

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

DERIVATIVES OF PARA-NITRO-BENZALDEHYDE.¹

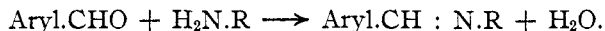
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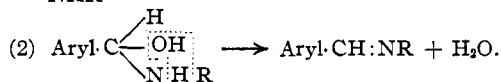
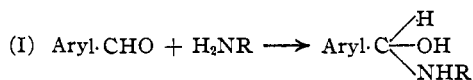
This investigation upon the derivatives of *p*-nitro-benzaldehyde was undertaken for the following reasons.

(1) Investigations are being carried out in these laboratories upon derivatives of 2,4-dinitro-benzaldehyde² and 2,4,6-trinitro-benzaldehyde, and it was desirable to have parallel work done upon *p*-nitro-benzaldehyde. (2) Benzaldehyde is an important dye intermediate, and since *p*-nitro-benzaldehyde may form analogous compounds³ it seemed probable that further uses for it might be found in that field. (3) A great many compounds have been prepared from benzaldehyde, and it was thought that similar compounds should be prepared from *p*-nitro-benzaldehyde. (4) Information regarding "steric hindrance" might be obtained from condensations with molecules having substituted groups in the *ortho* position. (5) It should be possible to obtain compounds having syn- and anti-isomers, and also the intermediate addition products. A few such cases have been noted in the literature,⁴ but in most cases isomers or addition products have not been obtained.

The reactions carried out in the study of *p*-nitro-benzaldehyde were of the general type known as condensations. The first type of condensation studied was that of the reaction between *p*-nitro-benzaldehyde and different aromatic amines. The reaction is accompanied by the elimination of 1 molecule of water and may be expressed by the general type reaction



Such condensation products are commonly known as "Schiff's bases."⁵ According to the present accepted theory the condensation takes place in 2 steps. The first is marked by the formation of an addition compound. The second step consists of the splitting off of one molecule of water.



¹ This report represents an abstract of a thesis presented by Charles G. King, in partial fulfilment of the requirements for the degree of Master of Science, October, 1920.

² THIS JOURNAL, 42, 849 (1920).

³ Ber., 13, 669 (1880); 15, 677 (1882); 39, 292 (1906); 28, 207 (1897).

⁴ J. Chem. Soc., 103, 1613 (1913); 109, 582 (1916); 109, 650 (1916); Atti accad. Lincei, 18, [2], 621 (1910).

⁵ Ber., 35, 984 (1902).

The complete condensation may take place immediately upon mixing the 2 reacting substances or in a non-dehydrating solvent, but in many cases a solvent must be used which also exerts a dehydrating effect, such as alcohol or glacial acetic acid. Thus *o*-phenetidine and 1,3,4-xylydine condense readily with *p*-nitro-benzaldehyde upon warming them together. 3-Nitro-4-toluidine did not condense with *p*-nitro-benzaldehyde upon refluxing for 4 hours in absolute alcohol, but did condense upon heating the 2 constituents together on a hot plate, after adding a few drops of glacial acetic acid.

The effect of steric hindrance upon the condensation was shown by the relative difficulty with which *o*-nitro-aniline and tribromo-aniline react. *o*-Nitro-aniline did not condense to an appreciable extent after 4 hours' refluxing in glacial acetic acid or absolute alcohol. Tribromo-aniline did not condense satisfactorily after 10 hours' refluxing. Both of these compounds condensed fairly readily with 2,4-dinitro-benzaldehyde in glacial acetic acid. Further investigation regarding the condensation of *o*-nitro-aniline and tribromo-aniline with *p*-nitro-benzaldehyde will be made.

The same type of reaction is possible with either substituted aldehydes, amines or both. Condensations were carried out between *p*-nitro-benzaldehyde and the following substituted amines: *o*-phenetidine, *p*-bromo-aniline, *o*-toluidine, *p*-toluidine, 1,3,4-xylydine, 3-nitro-4-toluidine, *p*-nitro-aniline and *m*-nitro-aniline.

The intermediate addition product of the aldehyde-amine condensation is often very difficult to isolate, due probably to its instability, or the rapidity with which the second step takes place, splitting off the molecule of water. No compounds of the addition product type were isolated. This phase of the work is being investigated.

It should be possible to obtain 2 stereo-isomers of the condensation products, having a double-bond nitrogen atom,¹ but no evidence of the existence of such isomers was found. Work upon this phase of the subject will be continued.

A second type of condensation is that taking place in the reaction of 1 molecule of an aromatic aldehyde or a substituted aromatic aldehyde and 2 molecules of another aromatic compound, with the elimination of 1 molecule of water. For example, 1 molecule of *p*-nitro-benzaldehyde was condensed with 2 molecules of aniline.² Similar condensations have been carried out with benzene³ and various phenolic bodies.⁴ Reactions of this type are being investigated by the writers.

¹ *J. Chem. Soc.*, 109, 659 (1916).

² *Ber.*, 13, 669 (1880).

³ *Ibid.*, 23, 1621 (1890).

⁴ *Ibid.*, 42, 4163 (1909).

Experimental.

The method used in the preparation of *p*-nitro-benzaldehyde was that described by V. v. Richter.¹

In the preparation of compounds listed below the ratio of 1 mole of *p*-nitro-benzaldehyde to 1 mole of the substituted amine was used in all cases. The reacting mixtures were refluxed on a water-bath. The condensation products were recrystallized several times from either alcohol, acetone, carbon tetrachloride or acetic acid. These products are soluble in chloroform, benzene, alcohol, acetic acid or acetone and insoluble in water except *p*-nitrobenzal-3-nitro-4-toluidine and *p*-nitrobenzal-*p*-nitro-aniline which are slightly soluble in water. On hydrolysis with 1 : 5 hydrochloric acid they yield *p*-nitro-benzaldehyde and the respective substituted amines.

The table given below contains the essential results obtained.

Name of Product.	M. p. ° C.	Color and crystal form.	Condens- ing medium.	Yield. %.	Time of heat- ing. Hours.	Analysis.	
						Calculated. %.	Found. %.
<i>p</i> -Nitrobenzal- <i>o</i> -phenetidine	81	yellow plates	alcohol	90	3	N, 10.37	10.48; 10.51
<i>p</i> -Nitrobenzal- <i>p</i> -bromo-aniline	160.5	yellow needles	alcohol	92	2	Br, 26.20	26.05; 26.25
<i>p</i> -Nitrobenzal- <i>o</i> -toluidine	89	yellow plates	alcohol	94	2	N, 11.67	11.54; 11.49
<i>p</i> -Nitrobenzal- <i>p</i> -toluidine	122.5	yellow needles	alcohol	95	1	N, 11.67	11.59; 11.79
<i>p</i> -Nitrobenzal-1,3,4-xylylidine	88.5	yellow needles	glacial acetic acid	85	1	N, 10.99	11.03; 11.15
<i>p</i> -Nitrobenzal-3-nitro-4-toluidine	161.5	yellow needles	glacial acetic acid	70	1/3	N, 14.74	14.79; 14.71
<i>p</i> -Nitrobenzal- <i>p</i> -nitro-aniline	198.5	yellow needles	glacial acetic acid	95	1/2	N, 15.50	15.33; 15.63
<i>p</i> -Nitrobenzal- <i>m</i> -nitro-aniline	152	yellow needles	alcohol	90	2	N, 15.50	15.67; 15.54

Analogous derivatives prepared from 2,4-dinitro-benzaldehyde² and 2,4,6-trinitro-benzaldehyde³ are affected by the action of light while these derivatives seem to be stable upon exposure to sunlight.

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¹ *Ber.*, **19**, 1060 (1886).

² *THIS JOURNAL*, **42**, 849 (1920); *ibid.*, **43**, 346 (1921).

³ *Ibid.*, **43**, 341 (1921).