

Their results were checked satisfactorily. A different compound, however, was obtained when glacial acetic acid was used as a solvent. Its melting point was 220°. The carbon, hydrogen and nitrogen determinations showed it to be an anil. These 2 compounds are probably isomers of the syn- and anti-type. Attempts to prepare similar isomers of the toluidines were unsuccessful. The same compound was obtained if alcohol instead of glacial acetic acid was employed in the reaction.

2. Fifteen derivatives of 2,4,6-trinitro-benzaldehyde were prepared, analyzed and certain physical properties determined.

3. The intermediate addition products were prepared in the case of aniline, *o*-toluidine and of the naphthylamines. The aniline and *o*-toluidine compounds lose aniline and *o*-toluidine respectively, while the naphthylamine products lose water and are converted into the condensation products.

4. The intermediate products are all reddish-brown in color and are very soluble in alcohol, while the condensation products have yellow to brick red colors, are not easily soluble and have much higher melting points.

5. These compounds, like many other similar condensation products, are affected to a greater or less extent by the action of light.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

DERIVATIVES OF 2,4-DINITRO-BENZALDEHYDE.¹ II.

BY ALEXANDER LOWY AND THOMAS B. DOWNEY.

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In the previous report,² the object of the research and references to the literature were given together with the theoretical phase of the subject.

The reactions investigated were all of the general type condensations previously described² for the preparation of modified "Schiff's bases."³ Condensations were carried out between 2,4-dinitro-benzaldehyde and the following substituted amines: *p*-bromo-aniline, 2,4,6-tribromo-aniline, *o*-nitro-aniline, *m*-nitro-aniline, *p*-nitro-aniline, *o*-phenetidine, *o*-anisidine and *p*-anisidine.

Some of these reactions offer additional evidence on the subject of steric hindrance. 2,4,6-Tribromo-aniline would not condense with 2,4-dinitro-benzaldehyde with 95% alcohol as the condensing medium when heated for 6 hours. In glacial acetic acid, however, the condensation took place within 3 hours.

¹ This report represents the experimental part of a thesis presented by Thomas B. Downey in partial fulfilment of the requirements for the degree of Master of Science, August, 1920.

² THIS JOURNAL, 42, 849 (1920).

³ Ber., 35, 984 (1902).

Another type of condensation is that taking place in the reaction of one molecule of an aromatic aldehyde or a substituted aromatic aldehyde and 2 molecules of a tertiary alkylated aromatic amine, or substituted aromatic amines, such as *o*-toluidine. For example, benzaldehyde condenses with 2 molecules of dimethylaniline to give malachite green. Lowy and Wescott¹ in these laboratories condensed 2,4-dinitro-benzaldehyde and dimethylaniline (in the proportion of one mol. to 2 mols.), and obtained a bluish-green coloring matter closely resembling malachite green. Condensations have been made by Danckwortt² with one molecule of *p*-nitro-benzaldehyde and 2 molecules of phenolic substances. Similar condensations will be tried in these laboratories using 2,4-dinitro-benzaldehyde and 2,4,6-trinitro-benzaldehyde, which should give compounds with characteristic colors.

Experimental Part.

Preparation of 2,4-Dinitro-benzaldehyde.—The method used in the preparation of the base compound of these derivatives, 2,4-dinitro-benzaldehyde is essentially that described by F. Sachs and R. Kempf.³ Certain modifications of this method worked out by Lowy and Wescott⁴ in these laboratories were followed.

The table given below contains the essential results obtained.

No.	Name of Product.	M. p. °C.	Yield. %.	Time of heating. Hours.	Analysis, %	
					Calc.	Found.
1.	2,4-Dinitro-benzal- <i>p</i> -bromo-aniline.....	162.5	90	1	Br = 22.83	22.66; 22.75
2.	2,4-Dinitro-benzal-2,4,6-tribromo-aniline.....	185	80	2	Br = 47.22	47.27; 47.32
3.	2,4-Dinitro-benzal- <i>o</i> -aniline.....	174.5	89	1.5	N = 17.73	17.53; 17.86
4.	2,4-Dinitro-benzal- <i>m</i> -nitro-aniline.....	138	92	4	N = 17.73	17.78; 17.94
5.	2,4-Dinitro-benzal- <i>p</i> -nitro-aniline.....	169.5	95	1	N = 17.73	17.78; 17.90
6.	2,4-Dinitro-benzal- <i>o</i> -phenetidine.....	141.5	94	1	N = 13.33	13.65; 13.54
7.	2,4-Dinitro-benzal- <i>o</i> -anisidine.....	140	89	0.5	N = 13.95	14.11; 14.21
8.	2,4-Dinitro-benzal- <i>p</i> -anisidine.....	129	90	0.5	N = 13.95	13.76; 14.07

In the preparation of compounds listed above the ratio of one mole of 2,4-dinitro-benzaldehyde to one mole of the substituted amine was used in all cases. The condensation products were recrystallized several times from alcohol, acetone or toluene. These products are very soluble

¹ Lowy and Wescott, *THIS JOURNAL*, **42**, 849 (1920).

² Danckwortt, *Ber.*, **42**, 4163 (1909).

³ Sachs and Kempf, *ibid.*, **35**, 2704 (1902).

⁴ *Loc. cit.*

in chloroform, benzene, alcohol, acetic acid, acetone and insoluble in water. On hydrolysis with 1:1 hydrochloric acid they yield 2,4-dinitrobenzaldehyde and the respective substituted amines.

The condensing medium was alcohol for all but Nos. 2 and 3. The products consisted of yellow needles except in 2 and 8; these were orange needles.

These compounds like many other similar condensation products are affected to a considerable extent by the action of light. It was noted that the halogenated derivatives were particularly susceptible to light.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

THE PREPARATION OF SOME ALKYL DERIVATIVES OF RESORCINOL AND THE RELATION OF THEIR STRUCTURE TO ANTISEPTIC PROPERTIES.

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Introduction.

A review of the literature reveals the fact that, in spite of the work of Ehrlich² and others, our knowledge of the relation of the structure of phenolic bodies to their antiseptic and toxic properties is still very incomplete. Therefore, any additional facts contributing to a better understanding of this relationship should be of considerable assistance in directing the search for new and more valuable antiseptics. It is believed by the writers that the present work adds a new and fundamental conception in the relationship consideration.

It is well understood,³ that the substitution of one or more methyl groups into the nucleus of phenol increases the germicidal value as well as lowers the toxic properties of that substance. Nothing, however, appears to be definitely known as to how the *antiseptic* strength would be affected by replacing the methyl group with alkyl radicals of greater weight. It is this phase of the subject in which the writers are especially interested.

Inasmuch as phenol and many of its derivatives have been found

¹ This paper is constructed from a thesis presented by Frederick W. Lane in 1920 to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. T. B. J.

² Bechhold and Ehrlich, *Z. physiol. Chem.*, **47**, 173 (1906); Baglioni, *Z. allgem. Physiol.*, **3**, 313 (1904); Pyman, *J. Chem. Soc.*, **III**, 1103 (1917); Bechhold, *Z. angew. Chem.*, **22**, 2033 (1909); May, "The Chemistry of Synthetic Drugs," p. 152. Longmans, 1918; Frankel, "Die Arzneimittel-Synthese," p. 483, Springer, Berlin, 1906.

³ Bechhold and Ehrlich, *loc. cit.*; Baglioni, *loc. cit.*; May, *loc. cit.*; compare also Schmiedeberg, *Arch. exp. Path. Pharm.*, **20**, 203 (1886).