into the water layer. The ether layer was removed and the aqueous phase extracted with four additional 50-ml. portions of ether. In some cases centrifugation was necessary to ensure complete separation. After drying the combined ether extracts over Drierite, filtering, and removing the solvent on the steam-bath, the residue was distilled at 8 mm. Forty-nine grams (40%) of a colorless, mobile, oily liquid with a faint ester odor was collected at 163–165°. It shows the same solubility behavior as the dipropionate.

Erythryl Dipalmitate.—Fifty-three grams (0.20 mole) of palmitic acid and 2 g. of anhydrous iron(III) chloride were brought into solution with the aid of heat in a 250-ml. round-bottom flask fitted with a stirrer, condenser and separatory funnel. The solution was cooled, and 14.1 g. (0.20 mole) of butadiene monoxide in 50 ml. of benzene was added over a five-minute period. The reaction mixture was then refluxed for three hours, after which 50 ml. of dry pyridine and 60 g. (0.22 mole) of palmitoyl chloride was added with cooling. This was followed by an additional reflux time of two hours. After cooling, 200 ml. of ethyl ether was added and the organic layer was washed with 200 ml. of 3 *N* hydrochloric acid, with water till neutral, then with 200 ml. of 5% sodium hydroxide and finally with water to neutrality. The organic layer was dried over Drierite and, after filtration, the filtrate was stripped of solvent by evaporation under reduced pressure, leaving a residue of crude erythryl dipalmitate. For purification the crude material was first crystallized four times from 250 ml. of petroleum ether (b. p. 23–38°) at −30°. This was followed by four crystallizations from acetone at −25°, and finally four crystallizations at −10° from a methanol-acetone mixture. After drying, 25 g. (22%) of soft cream-colored solid was obtained. The compound is soluble in methanol, slightly soluble in ethanol and acetic acid; very soluble in ethyl ether, chloroform, carbon tetrachloride, benzene, and petroleum ether; insoluble in water.

Erythryl Divalerate.—Eighty-four grams (0.7 mole) of valeryl chloride was slowly added to a mixture of 110 ml. of dry pyridine (1.4 moles) and 100 ml. of dry benzene in a 1-liter round-bottom flask with a reflux condenser fitted with a Drierite tube on top. The formation of the yellow pyridinium salt evolved much heat. A solution of 29 g. of erythrol (0.33 mole) in 50 ml. of dry benzene was slowly added with shaking and the reaction mixture then refluxed for two hours. After cooling, 100 ml. of ethyl ether was added, and the organic layer was washed respectively with 200 ml. of 3 *N* hydrochloric acid, water till neutral, 200 ml. of 5% sodium hydroxide and again with water till neutral. The ether solution was then dried over Drierite. After filtration, the solvent was removed by evaporation under reduced pressure, and the residue was distilled in vacuum. The fraction coming over at 146–147° at 7 mm. was retained. The yield was 40 g. (47%) of a colorless, mobile, oily liquid with a faint ester odor. The solubility behavior was the same as for the dipropionate.

Erythryl Distearate.—This reaction was carried out in essentially the same way as the divalerate. The reflux time, in this case, was increased to three hours. The crude ester was recrystallized once from absolute ethanol; once from a 3:1 ethanol:ether mixture; and once from petroleum ether (38–40°). After drying, a 97% yield of small soft white crystals was obtained. The solubility is the same as found for the dipalmitate.

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Summary

1. Butadiene monoxide was found to form a minimum boiling azeotrope with water at 64.5°. The boiling point, refractive index and density of the highly purified oxide were measured. It was established that butadiene monoxide absorbs bromine quantitatively after forty-eight hours contact time.

2. The preparation and properties of the following diesters of erythrol are described: diacetate, dipropionate, dibutyrate, divalerate, dicaprylate, dipalmitate and distearate.

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Decarboxylation of *p*- and *o*-Formylcinnamic Acids to *p*-Formylstyrene and 1-Indanone

BY RICHARD H. WILEY AND PATRICK H. HOBSON[1]

Many of the substituted styrenes recently reported[2] have electrophilic substituents in the nucleus, and, at least with *m*-nitrostyrene,[3] the presence of this type group modifies the polymerizability of the substituted styrene. In continuing our studies of these phenomena, we wish to record our observations on the synthesis of *p*-formylstyrene by decarboxylation of *p*-formylcinnamic acid and the decarboxylation of *o*-formylcinnamic acid to 1-indanone.

p-Formylstyrene was prepared from terephthalaldehyde by condensation with malonic acid followed by decarboxylation of the cinnamic acid. Condensation in a one to one mole ratio gave 62% of *p*-formylcinnamic acid along with an undetermined amount of phenylenediacrylic acid. The two were separated by extraction of the *p*-formylcinnamic acid from the solid reaction mixture with chloroform. A one to two mole ratio gave 70–80% of *p*-phenylenediacrylic acid. Decarboxylation of *p*-formylcinnamic acid to *p*-formylstyrene gave low yields by previously described techniques[3,4] but 52–55% was obtained by dropping a quinoline solution of the aldehyde into a flask containing copper at 310°. Decarboxylation of *p*-phenylenediacrylic acid gave 45–54% of *p*-divinylbenzene.

The condensation of phthalaldehyde with malonic acid in a one to one mole ratio gave 67% of *o*-formylcinnamic acid, m. p. 163–164°. Re-

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(1) Du Pont Company Postgraduate Fellow, 1948–1949.

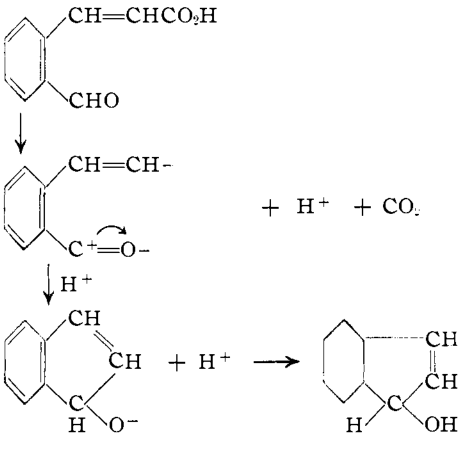
(2) Wiley and Smith, THIS JOURNAL, **70**, 1560 (1948).

(3) Wiley and Smith, *J. Polymer Science*, **3**, 444 (1948).

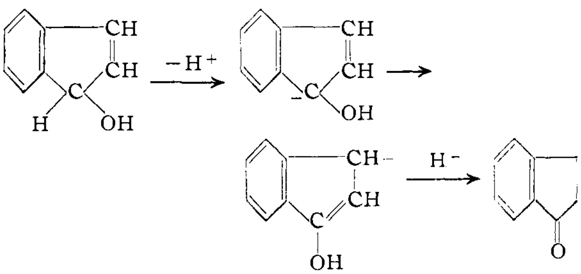
(4) Walling and Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

gardless of the ratio of aldehyde to acid no *o*-phenylenediacrylic acid was isolated although formation of this diacrylic acid in the Perkin reaction has been reported.[5] The decarboxylation of this compound takes place with remarkable ease. Evolution of carbon dioxide begins at room temperature when the acid is dissolved in quinoline although the *p*-derivative undergoes practically no decarboxylation at 150°. Addition of copper powder to this solution accelerates evolution of carbon dioxide but it is not known whether the effect is catalytic or mechanical. From this reaction 68% of 1-indanone, m. p. 41–42°, was isolated and identified by comparison with a sample prepared by an independent synthesis.[6]

The formation of 1-indanone in this reaction may be accounted for by the tendency of the ion formed on decarboxylation of *o*-formylcinnamic acid to combine with the carbonyl carbon rather than the proton with resultant addition of the proton to the carbonyl oxygen

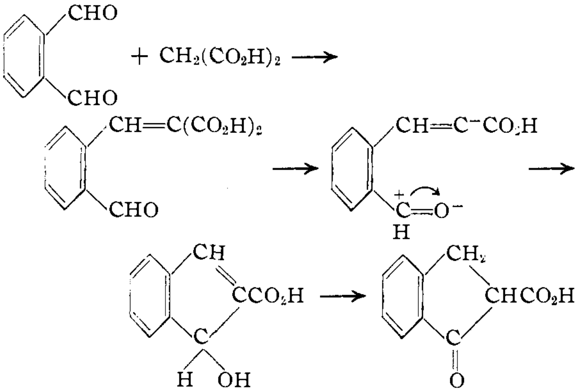


The reaction is similar to the formation of a carbinol on decarboxylation of quinaldic acid in the presence of benzaldehyde.[7] The rearrangement of the carbinol to 1-indanone



is similar to the prototropic change of α-phenyl allyl alcohols to propiophenones which has previously been noted[8] as occurring quantitatively in the presence of alcoholic alkali.

There is a possibility that the acid obtained from phthalaldehyde and malonic acid has also cyclized by a similar mechanism to form 1-indanone-2-carboxylic acid.



This reaction will explain the failure to condense two moles of aldehyde with one of acid. Furthermore, this structure is not clearly eliminated by the use of classification reagents which do not give unequivocal evidence of the presence of an aldehyde group. The ease with which carbon dioxide is lost is also unusual for a cinnamic acid. This possibility has, however, been eliminated by a synthesis of 1-indanone-2-carboxylic acid, m. p. 98–100 °, which was found to differ from the condensation product, m. p. 163–164°. The previously reported[9] synthesis of 1-indanone-2-carboxylic acid was satisfactory. The characterization data on this acid are, however, reported here for the first time.

Experimental

All melting points are corrected.

Terephthalaldehyde[10] and **phthalaldehyde**[11] were prepared from the corresponding tetrabromides.

***p*-Formylcinnamic Acid.**—Ninety-five grams (0.71 mole) of terephthalaldehyde, 75 g. (0.72 mole) of malonic acid, 200 cc. of ethanol, and 200 cc. of pyridine were heated on a steam-bath overnight. The pasty mass was broken up, 400 cc. of *N* hydrochloric acid added, the solid filtered off and washed with 1 liter of water. After air-drying for twenty-four hours the *p*-formylcinnamic acid was separated from the phenylenediacrylic acid by extraction with chloroform in a Soxhlet extractor for 100 hours; yield, 76 g. (0.43 mole) (61%), m. p. 249–250° (from ethanol). Reported melting point of acid prepared by Perkin reaction[12] is 247°.

Anal. Calcd. for $C_{10}H_8O_3$: neut. equiv., 176. Found: N. E., 175.

***p*-Phenylenediacrylic acid** was prepared from terephthalaldehyde and malonic acid by the method of Ruggli[13] in 70–80% yield.

Anal. Calcd. for $C_{12}H_{10}O_4$: neut. equiv., 109. Found: neut. equiv., 108.

***p*-Divinylbenzene.**—Thirteen grams (0.060 mole) of phenylenediacrylic acid was decarboxylated with quinoline and copper according to the method of Walling and Wolfstirn[4] with the addition of 2.5 g. of quinone as anti-

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[5] Thiele and Falk, *Ann.*, **347**, 117 (1906).

[6] Pacaud and Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 336.

[7] Ashforth, Daffern and Hammick, *J. Chem. Soc.*, 809 (1939).

[8] Tiffeneau, *Bull. soc. chim.*, **1**, 1209 (1907); *cf.* Burton and Ingold, *J. Chem. Soc.*, 904 (1928).

[9] Prescott and Robinson, *J. Chem. Soc.*, **113**, 879 (1918).

[10] Snell and Weissberger, "Organic Syntheses," Vol. 20, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 92.

[11] Thiele and Gunther, *Ann.*, **347**, 107 (1906).

[12] Low, *Ann.*, **231**, 374 (1885).

[13] Ruggli and Theilheimer, *Helv. Chim. Acta*, **24**, 899 (1941).

oxidant. Yield of crude divinylbenzene was 3.5 g. (0.027 mole) (45%), m. p. 30–31° (from dilute acetic acid); reported[14] m. p. 31°.

***p*-Formylstyrene.**—Eighteen grams (0.102 mole) of *p*-formylcinnamic acid was dissolved in 120 cc. of quinoline and 0.1 g. of copper acetate added. The solution was added dropwise to 5 g. of copper powder in a 50-cc. distilling flask heated at 300–310°. The rate of addition was regulated so that there was no appreciable quantity of liquid in the distilling flask at any time. The distillate was poured into 400 cc. of 3 *N* sulfuric acid and the *p*-formylstyrene removed by steam distillation. The steam distillate was extracted with three 100-cc. portions of ether. The ether extracts were washed with dilute sulfuric acid, dilute sodium carbonate solution, and with water. After drying over "Drierite" the ether was removed under reduced pressure and the distillate fractionated; yield, 7.02 g. (0.053 mole) (52%), b. p. 92–93° (14 mm.), n^{25}_D 1.5960, d^{25}_4 1.036.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.77; H, 6.09.

The phenylhydrazone was prepared[15] and recrystallized from 50% water and 50% ethanol (with small amounts of hydroquinone present), m. p. 130–131°.

Anal. Calcd. for $C_{15}H_{14}N_2$: N, 12.61. Found: N, 12.45.

One gram (0.0076 mole) of *p*-formylstyrene was oxidized to *p*-carboxystyrene with silver oxide,[16] yield, 0.84 g. (0.0057 mole) (75%), m. p. 142–143°; reported[17] m. p. 143–144°.

Anal. Calcd. for $C_9H_8O_2$: neut. equiv., 148. Found: neut. equiv., 149.

***o*-Formylcinnamic Acid.**—Twenty and one-tenth grams (0.150 mole) of phthalaldehyde was mixed with 17.7 g. (0.170 mole) of malonic acid in an erlenmeyer flask and warmed on a water-bath at 70–80° until the aldehyde melted. Two cc. of pyridine was added. There was an immediate evolution of carbon dioxide. After heating the solution at 55–60° for thirty to forty minutes it became a brown solid mass. Heating was continued for an additional sixty minutes at 60°. The somewhat pasty mass was cooled and washed with two 30-cc. portions of chloroform and then extracted with chloroform in a Soxhlet extractor for four hours; yield, 17.5 g. (0.100 mole) (67%), m. p. 159–161°. After recrystallizing from water and again from chloroform the colorless crystals melted at 163–164°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58; neut. equiv., 176. Found: C, 68.00; H, 4.63; neut. equiv., 174.

The above compound slowly absorbed bromine in chloroform in the absence of oxygen without evolution of hydrogen bromide, and rapidly decolorized an aqueous solution of potassium permanganate. It gave no color with Schiff reagent and formed a black precipitate but no silver mirror with Tollens reagent. With ferric chloride solution a reddish color was obtained. It was stable at room temperature and on boiling with water, but was slowly decomposed upon boiling with dilute sodium hydroxide solution. *p*-Formylcinnamic acid also gave no color with Schiff reagent.

A phenylhydrazone was prepared by heating the reactants on the steam-bath for three hours without solvent. The solid separated on pouring the reaction mixture into dilute acid and was recrystallized from alcohol, m. p. 128–129°, mixed m. p. with phenylhydrazone prepared from 1-indanone, 127–128°. Customary procedures for preparation of a phenylhydrazone gave a product which could not be purified.

The oxime of the acid was prepared by heating 0.2 g. of the acid with 0.5 g. of hydroxylamine hydrochloride and 4 cc. of 3 *N* sodium hydroxide for three hours on the steam-bath. The excess alkali was neutralized with carbon dioxide and a small amount of the oxime of 1-indanone, m. p. 144–145°, separated. The solution was acidified with dilute hydrochloric acid whereupon the oxime of the acid separated, m. p. (on slow heating) 143–144°. When the melting point tube was placed in a bath preheated to 130–140° the compound liquified, rapidly evolved a gas, presumably carbon dioxide, solidified, and remelted at 143–144°. Placed in the bath at temperatures below 130° no liquifaction below 143° or evolution of gas was observed.

Anal. Calcd. for $C_{10}H_9O_3N$: N, 7.32; neut. equiv., 191. Found: N, 7.17; neut. equiv., 189.

1-Indanone.—Eleven grams (0.063 mole) of the above acid was dissolved in 25 cc. of quinoline. Decarboxylation began immediately, as was evidenced by the evolution of carbon dioxide and was accelerated by the addition of a small amount (0.01 g.) of copper powder. After standing at room temperature for four hours, the solution was heated on the steam-bath for ten minutes. After cooling, 150 cc. of 3 *N* sulfuric acid was added, and the mixture steam distilled into a cooled receiver. The white crystals of 1-indanone were separated from the chilled distillate, which was then extracted with three 50-cc. portions of ether. The ether extracts were dried over anhydrous sodium sulfate, the ether removed under reduced pressure and the 1-indanone thus obtained combined with the main portion. The total yield was 5.61 g. (0.043 mole) (68%) m. p. 37–39°; after recrystallizing from petroleum ether at 0°, m. p. 41–42°.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.52; H, 6.06.

The oxime,[18] m. p. 143–144°, and phenylhydrazone,[14] m. p. 128–130° (from ethanol), were prepared by usual techniques.

A sample of 1-indanone prepared from indene,[6] melted at 40–40.5°; mixed m. p. 40–40.8°. The oxime of the authentic sample melted at 143–144°; mixed m. p. with above oxime, 142–143°.

1-Indanone-2-carboxylic Acid.—A mixture of 3.0 g. of sodamide and 4.0 g. of indanone in 50 ml. of dry ether at 0–25° for three hours was treated with Dry Ice, then water. The acidified aqueous layer deposited 2.0 g. of 1-indanone-2-carboxylic acid which was purified by reprecipitation from alkali; m. p. 98–100° with evolution of a gas.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58; neut. equiv., 176. Found: C, 68.30; H, 4.78; neut. equiv., 177–178.

Summary

Terephthalaldehyde has been condensed with malonic acid to give *p*-formylcinnamic acid in 62% yield or phenylenediacrylic acid in 70–80% yield. These acids have been decarboxylated to *p*-formylstyrene in 52% yield and to divinylbenzene in 45% yield.

Phthalaldehyde has been condensed with malonic acid to give 67% yield of *o*-formylcinnamic acid. This acid has been decarboxylated to 1-indanone in 68% yield. A mechanism for the reaction is discussed.

1-Indanone-2-carboxylic acid has been prepared from 1-indanone and characterized.

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[14] Lespieau and Deluchat, *Compt. rend.*, **190**, 683 (1930).

[15] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 64.

[16] Delépine and Bonnet, *Compt. rend.*, **149**, 39 (1909).

[17] Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945).

[18] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 167.