

The direct nitration of the so-called water-insoluble form of furfuryl alcohol proceeds smoothly, but decomposition sets in on subsequent treatment with pyridine.¹ Apparently nitrofurfuryl nitrate is among the products which are being investigated.

Hydrolysis of Nitrofurfuryl Acetate.—Eighteen and one-half g. (0.1 mole) of nitrofurfuryl acetate is refluxed for twenty minutes with 200 cc. of 5% sulfuric acid. The solution is chilled and filtered by suction to remove 0.2 g. of an as yet unidentified compound⁶ melting at 73°. The filtrate is extracted thrice with 50-cc. portions of ether and the combined ether extracts are dried over sodium sulfate. The residue, after removal of the ether, is distilled under reduced pressure (157°, 8 mm.), to give a yellow oil which solidified overnight to the nitrofurfuryl alcohol melting at 32°. The yield is 9–10 g. or 49–55%.

Anal. Calcd. for C₅H₆O₄N: C, 41.95; H, 3.52. Found: C, 41.96; H, 3.76.

Oxidation of Nitrofurfuryl Alcohol.—The nitrofurfuryl alcohol was oxidized by heating for two days at 40–50° with a mixture of manganese dioxide and 50% sulfuric acid. The ether extract from this oxidation gave nitrofurfural melting at 36°. This showed no depression in a mixed melting point determination with an authentic specimen.¹

The authors are grateful to R. R. Burtner for assistance in this study. He has shown that furfuryl chloride and furfuryl methyl ether also undergo ready substitution, the chloromethyl and alkoxyethyl groups orienting like the acetate group.

Summary

The first nitrofurfuryl alcohol has been prepared by the hydrolysis of nitrofurfuryl acetate, which was obtained by the direct nitration of furfuryl acetate. The nitro group markedly stabilizes the furan nucleus.

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[194TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND THE MICROANALYTICAL LABORATORY, FOOD AND DRUG ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

THE IDENTIFICATION OF PHENOLS AS THE ESTERS OF 3,5-DINITROBENZOIC ACID

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In connection with an investigation on the chemistry of lignin which one of the authors has been conducting, an occasion arose requiring the identification of the phenols produced when lignin is subjected to destructive distillation or is distilled with zinc dust in an atmosphere of hydrogen. Attempts were made to prepare the usual derivatives of phenols such as the benzoyl derivatives, the phenyl, diphenyl and α -naphthyl urethans, and the *p*-nitrobenzyl ethers, but all these were found to be liquid at room temperature and therefore unsuitable for the purpose of identification. It was found, however, that 3,5-dinitrobenzoyl chloride condensed with the phenols under investigation and yielded products which could be

⁶ The same compound has been isolated in small quantities from the direct nitration of water-insoluble furfuryl alcohol in acetic anhydride.

readily purified by crystallization. The 3,5-dinitrobenzoyl chloride was first used as a reagent for the identification of alcohols¹ and has been applied by Brown and Kremers² to the identification of phenols. The method prescribed by these investigators is, however, difficult to carry out, particularly when only a small quantity of a phenolic substance is available.

In this paper a new and simple method for the preparation of the 3,5-dinitrobenzoyl derivatives of phenols is described. Some of the more important physical properties of these derivatives, including the data on the optical properties of the crystals, are recorded.

Experimental

Materials Used.—The 3,5-dinitrobenzoyl chloride used in all our experiments was obtained from the Eastman Kodak Company.

Phenols.—All the phenols except those listed below were obtained from the Eastman Kodak Company.

Phenol.—This was the regular U. S. P. product.

5-Hydroxy-1,3-dimethylbenzene.—This was prepared through the diazo reaction from 5-amino-1,3-dimethylbenzene.

Thymol.—This was the U. S. P. product.

Isoeugenol.—This was a Kahlbaum product.

Creosol (1-Methyl-3-methoxy-4-hydroxybenzene).—The creosol was synthesized from vanillin by the application of the Clemensen³ reduction method. The procedure was briefly as follows. To 20 g. of vanillin and 400 cc. of hydrochloric acid (200 cc. of hydrochloric acid *d* 1.19 and 200 cc. of water), 100 grams of amalgamated zinc was added, and the mixture was boiled under a reflux condenser for eight hours. The reaction product was allowed to cool to room temperature, and extracted with ether. The ether solution was extracted with a solution of sodium bisulfite, dried over anhydrous sodium sulfate, and the ether distilled off. The residue was fractionally distilled, and the fraction which distilled over at 219–221° was retained; yield, 5 g. (27.6%). A methoxyl determination gave the following results.

Anal. Subs., 0.1254: AgI, 0.2111. Calcd. for C₈H₁₀O₂: CH₃O, 22.46. Found: CH₃O, 22.23.

1-*n*-Propyl-3-methoxy-4-hydroxybenzene.—This was prepared by the catalytic reduction of eugenol. The procedure was as follows. One-tenth of a mole of eugenol (16.4 g.) was dissolved in 150 cc. of 95% ethanol, 0.2 g. of platinum catalyst was added (prepared according to the directions given by Adams, Voorhees and Shriner)⁴ and the mixture was shaken in a shaking machine in an atmosphere of hydrogen until the calculated amount of hydrogen was absorbed. The platinum was filtered off and the filtrate distilled. At first alcohol came over, then the temperature rose rapidly and an oil distilled over at 250–255°. This was redistilled, and the main portion came over at 251–253° (corrected for stem exposure) (765.8 mm.); yield, 12 g. (72.2%).

¹ S. P. Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, New York, 1905, p. 168.

² Brown and Kremers, *J. Am. Pharm. Assoc.*, 11, 607 (1922).

³ Clemensen, *Ber.*, 46, 1837 (1913); 47, 51 (1914).

⁴ Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, John Wiley and Sons, New York, 1928, p. 92.

Anal. Subs., 0.1552: AgI, 0.2170. Calcd. for $C_{10}H_{14}O_2$: CH_3O , 18.67. Found: CH_3O , 18.47.

Preparation of the 3,5-Dinitrobenzoyl Esters of the Phenols.—0.01 mole of the phenol and 2.3 g. (0.01 mole) of 3,5-dinitrobenzoyl chloride were added to 20 cc. of *c. p.* pyridine, and the mixture was heated over a free flame under the reflux condenser for one hour. The reaction product was cooled and poured into about 400 cc. of cold 5% sulfuric acid. If the crude reaction product separated as a solid, it was filtered off and washed with water until the wash water was acid free. The product was added to 200 cc. of 2% sodium hydroxide solution, the mixture was well stirred, filtered, washed with water, and then crystallized. When the reaction product separated out as an oil or as a gummy mass, it was dissolved in ether and the ether solution washed successively with water, 2% sodium hydroxide, and finally with water. The ether was distilled off and the residue crystallized. In all cases except one the reaction products were crystallized from 95% ethanol. The 3,5-dinitrobenzoyl derivative of isoeugenol was crystallized from *n*-butyl alcohol.

Melting Point Determinations.—The melting points were determined in a Roth⁵ type of apparatus with Anschütz thermometers which had been standardized by the Bureau of Standards.

Nitrogen Determinations.—The nitrogen was determined by the Kjeldahl method, modified for the determination of nitrogen in nitro compounds. The modified Parnas-Wagner micro Kjeldahl apparatus⁶ was used. Approximately twenty milligrams of substance were taken for each determination.

The results of the melting point and nitrogen determinations are given in Table I.

TABLE I
MELTING POINTS AND NITROGEN CONTENT OF 3,5-DINITROBENZOYL DERIVATIVES OF PHENOLS

3,5-Dinitrobenzoyl derivatives	M. p., (corr.), °C.	Formula	Nitrogen, %	
			Calcd.	Found
Phenol	145.8	$C_{13}H_8O_6N_2$	9.72	9.69
<i>o</i> -Cresol	138.4	$C_{14}H_{10}O_6N_2$	9.27	9.14
<i>m</i> -Cresol	165.4	$C_{14}H_{10}O_6N_2$	9.27	9.14
<i>p</i> -Cresol	188.6	$C_{14}H_{10}O_6N_2$	9.27	9.14
4-Hydroxy-1,2-dimethylbenzene	181.6	$C_{15}H_{12}O_6N_2$	8.86	8.83
2-Hydroxy-1,3-dimethylbenzene	158.8	$C_{15}H_{12}O_6N_2$	8.86	8.82
4-Hydroxy-1,3-dimethylbenzene	164.6	$C_{15}H_{12}O_6N_2$	8.86	8.96
5-Hydroxy-1,3-dimethylbenzene	195.4	$C_{15}H_{12}O_6N_2$	8.86	8.90
2-Hydroxy-1,4-dimethylbenzene	137.2	$C_{15}H_{12}O_6N_2$	8.86	8.68
Thymol	103.2	$C_{17}H_{16}O_6N_2$	8.13	8.17
<i>p</i> -Cyclohexylphenol	168.0	$C_{16}H_{18}O_6N_2$	7.56	7.43
Guaiacol	141.2	$C_{14}H_{10}O_7N_2$	8.80	8.60
Cresol (1-methyl-3-methoxy-4-hydroxybenzene)	170.6	$C_{15}H_{12}O_7N_2$	8.43	8.33
1- <i>n</i> -Propyl-3-methoxy-4-hydroxybenzene (<i>n</i> -propylguaiacol)	116.2	$C_{17}H_{16}O_7N_2$	7.77	7.72
Eugenol	130.8	$C_{17}H_{14}O_7N_2$	7.82	7.86
Isoeugenol	158.4	$C_{17}H_{14}O_7N_2$	7.82	7.70
α -Naphthol	217.4	$C_{17}H_{10}O_6N_2$	8.28	8.08
β -Naphthol	210.2	$C_{17}H_{10}O_6N_2$	8.28	8.29

⁵ Roth, *Ber.*, 19, 1970 (1886).

⁶ Parnas and Wagner, *Biochem. Z.*, 125, 253 (1921); Clark and Collip, *J. Biol. Chem.*, 67, 621 (1926).

TABLE II
OPTICAL PROPERTIES OF CRYSTALS OF 3,5-DINITROBENZOYL DERIVATIVES OF PHENOLS

3,5-Dinitrobenzoyl deriv. of	Habit	Color	Extinction	Elongation	Class	Figures	Refractive indices			Common index
							α	β	γ	
Phenol	Rods	Colorless	Parallel	Negative	Biaxial	Rare	1.505	1.690	>1.740	α
<i>o</i> -Cresol	Plates	Colorless	Biaxial	Infrequent	1.490	Indet.	>1.720	α
<i>m</i> -Cresol	Plates	Colorless	Parallel	Negative	Biaxial	Rare	1.475	1.700	1.740	α and γ
<i>p</i> -Cresol	Plates	Colorless	Biaxial	Rare	1.500	Indet.	1.740	α and γ
4-Hydroxy-1,2-dimethylbenzene	Rods, needles	Colorless	Parallel	Negative	Biaxial	Rare	1.508	1.670	>1.740	α and γ
2-Hydroxy-1,3-dimethylbenzene	Rods, plates	Cream-white	Parallel	Negative	Biaxial	Rare	1.512	1.670	>1.740	α and γ
4-Hydroxy-1,3-dimethylbenzene	Rods, plates	Colorless	Parallel	Negative	Biaxial	Rare	1.517	1.645	>1.690	α
5-Hydroxy-1,3-dimethylbenzene	Rods	Cream-white	Parallel	Negative	Biaxial	Rare	1.485	1.650	>1.740	α and β
2-Hydroxy-1,4-dimethylbenzene	Needles	Cream-white	Parallel	Negative	Biaxial	Rare	1.487	1.665	1.740	α
Thymol	Needles	Colorless	Parallel	Negative	Biaxial	Rare	1.480	1.625	1.705	α
<i>p</i> -Cyclohexylphenol	Needles	Brownish-white	Parallel	Positive or negative	Biaxial	Frequent	1.515	1.625	1.702	All
Guaiacol	Needles	Yellow	Biaxial	Rare	1.530	Indet.	>1.740	α
Creosol (1-methyl-3-methoxy-4-hydroxybenzene)	Rods, needles	Colorless	Parallel	Positive	Biaxial	Rare	1.550	1.570	1.640	γ
1- <i>n</i> -Propyl-3-methoxy-4-hydroxybenzene (<i>n</i> -propylguaiacol)	Needles	Light yellow	Parallel	Positive	Biaxial	Infrequent	1.520	Indet.	1.650	α and γ
α -Naphthol	Needles	Yellow	Parallel	Negative	Biaxial	Rare	1.490	1.615	>1.740	β
β -Naphthol	Needles	Colorless	Parallel	Negative	Biaxial	Rare	1.475	1.740	>1.740	α

Optical Properties of the Crystals.—The optical properties of the crystals were determined by the immersion method⁷ which has been used successfully by one of the authors in the identification of several types of organic compounds.⁸ The 3,5-dinitrobenzoyl derivatives of the phenols were most satisfactorily studied in solutions of potassium mercuric iodide in glycerol and water, although for rapid determinative work, oily liquids consisting of mixtures of mineral oils, monochloronaphthalene and methylene iodide can be used.

The results obtained are given in Table II. Because of the peculiar cleavage properties of the 3,5-dinitrobenzoyl derivatives of eugenol and isoeugenol the optical properties of the crystals could not be determined with any degree of accuracy and therefore are not included in the table.

Summary

1. A method for the preparation of the 3,5-dinitrobenzoyl derivatives of phenols is described. This method can be conveniently used for the identification of phenols.
2. The melting points and the optical properties of the crystals of the 3,5-dinitrobenzoyl derivatives of several phenols were determined.
3. Methods for the preparation of creosol and of 1-*n*-propyl-3-methoxy-4-hydroxybenzene are given.

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THE REARRANGEMENT OF SATURATED ALKYL PHENYL ETHERS. SYNTHESIS OF ISOPROPYL PHENOL AND CRESOLS¹

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Theoretical Part

In an earlier publication² a report was given on the condensation of olefins with phenols under the influence of concentrated sulfuric acid in the cold. The results obtained differed from those already reported in the literature, ethers being obtained and not the corresponding substituted phenols. It was suggested that the condensation process used by the other authors brought about rearrangement of the ethers first formed.

⁷ Wilson and Keenan, *J. Assoc. Official Agr. Chem.*, **13**, 389 (1930).

⁸ Keenan, *J. Biol. Chem.*, **62**, 163 (1924); *J. Wash. Acad. Sci.*, **16**, 433 (1926); Keenan and Weisberg, *J. Phys. Chem.*, **33**, 791 (1929).

¹ Constructed from the second half of the thesis presented by Samuel Natelson to the Faculty of the Graduate School of New York University in candidacy for the degree of Doctor of Philosophy, 1931. Presented at the Indianapolis meeting of the American Chemical Society, April 3, 1931.

² Niederl and Natelson, *THIS JOURNAL*, **53**, 272 (1931).