2,3-xylenol. The compound in the top zone was eluted with methyl alcohol, recrystallized from absolute alcohol. It melted at 126.5–127.2° and the absorption spectrum checked with that found for a pure sample of 2,6-dinitro-3,4-xylenol.

(b) **Nitration of 2-Nitro-3,4-xylenol.**—30 mg. of 2-nitro-3,4-xylenol was nitrated and chromatographed as in the above procedure for 6-nitro-2,3-xylenol. The compound in the top yellow zone had a melting point 125.9–126.5°, and the absorption spectrum was the same as that for a pure sample of 2,6-dinitro-3,4-xylenol. A mixed melting point showed no depression.

(c) **Amination of 2,6-Dinitro-3,4-xylenol.**—2 g. of 2,6-dinitro-3,4-xylenol were mixed with 1 g. of ammonium chloride and 20 ml. of ammonium hydroxide (22%). These were placed in a thick-walled Pyrex tube and the tube sealed off. The tube and contents were placed in a bomb furnace and heated at 150° for six hours. The tube was then cooled, carefully opened and the contents washed out with water.

Two grams of solid potassium hydroxide was added and the solution extracted with ether. The ether was evaporated off, the residue dissolved in petroleum ether, and the solution chromatographed on a column of silicic acid-celite (2:1). The chromatogram was developed with 0.9 volume of ether–petroleum ether (1:10). The lower yellow band was eluted with ether, the ether evaporated off, and the 2,6-dinitro-3,4-xylidine recrystallized from absolute alcohol, giving orange-red needles melting at 142.5–143.0°; literature[20] gives 143°.

3,5-Xylenol. (a) **2-Nitro-3,5-xylenol** was prepared by the nitration of 3,5-xylenol in acetic acid.[11]

3,6-Xylenol.—2-Nitro-3,6-xylenol and 4-nitro-3,6-xylenol were prepared by the nitration of 3,6-xylenol in glacial acetic acid.[13]

Ionization Constants of Nitroxylenols

The ionization constants of the various nitroxylenols given in this paper were determined. Approximately 0.01 *M* solutions of the nitroxylenol in absolute alcohol were made up. This solution was then one-half neutralized with 0.01 *N* sodium hydroxide and enough conductivity water was added so that the final solution contained 50–50 water–alcohol by weight. The pH of the solution was measured on a Leeds–Northrup pH meter, and the pH of this half-neutralized solution was taken as the pK_a for the nitro derivative. For example: 61.5 mg. of 6-nitro-2,4-xylenol was dissolved in 50 ml. of absolute alcohol, and 18.00 ml. of 0.1026 *N* sodium hydroxide added to half-neutralize the 6-nitro-2,4-xylenol. 21.44 ml. of water was mixed with the solution to make the final solution 50–50 water–alcohol by weight. The pH of the solution was measured and found to be 9.20 ± 0.05. The pK_a was then said to be 9.20 ± 0.05.

A neutralization curve was run on 6-nitro-2,4-xylenol against sodium hydroxide; 163.0 mg. of 6-nitro-2,4-xylenol was dissolved in 100 ml. of water–alcohol (50–50 by weight) and the solution placed under the electrodes of the L. and N. pH meter. The solution was titrated with a 0.01309 *N* solution (50–50 H_2O–C_2H_5OH; by weight) sodium hydroxide, and the pH of the solution measured after each addition of sodium hydroxide. The data were plotted and the equivalence point calculated mathematically.[22] From these data the pH of the solution at one-half neutralization was determined. The pH was found to be 9.20, thus giving the pK_a of 9.20, which checks with that given above.

Summary

1. The preparation, absorption spectra and ionization constants for the ortho-nitro derivatives of five isomeric xylenols are given.

2. Two new compounds, 6-nitro-2,3-xylenol and 2-nitro-3,4-xylenol, have been prepared and their structure proved.

3. From a study of the ionization constants for the various orthonitroxylenols, one case of the steric inhibition of resonance is shown by 2-nitro-3,4-xylenol (pK_a 8.95) as compared with 6-nitro-3,4-xylenol (pK_a 8.55)

[22] Kolthoff and Laitinen, "pH and Electro Titrations," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 106–109.

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 14, 1949

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Vinyl Aromatic Compounds. VII. 1,3,5-Trivinylbenzene[1]

BY DAVID T. MOWRY AND EUGENE L. RINGWALD

Because of the theoretical and commercial interest in divinylbenzenes as insolubilizing or cross-linking agents in high polymer preparations it was of interest to prepare 1,3,5-trivinylbenzene for comparison.

1,3,5-Triacetylbenzene, which is readily available from acetone and formic esters,[2,3] was hydrogenated catalytically over copper chromite at about 1000 p.s.i. and at 110–130° in nearly quantitative yield. The crude product, m. p. 124–130°, was a mixture of the two racemic forms, (*ddd–lll*) and (*dll–ldd*), of 1,3,5-tris-(α-hydroxyethyl)-benzene. The most abundant form, which from considerations of probability would be (*dll–ldd*), melted at 137°.

Catalytic vapor-phase dehydration[4] of an aqueous solution of the triol over activated alumina at 400° and 125 mm. pressure gave an 85% yield of 1,3,5-trivinylbenzene, which was indicated to be approximately 98% pure by bromine number analysis. The material was found to be slightly more effective than pure *p*-divinylbenzene[4,5] as a cross-linking agent in styrene polymerization.

A facile synthesis of pure trimesic acid is provided by the oxidation of 1,3,5-triacetylbenzene which proceeds smoothly in 94% yield by the action of sodium hypochlorite.

Experimental

1,3,5-Triacetylbenzene.—The following modification of the method of Claisen and Stylos[2] gives somewhat better

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[1] Preceding paper in this series, THIS JOURNAL, **71**, 120 (1949).

[2] Claisen and Stylos, *Ber.*, **21**, 1145 (1888).

[3] Frank and Varland, "Organic Syntheses," Vol. 27, p. 91 (1947).

[4] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[5] Deluchat, *Ann. chim.*, [11] **1**, 181 (1934).

yields than those reported by Frank and Varland.[5] Three moles (162 g.) of dry sodium methylate and 2 l. of dry benzene were placed in a 3-necked 5-l. flask equipped with an efficient stirrer. A mixture of 174 g. (3.0 moles) of dry acetone and 180 g. (3.0 moles) of methyl formate was added dropwise at such a rate that the temperature did not exceed 50–60°. After stirring for four hours, the solid sodium salt of formylacetone was filtered rapidly with exclusion of moisture and dried in a vacuum oven at 50–60°. The dry powder (300 g.) was added rapidly with stirring to a solution of 230 g. of 85% phosphoric acid in 500 ml. of water. The resultant aqueous solution (*p*H 4–5) was kept at 50–60° until precipitation of the 1,3,5-triacetylbenzene was complete (four to six hours). A 56% yield (84 g.) of pale yellow crystals, m. p. 153–157°, was obtained by filtration and drying. Recrystallization from aqueous ethanol or a mixture of benzene and hexane or distillation at 170–200° (10 mm.) through a short Vigreux column gave 76 g. (51%) of nearly colorless product, m. p. 160–161°, which was sufficiently pure for hydrogenation.

In a similar run in which the phosphoric acid condensation was carried out at 80° an appreciable amount of acetone (19 g., 11%) was recovered by condensing the volatile material liberated. A negative sodium nitroprusside–piperidine test of this fraction indicated the absence of acetaldehyde. This indicated that at least one of the side reactions involved hydrolytic cleavage of formylacetone to acetone and formic acid. This type of cleavage was found to take place rapidly in warm alkaline solution.

Preparation of the sodium methylate *in situ* from sodium sand prior to the formylation gave similar yields. Extraction of the sodium salt of formylacetone from the benzene suspension with water followed by acidification gave crude yields of about 50%. Acidification with acetic, formic or boric acids gave results comparable to phosphoric acid, but the use of hydrochloric or sulfuric acids led to a darker and more tarry product.

1,3,5-Tris-(α-hydroxyethyl)-benzene.—Three hundred sixty-four grams of 1,3,5-triacetylbenzene, 18 g. of copper chromite catalyst[6] and 400 ml. of absolute ethanol were placed in an American Instrument Co. rocking hydrogenation autoclave. Absorption of hydrogen began at 115° and 1400 p. s. i. and was complete in one hour, the maximum temperature being 140°. The solution was then filtered free of catalyst and evaporated to give three crops of crystals: 209 g., m. p. 135–136°; 116 g., m. p. 125–128°; and 47 g., m. p. 114–119°. The total yield of triol isomers was essentially quantitative. Recrystallization of any of the fractions from dioxane gave the predominant isomer, m. p. 137°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.5; H, 8.57. Found: C, 68.7; H, 8.55.

1,3,5-Trivinylbenzene.—A hot solution of 105 g. (0.5 mole) of 1,3,5-tris-(α-hydroxyethyl)-benzene and 1 g. of hydroquinone in 80 ml. of water was slowly dropped during a forty-five minute period through a 25 mm. i. d. Pyrex tube 1 meter long which was packed with 4–8 mesh activated alumina. The tube was heated by a vertical nitrate–nitrite bath maintained at 400°, and the product was trapped in an ice-cooled receiver. The system was evacuated to 125 mm. pressure. After flushing the catalyst bed with steam, the organic layer was separated, 1 g. of *t*-butylcatechol was added, and the product was distilled rapidly through a 100-cm. Vigreux column, taking the fraction boiling at 72–73° (0.5 mm.), d^{26} 0.938, $n^{25}\text{D}$ 1.5967. A bromide–bromate determination of unsaturation indicated a purity of 98.9% as trivinylbenzene.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.2; H, 7.7. Found: C, 91.5; H, 7.64.

Similar dehydrations at 350 and 300° resulted in yields of 75 and 34%, respectively. No monomeric product was obtained when the liquid-phase dehydration technique of Gauthier using fused potassium acid sulfate[7] was attempted.

An approximate comparison of the cross-linking potency of this material with that of *p*-divinylbenzene[4] and with a commercial product containing 34% divinylbenzene was made by dissolving small amounts of the three materials in freshly redistilled styrene. The solutions were copolymerized by heating in the presence of 0.1% benzoyl peroxide for forty-eight hours at 100°. Examination of 1% benzene solutions of the mascerated polymer particles indicated that 0.02% or more of trivinylbenzene produced a swollen but insoluble gel, whereas 0.04% of pure *p*-divinylbenzene or 0.1% of the commercial product was required to produce the same effect.

Trimesic Acid.—The following is an adaptation of the general method of Newman and Holmes who oxidized β-naphthyl methyl ketone to β-naphthoic acid.[8]

In a 12-liter three-necked flask equipped with a mechanical stirrer, Dean–Stark trap and condenser was placed a solution of 1408 g. of sodium hydroxide (35.2 moles) in 1500 ml. of water. After cooling by adding seven kilograms of ice, chlorine was passed in rapidly until 1055 g. was absorbed. The solution was then heated to 85° and 202 g. (1.08 moles) of 1,3,5-triacetylbenzene was added in small portions over a period of two hours, keeping the temperature between 90–95°. Chloroform (202 g.) was collected as the lower layer in the Dean–Stark trap.

The clear solution was then stirred for several hours at 85°, allowed to cool overnight and the excess hypochlorite destroyed by the addition of 300 g. of sodium bisulfite. Acidification with excess (monosodium trimesate tends to precipitate) hydrochloric acid gave a precipitate of trimesic acid which was filtered and recrystallized from hot water containing a little hydrochloric acid. By concentration of the mother liquors there was obtained a total yield of 214 g. (94%) of good quality trimesic acid, m. p. 375°, neutral equivalent 71.8 (theory for monohydrate, 72.6).

Summary

1,3,5-Trivinylbenzene has been prepared by the catalytic vapor-phase dehydration of 1,3,5-tris-(α-hydroxyethyl)-benzene. The latter compound was obtained by hydrogenation of 1,3,5-triacetylbenzene. Oxidation of this ketone with sodium hypochlorite has provided a convenient synthesis of trimesic acid.

DAYTON 7, OHIO RECEIVED OCTOBER 20, 1949

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[6] Lazier and Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 44.

[7] Gauthier and Gauthier, *Bull. soc. chim.*, [4] **53**, 323 (1933); Marvel and Shertz, THIS JOURNAL, **65**, 2054 (1943).

[8] Newman and Holmes, "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, N. Y., 1943, p. 428.