

## 2. Preparation of *p*-Aminobenzaldehyde, and the Mechanism of the Reactions of Sodium Polysulphides with *p*-Nitrotoluene.

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An improved method of preparing *p*-aminobenzaldehyde in about 75% yield is based on a study of the reactions of *p*-nitrotoluene with sodium sulphide and polysulphides.

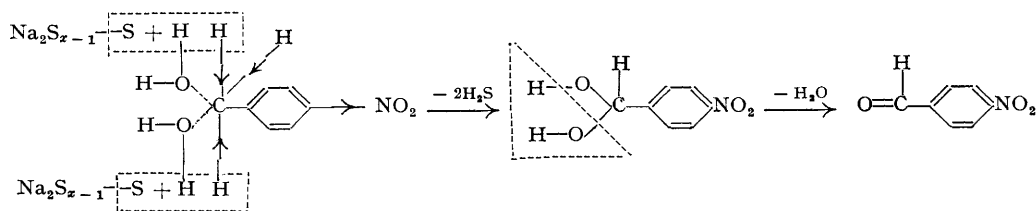
WHEN *p*-nitrotoluene reacts with a solution of sulphur in aqueous alcoholic sodium hydroxide (Geigy, D.R.-P. 86,874; Friedlander and Lenk, *Ber.*, 1912, **45**, 2083), *p*-aminobenzaldehyde and *p*-toluidine are formed. A study of the mechanism of this reaction has shown that the average yield of each product from 100 g. of *p*-nitrotoluene is 40 g. and that two simultaneous reactions are proceeding with approximately equal velocities, namely, (a) an oxidation-reduction, which produces *p*-aminobenzaldehyde, and (b) straight reduction to *p*-toluidine. The balance of the *p*-nitrotoluene (ca. 4%) is recovered unchanged, and no evidence of the intermediate formation of stilbene derivatives has been obtained.

In the preparation according to Geigy, sodium hydroxide (100 Parts) and sulphur (60 parts) were dissolved in boiling aqueous alcohol, and it was first ascertained experimentally that these quantities did react according to the equation usually given,  $6\text{NaOH} + 4\text{S} = 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$ . Since sodium thiosulphate does not react with *p*-nitrotoluene, it was concluded that sodium sulphide or a polysulphide used initially would not only be more efficient than Geigy's mixture, but would more readily provide data for the study of the reaction mechanism. Accordingly, a series of experiments was made in which sodium polysulphides,  $\text{Na}_2\text{S}_x$  ( $x = 1$  to  $5$ ), reacted under identical conditions with *p*-nitrotoluene in aqueous alcoholic sodium hydroxide. The yields of *p*-aminobenzaldehyde varied from ca. 40% with  $\text{Na}_2\text{S}$  to ca. 75% with  $\text{Na}_2\text{S}_4$ , and when the sulphur content was raised to  $\text{Na}_2\text{S}_5$ , by-products originated in further reactions of the primary amines formed. Of methyl, ethyl, and *n*-propyl alcohol, ethyl alcohol was the most efficient for the oxidation-reduction reaction (a); in the absence of an alcohol the yield of *p*-aminobenzaldehyde was only 31%. Free alkali (sodium hydroxide), however, appeared to be even more necessary than alcohol for reaction (a), since in its absence (or at small concentrations due to the equilibrium,  $\text{Na}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{NaSH}$ ) the yield of *p*-aminobenzaldehyde was less than 10%. Intermediate polysulphide formation during the reaction with sodium monosulphide was indicated by development of colour and confirmed, after completion of the reaction and removal of organic material by solvents, by analysis, the sulphur being allocated to  $\text{Na}_2\text{S}_2\text{O}_3$ , NaSH or  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_4$  (trace only), and polysulphide sulphur. The formation of polysulphide indicated its necessity for reaction (a), supporting evidence being obtained by the addition of pyrogallol to the various polysulphide mixtures, whereby removal of polysulphide prevented the formation of *p*-aminobenzaldehyde, the sole product being *p*-toluidine.

The above results clearly indicate that the oxidation of the methyl to the aldehyde group is brought about by the sodium polysulphide, probably on the lines developed by Robinson (J., 1941, 230), the loosely combined sulphur acting as oxidising agent as in the scheme on p. 5.

The hydrogen sulphide produced will be converted into sodium hydrosulphide by the alkali present and, together with the sodium sulphide also present, will then reduce the nitro- to the amino-group. When sodium sulphide is used alone, the sulphur necessary for polysulphide formation will be produced by its reaction with the nitro-group, and subsequent oxidation of the methyl group can then occur. When the amount of sodium sulphide is decreased to the minimum, as when the higher polysulphides are used, the amount of *p*-toluidine

formed becomes the minimum also. Too great an excess of sulphur, however, promotes thionation of the amines first formed (cf. Hodgson and France, J., 1933, 296).



An improved preparation (with R. R. Davies) of *p*-aminobenzaldehyde, by a modification of Geigy's directions, is described, together with one of *o*-chloro-*p*-aminobenzaldehyde from *o*-chloro-*p*-nitrotoluene.

#### EXPERIMENTAL.

*p*-Aminobenzaldehyde.—A mixture of *p*-nitrotoluene (10 g.), hydrated sodium sulphide (6.0 g.), sulphur (2.5 g.; ratio of 1 g.-mol. of *p*-nitrotoluene to 0.33 g.-mol. of sodium polysulphide), ethyl alcohol (60 c.c.), sodium hydroxide (4.5 g.), and water (120 c.c.), was refluxed for 90 minutes. The alcohol and *p*-toluidine (1.7 g.) were then removed by steam, and the non-volatile *p*-aminobenzaldehyde (6.6 g.; 74.6%, estimated as *p*-nitrophenylhydrazone) collected and preserved for subsequent use by conversion into the sulphate (cf. Geigy, *loc. cit.*). Alternatively, the steam distillation may be replaced by an ether extraction, and the procedure modified accordingly.

*Yields of p-aminobenzaldehyde from p-nitrotoluene (10 g.), with variations of sodium polysulphide only.*

Hydrated sodium sulphide, g.	Sulphur added, g.	Formula.	<i>p</i> -Aminobenzaldehyde, estimated as <i>p</i> -nitrophenylhydrazone.	
6	0.0	Na <sub>2</sub> S	3.0—3.5 g.	35—40%
6	0.8	Na <sub>2</sub> S <sub>2</sub>	4.0	45.3
6	1.6	Na <sub>2</sub> S <sub>3</sub>	4.75	53.4
6	2.4	Na <sub>2</sub> S <sub>4</sub>	6.35	72.0
6	3.2	Na <sub>2</sub> S <sub>5</sub>	Contaminated by by-products	

*Effect of variations of alcohol only in optimum preparation above.*

Alcohol.	Yield of <i>p</i> -aminobenzaldehyde,	
	g.	%.
Methyl .....	4.7	53.4
Ethyl .....	6.6	74.6
<i>n</i> -Propyl .....	5.28	59.2
None .....	2.74	31.8

*Preparation of p-Amino- and o-Chloro-p-amino-benzaldehyde by a Modification of Geigy's Process (with R. R. Davies).—*Boiling solutions of *p*-nitrotoluene (68.5 g.; 0.5 g.-mol.) and of *o*-chloro-*p*-nitrotoluene (86 g.; 0.5 g.-mol.) were each treated dropwise during 1 hour with a boiling solution of sulphur (41 g.) in 17% aqueous sodium hydroxide (500 g.); the mixtures were then boiled for a further 2 hours and cooled to 20°. The aldehydes were collected, washed with water (300 c.c.), and recrystallised from 50% acetic acid. The yields of pure products (by nitrite and hydroxylamine estimations) were: *p*-aminobenzaldehyde, 32 g. (52%); *o*-chloro-*p*-aminobenzaldehyde, 35.8 g. (46%).

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