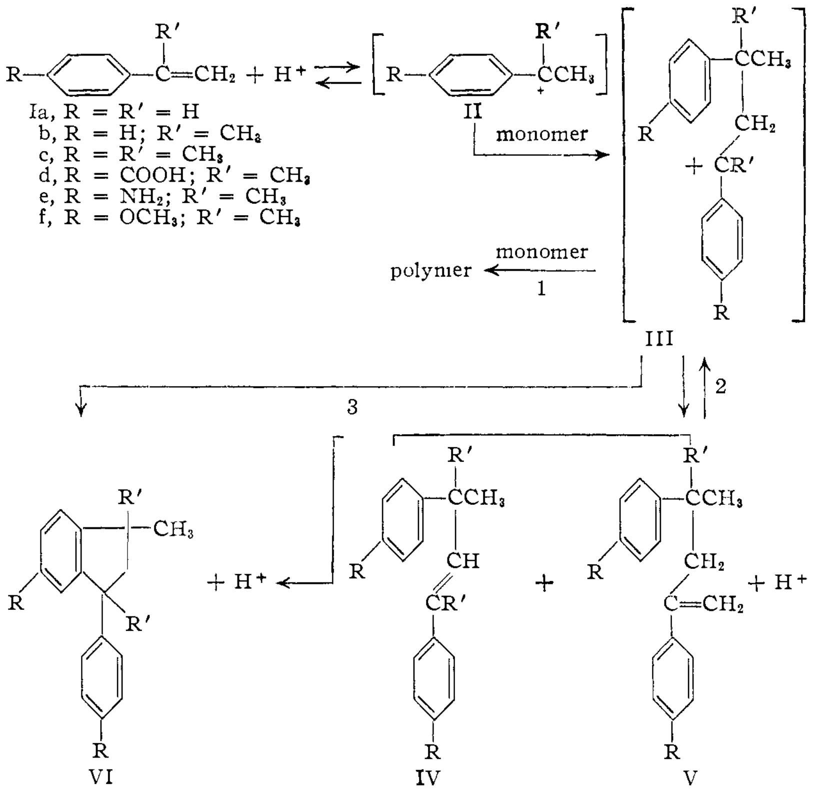

Fig. 1.

Similarly, *p*-isopropenylanisole (If) also was reported to undergo dimerization to the unsaturated dimer IVf after treatment with acid.[11] The structure of the dimer was established by degradation and by infrared analysis. An attempt to convert it to the cyclic dimer VIf with stannic chloride failed. In spite of this, however, it is felt that in view of the results reported herein and those reported by Rosen,[5] a more thorough examination of conditions for cyclization should lead to the successful conversion of IVf to VIf.

The structures for the cyclic dimers of α-methylstyrene and α,*p*-dimethylstyrene (VIb and VIc, respectively) were previously established by unequivocal syntheses.[3,12] Oxidation of VIc to the corresponding diacid VId was also previously demonstrated.[12] This diacid was identical in all respects to the cyclic dimer of *p*-isopropenylbenzoic acid. The latter dimer VId after decarboxylation gave VIb, further supporting the structure VId.

The cyclic dimer VIe of *p*-isopropenylaniline was found to be identical in all respects to the diamine produced from a Schmidt conversion of the diacid VId, and to the diamine prepared *via* the dinitration of VIb followed by reduction.[13]

All of the ring substituted α-methylstyrenes discussed above have the substituent in the *p*-position. In these cases only one isomer having the phenylindane structure (VI) is possible. This is readily seen by examining Fig. 1. In the cyclization of III to form VI, the ring alkylation can occur at either ring carbon atom adjacent to the alkyl carbonium ion side chain. In these systems both *o*-positions are equivalent; thus, only one dimer is formed.

In contrast, however, *m*-substituted styrenes may form two phenylindane dimers, since the two positions *ortho* to the alkylcarbonium ion side chain are not equivalent. This is illustrated in Fig. 2 where the intermediate dimer carbonium ion of α,*m*-dimethylstyrene (VII) is shown. If cyclization occurs *ortho* to the ring methyl group, then dimer VIII will be obtained, whereas ring closure at the position *para* to the ring methyl will lead to dimer IX.

Actually, with α,*m*-dimethylstyrene both dimers were formed as the result of acid treatment of the monomer. The dimer product was estimated by infrared analysis to contain approximately 65% of VIII and 35% of IX. The structures of these dimers were established by oxidation to the corresponding dibasic acids X and XI. Esterification rate studies on the diacids supported the assigned structures, since the hindered acid X, as would be expected, was found to esterify at a much slower

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[9] These same conditions also converted *p*-(1-hydroxy-1-methylethyl)-benzoic acid to the cyclic dimer VId in good yield. (*p*-Isopropenylbenzoic acid and *p*-(1-hydroxy-1-methylethyl)-benzoic acid are essentially equivalent in strong acid solution).

[10] J. V. Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, **472**, 1 (1929).

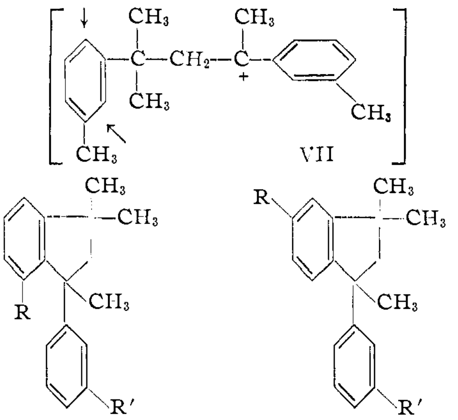
[11] J. M. Van der Zanden and Th. R. Rix, *Rec. trav. chim.*, **75**, 1166 (1956).

[12] V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948).

[13] In the dinitration of VIb one might expect the formation of two isomers as the predominant products. Only 1,3,3-trimethyl-1-(4'-nitrophenyl)-6-nitroindane was isolated and characterized. No effort was made to determine whether there was formed any of the other most probable isomer in which the second nitro group would be on the 5-position rather than the 6-position on the indane ring.

rate than acid XI. These data are in agreement with the infrared spectra of these compounds.

The corresponding dimethyl esters XII and XIII were isolated as the products of the rate studies in addition to the half-methyl ester XIV. The latter structure was assigned on the basis that the hindered carboxyl group would most likely be the unesterified group.



VIII, R = R′ = CH_3
X, R = R′ = COOH
XII, R = R′ = $COOCH_3$
XIV, R = COOH; R′ = $COOCH_3$

IX, R = R′ = CH_3
XI, R = R′ = COOH
XIII, R = R′ = $COOCH_3$

Fig. 2.

Several years ago, it was reported that *m*-cymene, on treatment with acid and a hindered olefin, was converted in part to a dimer *via* the intermediate VII.[14] On the basis of degradation studies, structure IX was assigned to this dimer. By oxidation the dimer was converted to a diacid which melted at 210°. This value is much lower than the melting points of either acid X (m.p. 254°) or acid XI (m.p. 257°), but it is close to the value obtained for a 1:1 mixture of X and XI (m.p. 218–220°). In view of these results, it now appears that the previously reported hydrocarbon dimer was a mixture of VIII and IX, rather than the single entity IX.

It is noteworthy that the major isomer was the result of cyclization *ortho* to a methyl group, rather than *para* to the methyl group (see VII, Fig. 2). Apparently steric hindrance was not sufficiently great to suppress *ortho* alkylation. (An examination of a Stuart and Briegleb atomic model of intermediate VII showed very little difference in steric hindrance between the *o*- and *p*-positions to the methyl group.) It would appear from these data that with the methyl group the inductive effect rather than resonance was the predominant influence in directing the course of this alkylation. A similar reasoning was advanced recently by de la Mare and co-workers to explain the predominantly *ortho* bromination of toluene.[15]

Acknowledgment.—The authors are indebted to several members of these laboratories for assistance in this work: Mr. William Furcht for the preparation of the mixed dimers; Dr. William Best for partial resolution of the mixed dimers; Mr. Norman Colthup for the infrared analyses; and the Microanalytical Group for the elemental analyses.

Experimental[16]

1,3,3,6-Tetramethyl-1-(4′-tolyl)-indane (VIc).—To 800 g. of toluene cooled to 5° was added 140 g. of concd. sulfuric acid. To this agitated mixture, held at 0–5°, was added slowly 260 g. (1.97 moles) of α,p-dimethylstyrene dissolved in 200 g. of toluene. After the addition the mixture was held for 0.5 hr. and then 120 g. of water was added. The organic layer was collected, washed with water until neutral and distilled. The product (230 g., 89%) was obtained as a colorless oil, b.p. 142–144° at 0.8 mm. This oil soon solidified, m.p. 37–38° (lit.[17] value 40°).

1,3,3-Trimethyl-1-phenylindane-4′,6-dicarboxylic Acid (VId).—Into an autoclave there was introduced 26.4 g. (0.1 mole) of VIc, 66.2 g. of 70% nitric acid and 61 g. of water. The temperature of the stirred mixture was slowly raised; at 150° an exothermic reaction developed and the temperature and pressure increased to 190° and 1000 p.s.i., respectively. After 10 min. at 190°, the autoclave was cooled and the product amounting to 26 g. (80%), m.p. 278–285°, was collected and washed free of mineral acid. Several recrystallizations from acetic acid raised the m.p. to 297° (lit.[11] value 294–295°).

Decarboxylation.—A mixture of 22 g. (0.068 mole) of VId, 100 g. of quinoline and 45 g. (0.7 g. atom) of copper powder was refluxed for 3 hr. The organic material was added to an excess of dilute hydrochloric acid and the insoluble hydrocarbon layer was isolated by an ether extraction. Evaporation of the ether gave 17 g. of a reddish colored oil. Several concd. sulfuric acid washings removed the colored impurities. The remaining colorless oil slowly crystallized (12 g., 77%), m.p. 52° after one recrystallization from methanol. This material did not depress the m.p. of a known sample of VIb.

1,3,3-Trimethyl-1-phenylindane (VIb) was prepared by dimerizing α-methylstyrene essentially according to the reported procedure for dimerizing styrene.[5] A mixture of 500 g. (2.36 moles) of α-methylstyrene and 2500 g. of 62% sulfuric acid was refluxed for 21 hr. The organic layer was separated and washed with concd. sulfuric acid; this removed unsaturated impurities and caused the oil to crystallize, yielding 405 g. (82%) of product, m.p. 48–50°. One recrystallization from methanol raised the m.p. to 52° (lit.[3] value 51–52°).

Dimerization of *p*-(1-Hydroxy-1-methylethyl)-benzoic Acid. (A) With 62% Sulfuric Acid to Form VId.—A mixture of 1.0 g. (6.7 mmoles) of the above carbinol acid and 125 g. of 62% sulfuric acid was refluxed for 22 hr. The crude solid product, 0.8 g. (90%), was collected and washed free of mineral acid with water, m.p. 283–285°. After recrystallization from acetic acid the m.p. was raised to 294–295°. It did not depress the m.p. of an authentic sample of VId.

(B) **With Concd. Hydrochloric Acid to Form IVd and Vd.**—A mixture of 2.0 g. (13.4 mmoles) of the above carbinol acid and 60 ml. of concd. hydrochloric acid was heated on a steam-bath for 30 hr. The solid product was collected, washed free of mineral acid and dried to give 1.8 g. (90%) of product, m.p. 245–265°. After three recrystallizations from acetic acid, it melted at 248–262°. The infrared spectrum of the material melting at 245–265° suggested the presence of olefinic unsaturation including terminal olefinic unsaturation. A mixture of this material and VId melted at 220–230°. The material is believed to be a mixture of IVd and Vd.

Cyclization.—The above acid of m.p. 245–265° (85 mg., 0.262 mmole) was treated with 20 ml. of 62% sulfuric acid for 22 hr. The product (70 mg., 83%) after being washed free of mineral acid melted at 280–285°. One recrystallization from aqueous acetic acid raised the m.p. to 294–297°. It did not depress the melting point of an authentic sample of VId.

Dimerization of *p*-Isopropenylaniline to Form IVe.—A mixture of 185 g. (1.37 moles) of *p*-isopropenylaniline and 2 g. of *p*-toluenesulfonic acid was heated on a steam-bath for 8 hr. The solid product was broken up in dilute base with

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(14) H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, **72**, 5521 (1950).

(15) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956).

(16) All melting points are uncorrected.

(17) M. Tiffeneau, *Ann. chim. phys.*, **10**, 197 (1907).

a Waring blender to remove the acid catalyst, filtered and dried to give 183 g. (99%) of crude product. After recrystallization from ethanol, it melted at 171–173° (lit.[10] value 173°). Infrared analysis indicated the absence of terminal olefinic unsaturation.

Conversion of IVe to VIe.—To 50 ml. of concd. sulfuric acid was added 10 g. (0.037 mole) of IVe. The resulting red colored solution was heated on a steam-bath for 45 min. and then poured onto 500 g. of ice. The acidic solution was made basic with sodium hydroxide. The gummy product was dissolved in ether, separated and dried. Removal of the solvent gave 6 g. (60%) of product, a light yellow oil which solidified after scratching, m.p. 85–87°. One recrystallization from hot heptane raised the m.p. to 93–94°. It did not depress the melting point of an authentic sample of VIe.

Conversion of VId to VIe via the Schmidt Reaction.—To a mixture of 1.62 g. (6.1 mmoles) of VId, 6 ml. of concd. sulfuric acid and 40 ml. of chloroform heated to 40–45° was added slowly 0.78 g. (0.012 mole) of sodium azide. The resulting mixture was heated at 55° for two hours and then hydroyzed with water. The aqueous layer was collected and made basic with sodium hydroxide to release the diamine product. It was washed free of base with hot water and crystallized from hot heptane, yield 0.80 g. (60%), m.p. 93–94°.

Anal. Calcd. for $C_{18}H_{22}N_2$: C. 81.18; H, 8.32; N, 10.52. Found: C, 81.26; H, 8.30; N, 10.45.

1,3,3-Trimethyl-1-(4′-nitrophenyl)-6-nitroindane.—To an agitated mixture of 236 g. (1.0 mole) of VIb and 750 ml. of chloroform at 0° was added slowly and separately over a 2-hr. period 396 ml. of concd. sulfuric acid and 132 ml. of 70% nitric acid while maintaining the reaction mass at 0–5°. After an additional 4 hr. of reaction, the chloroform layer was collected, washed free of acidic materials with dilute sodium bicarbonate solution and concentrated to give product, m.p. 149–150° after several recrystallizations from ethanol, yield 82 g. (25%).

Anal. Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.55; N, 8.58. Found: C, 66.34; H, 5.85; N, 8.44.

Reduction.—To an agitated mixture of 65.2 g. (0.2 mole) of the above dinitro compound, 67 g. (1.2 g. atoms) of reduced iron powder and 100 ml. of 50% ethanol heated at the reflux temperature was added slowly 5.2 ml. of concd. hydrochloric acid mixed with 25 ml. of 50% ethanol. The reaction mass was refluxed for one hour and then made basic with an excess of sodium hydroxide solution. The product was washed with hot water to remove inorganic salts, m.p. 93–94° after several recrystallizations from hot heptane. This material did not depress the m.p. of the diamine prepared by a Schmidt reaction of the diacid VId.

Dimerization of α,*m*-Dimethylstyrene.—To a mixture of 1000 ml. of toluene and 186 g. of 85% sulfuric acid heated to 40–50° was added slowly 339 g. (2.1 moles) of α,*m*-dimethylstyrene while maintaining the temperature at 40–50°. After the addition the reaction mass was held at this temperature for 3 hr. The toluene layer was separated, washed free of acidic materials with dilute base and vacuum distilled to give 225 g. (74%) of a cyclic dimer, b.p. 156–158° at 2–3 mm. Part of the dimer solidified after standing at room temperature for several weeks. The solid dimer (fraction A) was separated from the liquid portion (fraction B) and crystallized from methanol, m.p. 57°. The infrared spectrum of fraction A indicated the presence of 1,2,3-vicinal aromatic substitution, suggesting structure VIII in preference to structure IX. By infrared analysis it was estimated that the original dimer mixture contained about 65% of VIII and 35% of IX.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found for fraction A: C, 90.66; H, 9.16. Found for fraction B: C, 90.60; H, 9.26.

Oxidation of Fraction A (VIII).—To a refluxing mixture of 10 g. (0.039 mole) of fraction A, 250 ml. of acetic acid, 300 ml. of water and 50 ml. of concd. sulfuric acid was added slowly 70 g. of chromic acid. The reaction mixture was held at the reflux temperature for 16 hr. An additional 20 g. of chromic acid was added and the mixture was refluxed for 8 hr. and then diluted with water to a volume of three liters to give 5 g. of X as a white solid, m.p. 230–235°. After three recrystallizations from aqueous acetic acid the m.p. remained constant at 254°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22; COOH, 27.79. Found: C, 74.25; H, 6.22; COOH, 28.01.

Oxidation of Fraction B (Mixture of VIII and IX).—This material (10 g., 0.039 mole) was oxidized according to the procedure described above. The yield of crude product was 3 g., m.p. 130–140°. Five recrystallizations from aqueous acetic acid raised the m.p. of XI to a constant value of 257°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22; COOH, 27.79. Found: C, 74.14; H, 6.47; COOH, 27.73.

MELTING POINTS OF MIXTURES OF X AND XI

Composition, % by weight X	XI	M.p., °C.
100	0	254
80	20	220–231
70	30	227–247
60	40	124–127
55	45	120–123
50	50 (cmpd. form.[18])	218–220
45	55	118–122
40	60	122–126
20	80	119–122
0	100	257

Comparison of Esterification Rates of Acids X and XI.—Each acid (2.50 g., 7.6 mmoles) was dissolved in a 25-ml. aliquot of methanol containing 62.5 mg. of *p*-toluenesulfonic acid. The two solutions (labeled A for acid X and B for acid XI) were heated at the reflux temperature (69–70°). Aliquots (1 ml.) were removed periodically and were examined for degree of esterification by neutralization with a standard solution of alkali. The results are tabulated below. The degree of esterification is expressed in milliequivalents of potassium hydroxide needed to neutralize a 1-ml. aliquot to a phenolphthalein end-point. The higher the value, the lower the degree of esterification.

Reaction time, hours	Degree of esterification X	XI
0	34 (calcd.)	34 (calcd.)
1	30.5	28.3
5	. .	17.9
17	18.2	. .
24	16.2	5.6
30	. .	4.2
40	14	. .
49	13.4	. .

At the end of the rate studies, the remaining portions of solutions A and B were worked up to isolate the methyl ester derivatives.

Solution A was poured over ice to give a gummy white solid which was taken up in ether. The ether solution was extracted with dil. sodium bicarbonate solution, dried and evaporated leaving a solid which was partially soluble in hot hexane. The portion (XIV, 1.15 g.) that was insoluble in hexane melted at 160–165°. After several recrystallizations from aqueous methanol the m.p. remained constant at 165°; on further heating, the material resolidified and melted at 175–176°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55; COOH, 13.30. Found: C, 74.47; H, 6.62; COOH, 13.31.

The hexane soluble material (XII, 750 mg.) was collected by evaporation, m.p. 72° after several recrystallizations from hexane.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 74.60; H, 7.12.

Acidification of the sodium bicarbonate extract gave 30 mg. of starting material (X). Apparently sodium bicarbonate did not remove the acid ester XIV from ether solution.

Solution B was allowed to evaporate to dryness leaving 2.10 g. of XIII, m.p. 116–118°, m.p. 127–128° after several recrystallizations from hot heptane.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 75.15; H, 6.80.

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(18) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1945, p. 12.