

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

DERIVATIVES OF 2,4,6-TRINITRO-BENZALDEHYDE.¹

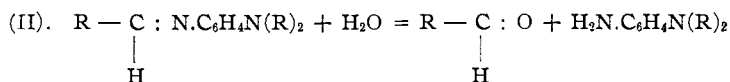
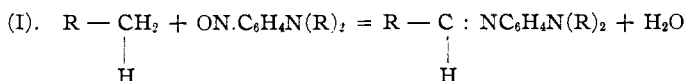
BY ALEXANDER LOWY AND EMIL HAROLD BALZ.

Received August 23, 1920.

The investigation of the derivatives of 2,4,6-trinitro-benzaldehyde was undertaken for several reasons. An examination of the literature revealed that, compared with the number of known derivatives of benzaldehyde and of mononitro-benzaldehydes, very few derivatives of this aldehyde² had been prepared. Undoubtedly, a comparison of the behavior of 2,4,6-trinitro-benzaldehyde and of benzaldehyde itself would show interesting facts regarding steric hindrance and the general effect of negative groups on the property of the compound. Consequently, one of the purposes of this research was to fill in the gaps in the list of derivatives of 2,4,6-trinitro-benzaldehyde reported in the literature.

Since 2,4,6-trinitro-benzaldehyde and its derivatives are explosive, they have been of considerable interest during the recent past. Benzaldehyde has been one of our important dye intermediates and, reasoning by analogy, it seemed possible that 2,4,6-trinitro-benzaldehyde might also find some use as a dye intermediate, provided some cheap process for its production could be developed. This seemed feasible, especially at the present time, since trinitro-toluene would furnish a cheap and plentiful source because of the large stocks of this material now on hand and the necessity for its disposal.

The method used for the preparation of 2,4,6-trinitro-benzaldehyde is essentially that described by F. Sachs and Kempf.³ They stated that the conversion of the methyl group to the aldehyde group may be accomplished by a condensation of the methyl derivative with a nitroso-dialkyl-aniline and subsequent hydrolysis of the condensation product.



They found that the above reactions proceeded easily in the preparation of 2,4,6-trinitro-benzaldehyde. They described the following method for its production.

¹ This report represents an abstract of a thesis presented by Emil Harold Balz in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August 1920.

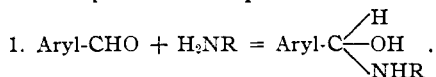
² *Ber.*, 35, 1236 (1902); 36, 960 (1903); 39, 2759 (1906); *Monatsh.*, 31, 192 (1910); *Ber.*, 35, 2704 (1902).

³ Sachs and Kempf, *ibid.*, 35, 2704 (1902); 36, 960 (1903); 35, 1224 (1902).

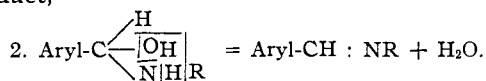
Seventy g. of 2,4,6-trinitro-toluene and 50 g. *p*-nitroso-dimethyl-aniline in an acetone solution were refluxed for one hour with 30 g. of anhydrous sodium carbonate. After the mixture cooled, the condensation product which precipitated was filtered, washed with several portions of 25% acetic acid and then boiled with water. The condensation product was then dissolved in conc. hydrochloric acid, and extracted in a separatory funnel with benzene.

This method¹ gave very poor results. The yield was only 15%. Our investigations led to numerous modifications of the details of operations, which will be described in the experimental part of the paper. This new method gave a yield amounting to 60% of that calculated.

The reactions investigated were of the general type known as condensations and take place in 2 steps.



The second step consists in the loss of one molecule of water by the addition product,



These condensation products are known as "Schiff's bases."² In some cases the 2 steps take place almost instantly while in others the intermediate product can be isolated. If a medium such as a dilute solution of alcohol and water is employed, the tendency is to form the addition product. On the other hand, in absolute alcohol, or in glacial acetic acid, the tendency is to yield the condensation product directly. Condensations were carried out between 2,4,6-trinitro-benzaldehyde and the following substituted amines: aniline, *o*-toluidine, β -naphthyl amine, α -naphthyl amine, *p*-toluidine, 1,3,4-xylydine, diphenylamine, *p*-aminoazobenzene, *p*-aminophenol, *o*-aminobenzoic acid, *m*-toluidine. In certain cases when the intermediate product is isolated and dried it undergoes change in either direction, *i. e.*, it either decomposes to form the original aldehyde and the amine, or it loses water to give the condensation product. The same type of reaction is possible with substituted aldehydes, or amines, or with both.

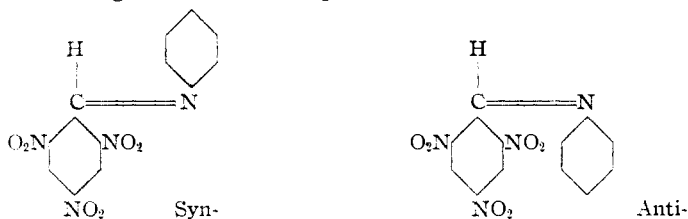
Steric hindrance also seems to exert considerable influence on the condensations. Spaeth³ could not condense the nitro-anilines with 2,4,6-trinitro-benzaldehyde. Attempts to condense them are under way. The nitro-anilines have been condensed with other nitro-benzaldehydes without great difficulty. It is interesting to note that sulfanilic acid fails to condense, while its sodium salt offers no difficulty. However, internal neutralization of the sulfanilic acid may account for this variation.

¹ *Monatsh.*, **31**, 192 (1910).

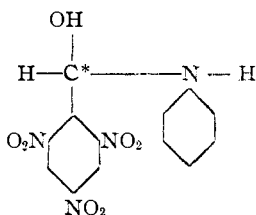
² *Ber.*, **35**, 984 (1902).

³ Spaeth, *Monatsh.*, **31**, 192 (1910)

Theoretically, 2 stereo-isomers are possible with carbon and nitrogen linked as they are in the case of these condensation products. For the anil, the following forms would be possible.



Furthermore, there should be 2 optically active isomers in the case of the addition products, since an asymmetric carbon atom is present.



Further experimental work on the identification of these optical isomers and the preparation of stereo-isomers of the double bond carbon-nitrogen type is being conducted in these laboratories. One molecule of 2,4,6-trinitro-benzaldehyde may be made to condense with 2 molecules of tertiary alkylated aromatic amines, substituted aromatic amines, or phenolic bodies to produce derivatives of triphenyl methane. Danckwortt¹ condensed *p*-nitro-benzaldehyde with phenolic bodies. Since these condensations present possibilities for the preparation of dye stuffs, they are now being investigated.

Experimental Part.

Preparation of 2,4,6-Trinitro-benzaldehyde.—The method used in the preparation of this compound was essentially that described by Sachs and Kempf and Everding.² When the details of their method were followed, very poor yields were obtained. Their method was modified so that finally 60% of the theoretical yield was obtained.

A solution of 70 g. of trinitro-toluene in 500 cc. of a mixture of equal parts of alcohol and acetone was warmed slightly to facilitate solution and placed in a jar equipped with an agitator. This solution was treated with 30 g. of anhydrous sodium carbonate and 50 g. of *p*-nitroso-dimethyl-aniline added gradually. The temperature was kept below 50°, while the mixture was stirred thoroughly and continuously. The addition of *p*-nitroso-dimethyl-aniline required an hour and after it had been stirred for another hour the mixture was allowed to stand for at least 24 hours. It was then a solid cake of the condensation product. By means of a large Büchner funnel, as much of the mother

¹ Danckwortt, *Ber.*, **42**, 4163 (1909).

² Sachs and Kempf, *ibid.*, **35**, 1236 (1902); Everding, **36**, 960 (1903).

liquor as possible was removed. The solid, placed in a jar, was macerated, thoroughly with 95% alcohol and the solution was filtered. This was repeated 3 times with the solid. Then it was washed with 25% acetic acid solution until all the sodium carbonate was removed. After the residual solid had been separated and dried, it was powdered until it was fine and gradually added to a jar containing 150 cc. of conc. hydrochloric acid. When the mixture was stirred thoroughly, the condensation product, nearly black in color, changed to a yellow substance almost immediately.

When the mixture had acquired a uniform yellow color, it was transferred to a large Erlenmeyer flask, the jar was rinsed with conc. hydrochloric acid and an equal volume of benzene was added to the mixture. After the flask had been shaken and heated in a pail of hot water, it was set aside for 5 minutes, when the upper layer of the warm benzene solution was decanted through a filter paper. More benzene was added to the residue and the extraction repeated until the aldehyde had been exhausted. At times considerable difficulty was encountered because of emulsification. The combined benzene extract was then distilled until about 250 cc. remained; this was filtered while still warm. As the solution cooled the aldehyde separated in crystals with benzene of crystallization which was lost as the solid dried. The pulverized aldehyde, purified by washing it with ether, was recrystallized from benzene. *M. p.* 119°.

The Product of 2,4,6-Trinitro-benzaldehyde and Aniline, $C_6H_2(NO_2)_3-CHO.C_6H_5NH_2$.—This compound was prepared by dissolving 2.41 g. of 2,4,6-trinitro-benzaldehyde in 30 cc. of boiling alcohol and adding to it 4 cc. of water, and finally 0.93 g. of aniline. This solution was shaken and cooled in an ice-bath. The product which separated as red plates was filtered rapidly with the aid of suction and washed with alcohol containing 8 cc. of water in 30 cc. of alcohol. After the product had been dried as completely as possible by application of suction, it was pressed between filter paper and finally placed in a desiccator over calcium chloride for a short time. *M. p.* 86°. On exposure to air, aniline was evolved, the product crumbled and lost its red color, to form trinitro-benzaldehyde. Aniline could be identified if some of the addition products was placed in a small test-tube and heated very gently. A rod moistened with conc. hydrochloric acid was held at the mouth of the test-tube; aniline hydrochloride was formed. The residual 2,4,6-trinitro-benzaldehyde was identified by its melting point. When the product was treated with glacial acetic acid a yellow compound resulted which was identified later as the condensation product. The property of decomposing into aniline and the aldehyde formed the basis of the analysis. A weighed quantity of the material was placed on a watch glass, allowed to stand at room temperature and the loss in weight determined.

Subs., 0.1909, 0.0573; loss, 0.0531, 0.0156.

Calc. for $C_6H_2(NO_2)_3CHO.(C_6H_5NH_2)$: $C_6H_5NH_2$, 27.84. Found: 27.81, 27.22.

In the preparation of the addition compounds listed below, the ratio of one mole of 2,4,6-trinitro-benzaldehyde to one mole of the substituted

Product.	M. P. ° C.	Color.	Solubility.	Analysis.	
				Calc. %.	Found %
2,4,6-Trinitro-benzaldehyde- o-toluidine.....	106	reddish	alcohol, chloroform,	$C_6H_4.CH_3NH_2$ = 30.74	30.54; 30.70
2,4,6-Trinitro-benzaldehyde- β-naphthylamine.....	...	reddish	alcohol, chloroform, N	$H_2O = 4.68$ = 14.58	4.60; 4.58 14.75; 14.76
2,4,6-Trinitro-benzaldehyde- α-naphthylamine.....	...	brown	alcohol, chloroform,	$H_2O = 4.68$	4.67; 4.51
2,4,6-Trinitro-benzaldehyde- diphenylamine.....	102	reddish	alcohol, acetic acid, N chloroform	= 13.65	13.75; 13.89

amine was used. These products were prepared by the same general method as that used for the aniline addition product described above. These products were converted into the condensation products when treated with glacial acetic acid or when heated, driving off the water. The table given above contains the essential results obtained.

2,4,6-Trinitrobenzal-aniline, $C_6H_2(NO_2)_3CH : NC_6H_5$.—This substance was made by dissolving 3 g. of 2,4,6-trinitro-benzaldehyde in 25 cc. of glacial acetic acid and adding to it 1.16 g. of aniline. The solution was heated for 5 minutes on a water-bath and cooled. A light yellow crystalline product separated. After 3 recrystallizations from glacial acetic acid, it melted at 220° , with decomposition. Yield, almost quantitative. This compound was almost insoluble in alcohol and in chloroform, but slightly soluble in hot glacial acetic acid.

Subs., 0.2000, 0.2000: 34.8 cc. N (34° , 733 mm.); 33.6 cc. N (28° , 733 mm.).

Calc. for $C_6H_2(NO_2)_3CH : N.C_6H_5 : N$, 17.72. Found: 17.83, 17.64.

Subs., 0.2000, 0.2000: CO_2 , 0.3621, 0.3653.

Calc. for $C_6H_2(NO_2)_3CH : NC_6H_5 : C$, 49.36. Found: 49.27, 49.80.

Subs., 0.2000, 0.2000: H_2O , 0.0460, 0.0481.

Calc. for $C_6H_2(NO_2)_3CH : NC_6H_5 : H$, 2.55. Found: 2.57, 2.64.

In the preparation of the condensation products listed below the same general method was used as described above for the preparation of the anil. Glacial acetic acid was used as solvent in all cases. The mixtures were heated on a water-bath for from 5 to 30 minutes to complete the reactions. The yields obtained were almost quantitative.

Product.	M. P. $^\circ$ C.	Color.	Crystallizing media.	Analysis for N.	
				Calculated. %.	Found. %.
2,4,6-Trinitro-benzal- <i>o</i> -toluidine.....	177	yellow	acetic acid chloroform	16.99	17.24; 17.10
2,4,6-Trinitro-benzal- β -naphthylamine.....	192	yellow	acetic acid	15.30	15.35; 15.30
2,4,6-Trinitro-benzal- α -naphthylamine.....	242	orange	acetic acid	15.30	15.17
2,4,6-Trinitro-benzal- <i>p</i> -toluidine.....	179.5	yellow	alcohol	16.99	17.09; 17.08
2,4,6-Trinitro-benzal-1,3,4-xylylidine.....	203	yellow	alcohol	16.28	16.24; 16.44
2,4,6-Trinitro-benzal- <i>p</i> -amino-azobenzene.....	189	brick red	acetic acid	20.00	19.95; 20.07
2,4,6-Trinitro-benzal- <i>p</i> -aminophenol.....	179	yellow	alcohol	17.11	16.95; 16.82
2,4,6-Trinitro-benzal- <i>o</i> -aminobenzoic acid.....	146	brick red	acetic acid	15.50	15.38; 15.60
2,4,6-Trinitro-benzal- <i>m</i> -toluidine.....	173.5	yellow	alcohol	16.99	17.05; 16.85

Summary.

1. The anil of 2,4,6-trinitro-benzaldehyde (m. p. 162°) prepared by Sachs and Everding¹ from an alcoholic solution was made and analyzed.

¹ Sachs and Everding, *Ber.*, **35**, 1236 (1902); *ibid.*, **36**, 960 (1903).

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.

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

BY ALEXANDER LOWY AND THOMAS B. DOWNEY.

Received September 1, 1920.

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).