[Contribution from the Research Laboratories of the Aerojet-General Corporation]

THE REDUCTION OF HALO NITRO COMPOUNDS WITH ZINC[1]

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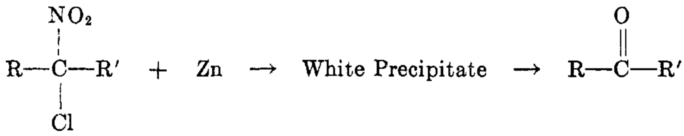
Zinc metal reacts with aliphatic nitro compounds to form hydroxylamines (1, 2). No information is available regarding the reaction of zinc metal and halo nitro compounds. It was found that halo nitro compounds, for example, bromonitrocyclohexane, react very rapidly with zinc metal with the formation of a white precipitate of unknown structure. The white precipitate was found to be insoluble in water and in all common organic solvents, thereby making purification impossible. It was found that the white precipitate contained zinc. It was also found to react with dilute mineral acids with the formation of a compound containing a keto group by the simultaneous displacement of the halogen and nitro groups. For example, when methyl 4-chloro-4-nitropentanoate was treated with zinc, the white precipitate formed was converted into the methyl 4-ketopentanoate after treatment with dilute hydrochloric acid. 1-Bromo-1-nitrocyclohexane yielded cyclohexanone by the same reaction sequence:



$$\mathrm{R{-}\overset{NO_2}{\underset{Cl}{C}}{-}R'} + \mathrm{Zn} \rightarrow \text{White Precipitate} \rightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}R'}$$

The analysis of the white precipitate is inconclusive and various values for Zn and halogen were obtained. However, the precipitate still contained nitrogen and the ratio of reactants to Zn for the formation of the precipitate is 1:2. A Zn-complex with the oxime of the ketone is probable and would explain the case of conversion of the metal complex into the corresponding ketone. The ketones were identified as crystalline semicarbazones. The reaction appears to be general with varying yields.

Methyl 4-nitropentanoate and its homologs were prepared by the Michael addition of methyl acrylate to chloronitroethane in a manner similar to that described for the addition of acrylonitrile to chloronitroethane (3).

EXPERIMENTAL[2]

1. *Methyl 4-nitro-4-chloropentanoate and zinc.* (*a*). A three-necked flask provided with a thermometer, stirrer, and reflux condenser was charged with 19.6 g. of methyl 4-nitro-4-chloropentanoate, 100 ml. of methanol, 10.2 g. of zinc dust, and 5 g. of ammonium chloride The mixture was stirred vigorously. The temperature rose to 48° and a white precipitate was formed. The mixture was kept stirring for 10 minutes at 60° until all zinc metal was consumed. The mixture then was cooled, and the precipitate was collected and washed with methanol and ether. The yield was 18 g. of white crystals carrying a high electric charge, which were analyzed without further purification.

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[2] The analyses were conducted by Dr. Adelbert Elek's Micro Analytical Laboratories, 4763 W. Adams Blvd., Los Angeles, California.

Found: C, 32.48; H, 3.82; N, 6.11; Zn, 22.81.

(*b*) The dry white precipitate (10 g.) was suspended in 100 ml. of water, and hydrochloric acid was added. The precipitate dissolved quickly to form a blue solution, from which an oil suddenly separated. The oil was extracted and distilled in a bulb tube at 80° air-bath temperature and 5 mm. pressure.

Anal. Calc'd for $C_6H_{10}O_3$: C, 55.37; H, 7.74; OCH_3, 24.40.
Found: C, 55.51; H, 7.79; OCH_3, 23.29.

(*c*). Two g. of the oil obtained under (*b*) was treated with a filtered solution of 3 g. of semicarbazide hydrochloride and 3 g. of sodium acetate in 70 ml. of methanol. After evaporation of the solvent a crystalline compound was obtained, which, upon recrystallization from water, had a m.p. 148 to 149°. The mixture m.p. with the semicarbazone of methyl 4-ketopentanoate was not depressed.

Anal. Calc'd for $C_7H_{13}N_3O_3$: C, 44.91; H, 7.00; N, 22.45.
Found: C, 45.31; H, 7.09; N, 21.78.

2. *1-Bromo-1-nitrocyclohexane and zinc.* (*a*). A three-necked flask provided with a stirrer, thermometer, and reflux condenser was charged with 20.8 g. of 1-bromo-1-nitrocyclohexane, 10.2 g. of zinc dust, 10 g. of ammonium chloride, and 250 ml. of methanol. The temperature rose to 45° and a white precipitate was formed instantly. After 10 minutes refluxing, all zinc metal was consumed. The mixture was cooled, and the precipitate was collected and dried in a desiccator. The yield was 18 g.

Found: C, 30.27; H, 5.17; N, 9.39; Br, 22.04.

(*b*). The precipitate (10 g.) was suspended in 100 ml. of water, and hydrochloric acid was added. The precipitate dissolved and a cyclohexanone odor was noticeable. The water phase was extracted with ether, and the ether was removed. The yield was 5.2 g. This oil was converted into the semicarbazone by treating it with clear solution of 5 g. of semicarbazide hydrochloride and 5 g. of sodium acetate in 100 ml. of methanol. The semicarbazone formed had m.p. 166 to 167° after recrystallization from water. The mixture m.p. with cyclohexanone semicarbazone was not depressed.

3. *Methyl 4-chloro-4-nitropentanoate.* (*a*). A three-necked flask provided with a stirrer, dropping-funnel, and thermometer was charged with 28 g. of potassium hydroxide and 200 ml. of water. Then 55 g. of 1-chloro-1-nitroethane was added dropwise at 0°. This was followed by 107 g. of methyl acrylate and the temperature increased to 43°. The mixture was stirred for 3 hours at 45–50° and allowed to stand overnight. The ether extract of the mixture was washed with water and dried over sodium sulfate. The residue of methyl 4-chloro-4-nitropentanoate distilled at 5 mm. and 95°, yield 53.5 g., n_D^{23} 1.4542.

Anal. Calc'd for $C_6H_{10}ClNO_4$: N, 7.64. Found: N, 7.48.

SUMMARY

1. The reduction of halo nitro compounds with zinc yields a white precipitate which, upon treatment with mineral acids, yields ketones.

2. The Michael addition of halo nitroparaffins with acrylate esters is described.

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