[CONTRIBUTION FROM THE NAVAL ORDNANCE RESEARCH LABORATORY, OAK STREET LABORATORIES, UNIVERSITY OF MINNESOTA]

Nitroxylenols—Absorption Spectra and Ionization Constants[1]

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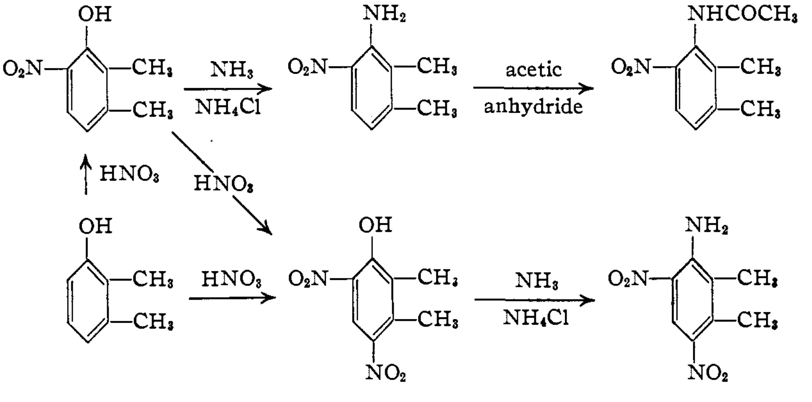
In a study on the isomeric xylenols as reagents for the colorimetric determination of nitrate[4] and nitric acid esters,[4] it was necessary to prepare, in a very pure state, for absorption spectra studies, the ortho nitro derivatives of the various isomeric xylenols. This paper describes the preparation, chromatographic purification, absorption spectra, and ionization constants of these compounds.

6-Nitro-2,3-xylenol and 2-nitro-3,4-xylenol,[5] which had not been prepared previously, are described and their structure proof given.

The visible and ultraviolet absorption spectra of the nitroxylenols have not been previously studied.

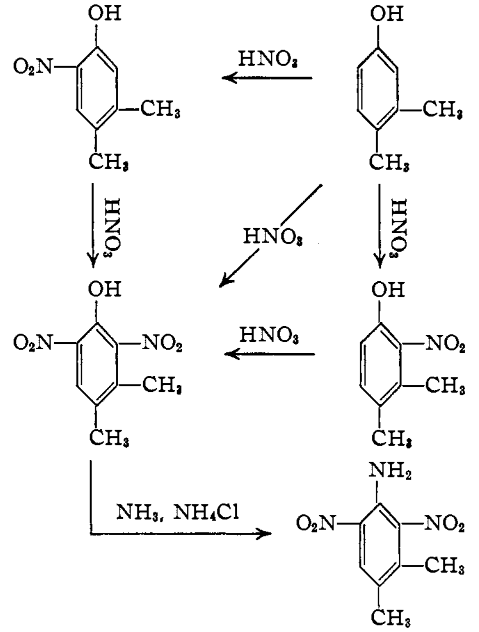
Preparation and Absorption Spectra of Nitroxylenols.—Below are given in brief the data concerning the preparation and absorption spectra of the various nitroxylenols.

2,3-Xylenol.—When 2,3-xylenol is nitrated, it yields 6-nitro-2,3-xylenol, 4,6-dinitro-2,3-xylenol, and presumably some 4-nitro-2,3-xylenol, although none of the 4-nitro derivative was isolated from the nitration mixture. Only the 4,6-dinitro compound had been prepared previously.[6] The structures were proved for 6-nitro- and 4,6-dinitro-2,3-xylenol in the following manner.



The spectrophotometric properties and pK_a values for these compounds, determined as described in Experimental, are given in Tables I and II.

2,4-Xylenol.—6-Nitro-2,4-xylenol was obtained by the nitration of 2,4-xylenol.[7,8] Only one mononitro derivative is obtained on nitration (see Tables I and II for the spectrophotometric data).



3,4-Xylenol.—3,4-Xylenol is very easily nitrated,[9,10] yielding 6-nitro-3,4-xylenol and 2-nitro-3,4-xylenol in the ratio of approximately 6 parts of the 6-nitro derivative to 1 part of the 2-nitro compound. With excess of nitric acid the 2,6-dinitro derivative is formed. 2-Nitro-3,4-xylenol had not been previously prepared.[5] The structure was proved for the 2-nitro, 6-nitro and 2,6-dinitro derivatives in the manner shown above (see Tables I and II for spectral data).

3,5-Xylenol.—3,5-Xylenol being a symmetrical molecule yields on nitration only one ortho nitro derivative (2-nitro-3,5-xylenol),[11] but also gives

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[2] Present address: Twin City Testing and Engineering Laboratory, 2440 Franklin Avenue, St. Paul, Minnesota.

[3] Present address: Rohm and Haas Company, Philadelphia, Pennsylvania.

[4] Holler and Huch, *Anal. Chem.*, **21**, 1385 (1949).

[5] After this paper was submitted for publication the preparation of this compound was described by Mueller and Pelton, THIS JOURNAL, **71**, 1504 (1949).

[6] Noelting and Pick, *Ber.*, **21**, 3159 (1888).

[7] Lako, *Ann.*, **182**, 32 (1876).

[8] Hodgkinson and Limpach, *J. Chem. Soc.*, **63**, 105 (1914).

[9] Diepolder, *Ber.*, **42**, 2916 (1909).

[10] Beilstein, "Handbuch der organischen Chemie," 4th ed., J. Springer, Berlin, Vol. VI, p. 480, 1918.

[11] Auwers and Borsche, *Ber.*, **48**, 1714 (1915).

a para nitro compound (4-nitro-3,5-xylenol).[12] The spectral data are given in Tables I and II. The 4-nitro compound was not prepared.

TABLE I

ABSORPTION SPECTRA OF THE SODIUM SALTS AND IONIZATION CONSTANTS OF THE NITROXYLENOLS

Xylenol derivative	Maximum[a] λ, mμ	Maximum[a] E	Minimum[a] λ, mμ	Minimum[a] E	pKa[b]
6-Nitro-2,3-	430	4741	362	1934	9.26
4,6-Dinitro-2,3-	378	11024	326	5256	5.62
6-Nitro-2,4-	446	4465	355–356	1021	9.20
2-Nitro-3,4-	418–420	780.8	325–332	456.4	8.95
6-Nitro-3,4-	432	5378	353	1346	8.55
2,6-Dinitro-3,4-	426	6049	336	997.0	5.23
2-Nitro-3,5-	412	1603	327	860.3	8.69
2-Nitro-3,6-	424	800.5	329	487.7	8.88
4-Nitro-3,6-	410	18412	291	709.2	8.36

[a] Sodium salts in water. [b] Measured at average temperature of 28.0°.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF THE FREE NITROXYLENOLS IN HEXANE

Xylenol derivative	Maximum		Minimum		Maximum		Minimum		Maximum		Minimum	
	mμ	E	mμ	E	mμ	E	mμ	E	mμ	E	mμ	E
6-Nitro-2,3-	292	9688	246–248	1516	352	3914	323	2750	...	..	...	..
4,6-Dinitro-2,3-[a]	270	12600	240	6912	355	4632	324	3792	...	..	...	..
6-Nitro-2,4-	282–283	8387	249	2137	366	3766	316	1210	...	..	...	..
2-Nitro-3,4-	278	5307	256	2822	360	2779	315	1460	244	3558	236	3393
6-Nitro-3,4-	282–284	9286	251	2100	356–358	4586	313	1707	...	..	...	..
2,6-Dinitro-3,4-[a]	274	6793	250	4914	350	3603	312	1983	424	1534	410–412	1448
2-Nitro-3,5-	287	9182	252	2445	352	3755	320–322	2691	...	..	...	..
2-Nitro-3,6-	284–286	5943	251	1642	358	2410	320	1524	...	...	...	..
2-Nitro-3,6-[b]	280	3442	259	2564	...	..	...	..	235–236	9360	227	8320
4-Nitro-3,6-	310	6685	...	..	...	..	...	..	234	5852	257	1472

[a] In ethyl alcohol. [b] Sodium salt in water.

3,6-Xylenol.—A mixture of 2-nitro and of 4-nitro-3,6-xylenols is formed on the nitration of 3,6-xylenol.[13] The two isomers can be separated by steam distillation, the 2-nitro compound distilling and leaving the 4-nitro derivative in the residue. The spectrophotometric data are given in Tables I and II.

2,6-Xylenol.—Since no ortho nitro derivatives can be formed from 2,6-xylenol, this isomer was not studied.

Discussion

Absorption Spectra of Sodium Salts.—An inspection of Table I on the sodium salts of the ortho-nitroxylenols shows that the absorption spectra may on the basis of the positions of the nitro group in relation to the methyl groups be divided into two groups. First are the spectra of 6-nitro-2,3-xylenol, 6-nitro-2,4-xylenol, and 6-nitro-3,4-xylenol, in which the nitro group is not adjacent to a methyl group, and in the second, the spectra of 2-nitro-3,4-xylenol, 2-nitro-3,5-xylenol, and 2-nitro-3,6-xylenol, in each of which the nitro group is adjacent to a methyl group. This grouping of the absorption spectra may be attributed to the fact that when a nitro group is adjacent to a methyl group, the methyl group forces the nitro group to twist out of the plane of the ring (steric hindrance) and the loss of coplanarity causes a shift of the absorption maximum and minimum to lower wave lengths, and causes a great reduction of the molecular extinction coefficient.

The ionization constants for these compounds were determined (see Table I) in 50–50 water–alcohol (by weight) by half neutralizing a 0.01 *M* alcoholic solution of the nitroxylenol with 0.01 *M* sodium hydroxide, and adding enough conductivity water so that the final solution was 50–50 water–alcohol (by weight). The *p*H of this half-neutralized solution was measured and this *p*H taken as the pK_a for the nitroxylenol.[14] From this datum and its correlation with absorption spectra the only clear-cut case of the steric inhibition of resonance[15] is shown by 2-nitro-3,4-xylenol (pK_a = 8.95) as compared with 6-nitro-3,4-xylenol (pK_a = 8.55).

The relations between the structures of the nitroxylenols and their acid strengths can at this time be correlated only in a qualitative way.[16]

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra for the mono-ortho and dinitro derivatives are quite similar (see Table II). They show maxima in the regions of 270–292 and 350–366 mμ, and minima in the regions of 236–256 and 312–324 mμ. The intense absorption in the region of 270–292 mμ is probably due to the benzenoid structure[17,18] of the compounds. The nitro group probably accounts for the absorption in the region of 350–366 mμ.[18] At this time the assignment of the other frequencies was not attempted.

Experimental

Apparatus.—The absorption spectra of the substances given in this report were determined on a Model DU Beck-

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[12] Wheland, Brownell and Mayo, THIS JOURNAL, **70**, 2494 (1948).

[13] Auwers and Michaelis, *Ber.*, **47**, 1289 (1914).

[14] Arnold and Sprung, THIS JOURNAL, **60**, 1163 (1938).

[15] Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 185–190.

[16] Wheland, University of Chicago, private communication.

[17] West in Weissberger, "Physical Methods of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946, p. 819.

[18] Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1939, p. 130.

man spectrophotometer; 1 cm. cells were used. The *p*H measurements were made on a Leeds-Northrup, *p*H meter, Catalog no. 7661 (Glass and calomel electrodes). The melting points were taken on a Kofler hot stage (Arthur H. Thomas Company, Catalog no. 6886A).

Adsorbents and Solvents.—Silicic acid–Celite (2 to 1) adsorbent was prepared by mixing 2 parts by weight of silicic acid (Merck Reagent) with 1 part by weight of Celite (Johns–Manville and Company). All solvents used in the chromatographic technique were redistilled. Petroleum ether (30–60°) was used throughout unless otherwise specified.

Preparation of Nitro Derivatives of the Isomeric Xylenols

2,3-Xylenol: (a) 6-Nitro-2,3-xylenol.—2.5 g. of 2,3-xylenol was dissolved in 50 ml. of glacial acetic acid, and cooled to 18–20°; 2.5 ml. of nitric acid (sp. gr. 1.42) which was dissolved in 10 ml. of glacial acetic acid was added dropwise with stirring. After the addition of the nitric acid, the reaction mixture was allowed to sit for fifteen minutes (18–20°), drowned in 500 ml. of water, and the solution neutralized with 20% sodium hydroxide. The alkaline solution was acidified with 10% sulfuric acid and steam distilled. The 6-nitro-2,3-xylenol was extracted from the distillate with petroleum ether. The solution was evaporated down and chromatographed on a column of silicic acid–celite (2:1). Prewash: 1 volume (the amount of solvent necessary to wet the column of adsorbent was taken as 1 volume) of ether and 2 volumes of petroleum ether. Developer: 0.8 volume of 5% ether in petroleum ether.

The chromatogram obtained was (the figures on the left designate the thickness of the zones in mm.): 100, empty section; 11, yellow, 6-nitro-2,3-xylenol; 20, empty section. The main zone was cut out and eluted with ether. The ether was evaporated off and the 6-nitro-2,3-xylenol was recrystallized twice from absolute alcohol, giving yellow needles melting at 48.5–49.0°; yield, 1.2 g. *Anal.* Calcd. for $C_8H_9NO_3$: C, 57.47; H, 5.43; N, 8.38. Found: C, 57.15; H, 5.46; N, 8.43.

(b) **4,6-Dinitro-2,3-xylenol.**—The residue remaining in the distilling flask after the first steam distillation of 6-nitro-2,3-xylenol (see above) was extracted with ether. The ether was evaporated and the crude 4,6-dinitro-2,3-xylenol dissolved in benzene–petroleum ether (4:10). The solution was chromatographed on a column of silicic acid–celite (2:1) and the chromatogram developed with 0.45 volume of benzene–petroleum ether (2:3).

The yellow zone was cut out and eluted with ether. The 4,6-dinitro-2,3-xylenol was recrystallized from absolute alcohol yielding 0.06 g. of yellow needles melting at 86.5–87.0 (lit., 82°[6]). *Anal.* Calcd. for $C_8H_8N_2O_5$: C, 45.29; H, 3.80; N, 13.21. Found: C, 45.27; H, 3.95; N, 13.30.

1. **Proof of Structure for 6-Nitro-2,3-xylenol: (a) Nitration of 6-nitro-2,3-xylenol**: 0.1 g. of 6-nitro-2,3-xylenol was dissolved in 10 ml. of glacial acetic acid and cooled to 20°. Three ml. of fuming nitric acid (sp. gr. 1.49) was added dropwise with stirring and the reaction mixture allowed to stand for ten minutes. The reaction was then stopped by adding 200 ml. of water and the solution neutralized with sodium hydroxide (20%). The solution was acidified with sulfuric acid (5%) extracted with benzene, and the benzene evaporated off. The residue was dissolved in benzene–petroleum ether (2:10) and chromatographed on a column of silicic acid–celite (2:1). The chromatogram was developed with 0.8 volume of benzene–petroleum ether (3:1). Both of the zones were eluted with methyl alcohol and the alcohol evaporated off. The compounds were then recrystallized from absolute alcohol. The compound in the top zone was identified by its melting point and absorption spectra as 4,6-dinitro-2,3-xylenol. The lower zone contained the unreacted 6-nitro-2,3-xylenol.

(b) **Amination of 6-nitro-2,3-xylenol**: 0.4 g. of 6-nitro-2,3-xylenol was mixed with 1 g. of ammonium chloride, 10 ml. of ammonium hydroxide (sp. gr. 0.90), and sealed in a thick-walled pyrex tube. The tube was placed in a bomb tube and heated in an oven for three hours at 150° ± 2°. After heating, the tube and contents were allowed to cool overnight. The tube was carefully opened and washed with water. The ammoniacal reaction mixture was extracted first with petroleum ether, and then with ether. The solvents were evaporated from the extracts, and the residues were dissolved in 5% ether in petroleum ether. The solutions were combined and chromatographed on a column of silicic acid–celite (2:1). The chromatogram was developed with 1 volume of ether–petroleum ether (1:6).

The greenish yellow band was eluted with ether and the ether evaporated. The compound was recrystallized from absolute alcohol yielding orange-red rhombohedra which melted at 120.0–120.2°. 6-Nitro-2,3-xylidine melts at 118–119° according to Noelting, Braun and Thesmar.[19] To confirm further that the isolated compound was 6-nitro-2,3-xylidine, the acetyl derivative was prepared, and found to have a melting point of 159.8–160.0°. Literature[19] gives the melting point at 160°.

(c) **Amination of 4,6-Dinitro-2,3-xylenol**: 0.35 g. of 4,6-dinitro-2,3-xylenol was mixed with 1 g. of ammonium chloride and 10 ml. of ammonium hydroxide. The reactants were placed in a thick-walled Pyrex tube and the amination carried out as in the case of 6-nitro-2,3-xylenol. The ammoniacal solution was extracted with ether and the ether then evaporated off. The residue was then dissolved in an acetone–ether (1:4) solution and chromatographed on a column of silicic acid–celite (2:1). The chromatogram was developed with 0.5 volume of acetone–ether (1:4).

The canary yellow zone was eluted with methyl alcohol and the alcohol evaporated. The residue was recrystallized from benzene, yielding yellow needles, which melted at 161.8–162.5°. The literature[20] gives the melting point of 4,6-dinitro-2,3-xylidine at 161°. To confirm further that the compound isolated was 4,6-dinitro-2,3-xylidine, the absorption spectrum of the compound in absolute alcohol was made. The spectrum[21] checked that as given by Morgan, Jobling and Barnett.

2,4-Xylenol: (a) 6-Nitro-2,4-xylenol was prepared by the nitration of 2,4-xylenol in glacial acetic acid.[7,8]

3,4-Xylenol: (a) 6-Nitro-3,4-xylenol and 2-nitro-3,4-xylenol.—One gram of 3,4-xylenol was dissolved in 10 ml. of glacial acetic acid and cooled to 15–20°; 1 ml. of nitric acid (sp. gr. 1.42) was dissolved in 5 ml. of glacial acetic acid and added dropwise to the reaction mixture with stirring. After the final addition of the nitric acid, the reaction mixture was allowed to sit for fifteen minutes, drowned in 200 ml. of water, and 1 g. of urea added. The mixture was then steam distilled and the distillate extracted with petroleum ether. The petroleum ether extract was evaporated to a small volume and chromatographed on a column of silicic acid–celite (2:1). Prewash: 1 volume ether, then 2 volumes petroleum ether. Developer: 0.6 volume of ether–petroleum ether (1:19). The chromatogram obtained was: 21, empty section; 20, light yellow, 2-nitro-3,4-xylenol; 45, empty section; 40, canary yellow, 6-nitro-3,4-xylenol; 30, empty section. Both zones were eluted with ether and the ether evaporated off. The top zone, consisting of 2-nitro-3,4-xylenol was recrystallized from petroleum ether (40–70°), yielding orange needles which melted at 71.8–72.4°; yield, 0.08 g. *Anal.* Calcd. for $C_8H_9NO_3$: C, 57.47; H, 5.43; N, 8.38. Found: C, 57.98; H, 5.54; N, 8.11. The lower zone on recrystallization from alcohol yielded yellow platelets of 6-nitro-3,4-xylenol melting at 86.7–87.7° (literature[9] gives 87°); yield, 0.5 g.

(b) **2,6-Dinitro-3,4-xylenol** was prepared by the nitration of 3,4-xylenol in glacial acetic acid.[9,10]

(1) **Proof of Structure for 6-Nitro, 2-Nitro, and 2,6-Dinitro-3,4-xylenol: (a) Nitration of 6-nitro-3,4-xylenol**: 0.1 g. of 6-nitro-3,4-xylenol was nitrated and chromatographed as in the procedure for the nitration of 6-nitro-

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(19) Noelting, Braun and Thesmar, *Ber.*, **34**, 2246 (1901).

(20) Crossley and Morrell, *J. Chem. Soc.*, **99**, 2348 (1911).

(21) Morgan, Jobling and Barnett, *ibid.*, **101**, 1215 (1912).

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 *p*H of the solution was measured on a Leeds-Northrup *p*H meter, and the *p*H 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 *p*H 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. *p*H meter. The solution was titrated with a 0.01309 *N* solution (50–50 H_2O–C_2H_5OH; by weight) sodium hydroxide, and the *p*H 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 *p*H of the solution at one-half neutralization was determined. The *p*H 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, "*p*H and Electro Titrations," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 106–109.

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[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).