

175. *The Preferential Reduction of Nitro-groups in Polynitro-Compounds. Part III. Picric Acid and 3 : 5-Dinitro-o-cresol. An Almost Quantitative Preparation of Picramic Acid.*

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Picric acid is reduced in aqueous methyl alcohol at 60° by sodium sulphide and sodium bicarbonate to give a 98% yield of picramic acid; the corresponding reduction in aqueous ethyl alcohol does not commence until *ca.* 80°, and then only with a 55% yield together with traces of sulphide dyes. Corresponding reductions of 3 : 5-dinitro-*o*-cresol are described.

In previous work (Hodgson and Birtwell, *J.*, 1944, 75) the rapid mono-reduction of 1 : 3-dinitronaphthalene in about 85% yield was effected by sodium sulphide in the presence of sodium bicarbonate with aqueous methanol as medium. Owing to the slight solubility of sodium carbonate in the medium the equilibrium, $\text{Na}_2\text{S} + \text{NaHCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{NaSH}$, was designed to produce the optimum concentration of sodium hydro-sulphide which was believed to be the main reducing agent. By-products were diminished to a minimum, and methanol was found to be superior to ethanol in every way. It seemed desirable, therefore, to extend the work to the mono-reduction of picric acid and of 3 : 5-dinitro-*o*-cresol.

In his review of previous work on the preparation of picramic acid Clayton (*J. Soc. Dyers and Col.*, 1930, 46, 365) concluded that optimum yields were obtained by the use of aqueous sodium picrate and prepared sodium hydrosulphide; in this respect, the methods described by Fierz-David (*Fundamental Processes of Dye Chemistry*, Churchill, 1921, p. 78) for the preparation of picramic acid are indirectly processes which involve sodium hydrosulphide, and the yields claimed of *ca.* 85% support the present authors' view that this compound is the prime reducing agent.

In the present investigation, alkaline solutions of picric acid in water and in aqueous methanol have been reduced with sodium hydrosulphide, sodium sulphide, sodium trisulphide and ammonium sulphide, either alone or in admixture, and an almost theoretical yield of picramic acid has been obtained in aqueous alcohol below 60° by the Hodgson and Birtwell procedure (*loc. cit.*). It is remarkable that when ethanol is used instead of methanol reduction is almost negligible at 60°, even when the reduction time is extended and twice the required amount of reducing agent employed, but at 80° a 55% yield was obtained in 30 minutes, accompanied, however, by traces of sulphide dyes which dyed cotton directly in light brown shades. This production of sulphide dyes, which is non-existent in methanol and incipient in ethanol, becomes appreciable in aqueous media, particularly when alkali is also present, and it can become the main reaction when either picric or picramic acid is heated under pressure with strongly alkaline sulphide solutions for 24 hours. It would appear, therefore, that one function of the special mixture is to maintain alkalinity of the medium below that required for sulphide dye formation.

One important feature which emerged from the 70% yield obtained in aqueous solution (Table III, Experiment 5) with sodium sulphide alone, was that the amount of reducing agent required to produce an excess of sulphide in the reaction mixture was less than the amount required by the equation, $4\text{RNO}_2 + 6\text{Na}_2\text{S} + 7\text{H}_2\text{O} = 4\text{RNH}_2 + 3\text{Na}_2\text{S}_2\text{O}_3 + 6\text{NaOH}$, viz., 1.3 mols. against 1.5 mols. per mol. of picric acid. This fact would appear to indicate that the by-products require less sodium sulphide for their production than does picramic acid. This is further demonstrated by the fact that picramic acid when submitted to the action of aqueous sodium sulphide at 55–60° in the presence of sodium hydroxide does not give any sulphide dye.

Both 3 : 5-dinitro-*o*-cresol and 2 : 4-dinitrophenol are less readily reduced by Hodgson and Birtwell's method (*loc. cit.*) than is picric acid, while in both cases there is concurrent formation of sulphide dyes favoured by increase of temperature and alkalinity. As expected (cf. Hodgson and Turner, *J.*, 1943, 318; Hodgson, *J. Soc. Dyers and Col.*, 1943, 59, 246) the monoreduction products are 5-nitro-3-amino-*o*-cresol and 4-nitro-2-aminophenol respectively.

In all the reductions investigated there appeared to be an initial induction period after all the sulphide mixture had been added which was the prelude to a rapid reaction, so that the first intermediate would appear to be only slowly formed. Further, while the addition of sodium bicarbonate to the sodium sulphide in alcohol greatly improved the reduction efficiency, this does not occur in water alone (see Table II, Experimental 6) since the water-soluble sodium carbonate formed (insoluble in the methanol medium) probably introduces the alkalinity necessary for by-product formation with 20% diminution in yield of picramic acid.

EXPERIMENTAL.

General Reduction Procedure.—Picric acid (10 g.) is dissolved in water or methanol at 55° and the appropriate amount of alkali (sodium hydroxide or ammonia), usually sufficient to neutralise the picric acid, then added. The reducing agent (see below) is stirred in gradually over 10–15 mins. at 55–60° until in excess (detected by ferrous sulphate paper). The mixture is cooled to 30° for the aqueous solutions and to 10° for those containing methanol to which water (150 c.c.) is also added, filtered, and the precipitate of sodium picramate washed with water or sodium chloride solution or saturated aqueous sodium picramate. The yield is determined by titration of the sodium picramate, suspended in hydrochloric acid (40 c.c., *d* 1.18) and water (1 l.) with a solution of sodium nitrite (35 g.) in water (1 l.).

The Sodium Hydrosulphide Solutions.—(A) Crystallised sodium sulphide (24 g., 0.1 g.-mol.), sodium bicarbonate (8.4 g.) dissolved in water (40 c.c.) at 40–50° containing sodium hydrosulphide (5.6 g., 0.1 g.-mol.) (Hodgson and Birtwell, *loc. cit.*). (B) Sodium hydroxide (4 g., 0.1 g.-mol.) dissolved in water (40 c.c.) and treated at 0° with hydrogen sulphide gas until the increase in weight corresponds with the complete formation of sodium hydrosulphide; vol. of this solution, *ca.* 50 c.c. (Clayton, *loc. cit.*). (C) Sodium carbonate (10 g.) added to (B), but it is impossible to effect complete dissolution without loss of hydrogen sulphide. (D) Crystallised sodium sulphide (27.6 g.) in water (21.8 g.) treated at 0° with hydrochloric acid (10.5 c.c., *d* 1.16); loss of hydrogen sulphide is diminished by using a tall cylinder, and running in the acid through a thistle tube to the bottom of the solution (Lapworth, *J.*, 1921, 119, 367).

TABLE I.

Reductions of picric acid (10 g.) in aqueous methanols (100 c.c.) containing sodium hydroxide (1.75 g.).

Expt.	Reducing agent.	Reaction mixture variation.	G.-mol. reducing agent/ g.-mol. picric acid.	Yield of picramic acid.	
				G.	%.
(1)	A	None	2.3	8.37	96
(2)	C	None	2.3	7.94	91
(3)	B	None	2.3	7.50	86
(4)	A	200 c.c. MeOH	1.5	6.7	73
(5)	A	0.9 g. NaOH	2.3	4.35	50
(6)	Na ₂ S, 9H ₂ O (12 g.) in water (50 c.c.)	None	2.3	Unsatisfactory	
(7)	B (with 2 g. Na ₂ CO ₃)	None	2.3	7.67	88

In the mother liquors from experiment (1) about 2% of dissolved picramic acid was estimated by titration and also by isolation, making the total yield 98%; no sulphide dyes were detected.

TABLE II.

Reductions of picric acid (10 g.) by sodium hydrosulphide in water containing sodium hydroxide or ammonia (d 0.88).
Reducing agent added in one batch.

Expt.	Reducing agent.	NaOH, g.	NH ₃ , c.c.	H ₂ O, c.c.	G.-mol. reducing agent/ g.-mol. picric acid.	Yield of picramic acid.	
						G.	%.
(1)	B	—	3	60	2.3	7.24	83
(2)	B	2	—	250	2.3	6.98	80
(3)	B	—	1	100	2.3	6.0	70
(4)	D	—	1	60	<2.3	5.65	65
(5)	D	2	—	250	<2.3	5.38	62
(6)	A	1.75	—	100	2.2	5.18	58
(7)	B (with 2 g. Na ₂ CO ₃)	1.75	—	100	2.3	6.98	80

TABLE III.

Reductions of picric acid (10 g.) by crystallised sodium sulphide in water (60 c.c.)
containing ammonia (1 c.c., d 0.88).

Expt.	Reducing agent, g. Na ₂ S.9H ₂ O.	Vol.,* c.c.	G.-mol. reducing agent/ g.-mol. picric acid.	Yield of picramic acid.	
				G.	%.
(1)	5.4	12	0.52	1.31	15
(2)	6.3	14	0.60	1.64	19
(3)	9.0	20	0.87	2.66	30
(4)	11.25	25	1.08	5.0	55
(5)	13.5	30	1.29	6.0	70
(6)	8.4 g. in 25 c.c. B	40	—	6.8	78

* Solution of sodium sulphide containing 45 g. cryst. sodium sulphide per 100 c.c.

TABLE IV.

Reductions of picric acid (10 g.) by crystallised sodium sulphide (13.5 g.; 1.3 g.-mols. reducing agent/g.-mol. picric acid) in water (90 c.c.) with additions to reduce alkalinity.

Expt.	Additions to reaction mixture.	Yield of picramic acid.	
		G.	%.
(1)	Ammonia (1 c.c., d 0.88). Then 1 g. NaHSO ₄ , 1 g. NaHSO ₃ or 1 g. Al acetate, after adding two-thirds of reducing agent.	6.0	70
(2)	Ammonia (1 c.c., d 0.88), NH ₄ Cl, or cryst. MgSO ₄ (5 g.).	5.27	57

Miscellaneous Reductions.—A solution of sodium trisulphide made up of crystallised sodium sulphide (12 g.) and sulphur (3 g.) in water (30 c.c.) when added to one of picric acid (10 g.) in water (250 c.c.) containing NaOH (2 g.) and maintained at 55–60° gave a 70% yield of picramic acid; a similar reduction of picric acid (10 g.) in water (60 c.c.) and ammonia (1 c.c., d 0.88) with a mixture of crystallised sodium sulphide (7.2 g.) in water (18 c.c.) and conc. ammonium sulphide (10 c.c.) gave only a 49% yield.

Examination of filtrate after removal of picramic acid by filtration at 30°, from an aqueous reduction with sodium sulphide. Sodium sulphide solution (150 c.c. containing 67.5 g. Na₂S.9H₂O) was stirred gradually into a solution of picric acid (50 g.) in water (300 c.c.) containing ammonia (5 c.c., d 0.88) at 55°. After the reaction was complete, the mixture was cooled to 30° and filtered, the filtrate just acidified with concentrated hydrochloric acid at 50° and heated to 100° (H₂S and SO₂ evolved) to coagulate the precipitate. The filtrate from the mixture, cooled to 15°, was evaporated to dryness and the residue extracted successively with benzene (100 c.c.), ethanol (200 c.c.) and hot water. The benzene extract gave picramic acid (0.7 g.), the alcohol extract a sulphur dye (11.12 g.), the water extract sodium chloride, and the final residue was a mixture of sulphur and tar (0.8 g.). The precipitate above contained picramic acid (1.8 g.) and sulphur dye (3.8 g.). The total yield of dissolved picramic acid was 5.6%.

*Reduction of 3 : 5-Dinitro-*o*-cresol.*—(A) *In methanol.* 3 : 5-Dinitro-*o*-cresol (10 g.), dissolved in methanol (200 c.c.) at 60° with addition of sodium hydroxide (2 g.) to give a neutral solution, was treated with mixture A (in amount, 2.4 g.-mol. NaSH/g.-mol. dinitrocresol). Reduction was negligible at 60° but became appreciable at 70°, and the mixture was maintained just above this temperature for 2 hrs., cooled to 10°, filtered, the alcohol removed, filtered again, and the filtrate steam distilled when about 15% of the unchanged 3 : 5-dinitro-*o*-cresol was recovered. The above residues of crude sodium derivative were combined, treated with HCl in excess, steam distilled to remove unchanged dinitrocresol and the insoluble residues mixed with calcium carbonate extracted repeatedly with boiling toluene. The pure 5-nitro-3-amino-*o*-cresol (7 g., 80% yield) was crystallised from toluene or boiling water, m. p. 176° (Cazeneuve, *Bull. Soc. chim.*, 1897, **17**, 206 gives m. p. 165°); diazotisation and Sandmeyer treatment gave 3-chloro-6-nitro-*o*-cresol which crystallised from 80% acetic acid in flesh coloured plates, m. p. 122° (Kehrmann, *Ber.*, 1915, **48**, 2024, gives m. p. 122°) (Found : N, 7.7. Calc. for C₇H₆O₃N₂: N, 7.5%); the intermediate 5-nitro-2-oxo-3-diazotoluene crystallised from hot water in light yellow crystals, m. p. 123° (decomp.) (Found : N, 23.6; C₇H₅O₃N₃ requires N, 23.4%); in this reduction no sulphur dye was detected.

(B) *In water.* 3 : 5-Dinitro-*o*-cresol (15 g.), dissolved in water (100 c.c.) containing sodium hydroxide (3 g.), was treated at 80° with mixture B (96 c.c., 2.3 g.-mols./g.-mol. dinitrocresol) and maintained at 85° for 2 hrs. To the mixture cooled to 0°, hydrochloric acid (20 c.c., d 1.18) was slowly added until a brown precipitate was formed (further addition precipitated a violet compound); the precipitate was separated, washed with water, mixed with excess calcium carbonate, extracted with toluene as in (A) above giving 5-nitro-3-amino-*o*-cresol (10.5 g., 80%). The residue (6 g.), insoluble in toluene, contained sulphur dyes which dyed cotton directly to intense black shades.

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