[CONTRIBUTION NO. 42 FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reduction of 2,4,6-Trinitro-*m*-xylene

BY STEPHEN S. VORIS AND PAUL E. SPOERRI

In the course of an investigation on cocoa red it was found that the methods of preparation of 2,4,6-triamino-*m*-xylene described in the literature are lengthy and give poor yields. A systematic investigation of the reduction of 2,4,6-trinitro-*m*-xylene therefore seemed justified, particularly since this reaction permits a study of a stepwise reduction complicated by the steric hindrance of two methyl groups.

In 1860 Bussenius and Eisentuch[1] reduced a trinitrated petroleum fraction with ammonium sulfide in alcoholic solution and obtained a diamine melting at 215° and a monoamine melting at 155°. Subsequently F. Beilstein[2] identified these products as 2-nitro-4,6-diamino-*m*-xylene and 2,4-dinitro-6-amino-*m*-xylene.

E. Luhmann[3] reduced 2,4,6-trinitro-*m*-xylene with tin and hydrochloric acid to form 2,4,6-triamino-*m*-xylene dihydrochloride but he did not obtain the free base. Later E. Grevnick[4] carried out the reduction with stannous chloride and hydrochloric acid and decomposed the triamine hydrochloride with sodium bicarbonate to obtain the free base which was purified by sublimation. The white crystalline 2,4,6-triamino-*m*-xylene sublimed between 140–150°.

A study of the recorded methods confirms in substance the reported findings. It was found, however, that the reduction with ammonium sulfide could be improved materially when carried out in dioxane solution instead of alcohol. A 70% yield of 2,2-dinitro-6-amino-*m*-xylene was obtained. No diamine was formed when the amount of ammonium sulfide calculated to reduce one nitro group was used.

In addition to the methods recorded in the literature the following reduction procedures were studied.

1. Alcoholic Stannous Chloride.—A 6% yield of 2,4-dinitro-2-amino-*m*-xylene was obtained without other reduction products.

2. Titanium Trichloride.—With amounts calculated to reduce one nitro group 3% of 2,4-dinitro-6-amino-*m*-xylene and 51% of 2-nitro-4,6-diamino-*m*-xylene were obtained.

(1) Bussenius and Eisentuch, *Ann.*, **113**, 65 (1860).
(2) F. Beilstein, *ibid.*, **133**, 45 (1864).
(3) E. Luhmann, *ibid.*, **144**, 277 (1867).
(4) E. Grevnick, *Ber.*, **17**, 2424 (1884).

3. Catalytic Hydrogenation.[5]—Reduction in a dioxane solution using Raney nickel catalyst with platinic chloride promoter at 70 to 90° and the subsequent separation as the hydrochloride gave a 99% yield of 2,4,6-triamino-*m*-xylene dihydrochloride of high purity.

The effect of the methyl groups on the 2-nitro group is quite pronounced. Titanium trichloride did not reduce the 2-nitro group and in the catalytic hydrogenation there was a distinct drop in the rate of hydrogenation after the introduction of $6H_2$.

Experimental

Preparation of the Starting Material.—2,4,6-Trinitro-*m*-xylene was prepared by a three-stage nitration[6] of *m*-xylene, b. p. 138–139°, obtained from the Eastman Kodak Company. The trinitro-*m*-xylene was purified by recrystallization from dioxane yielding white crystals, m. p. 181°.

Reduction with Ammonium Sulfide.—Ten grams of 2,4,6-trinitro-*m*-xylene was dissolved in 50 cc. of dioxane; to this was added 6 cc. of concd. ammonium hydroxide, the solution cooled and hydrogen sulfide introduced. After the reaction mixture was saturated with hydrogen sulfide, it was refluxed for one-half hour on a water-bath. The flask was then cooled again and the process repeated until there was a total gain in weight of 4.2 g. The reaction mixture was diluted with water, the precipitate filtered off, dried, extracted with alcohol, and the solvent evaporated. A yield of 6.2 g. of crude 2,6-dinitro-4-amino-*m*-xylene was obtained, 71%. The 2,6-dinitro-4-amino-*m*-xylene upon recrystallization from alcohol gave bright yellow needles, m. p. 191°.

2,6-Dinitro-4-amino-*m*-xylene is soluble in alcohol, ether and dioxane but insoluble in water or dilute acid. It is slightly soluble in concd. hydrochloric acid and 1:5 sulfuric acid but separates on dilution. The hydrochloride was prepared by dissolving the amine in dioxane and passing in dry hydrogen chloride. The hydrochloride formed white, leafy crystals which decomposed with water. *Anal.* Calcd.: Cl, 14.7. Found: Cl (Mohr method), 15.0, (Parr method) 14.5.

2,6-Dinitro-4-amino-*m*-xylene was diazotized and coupled with α-naphthol giving a deep brick red dye. The acetyl derivative consists of white crystals, m. p. 175°.

Reduction with Titanous Chloride.—Five grams of 2,4,6-trinitro-*m*-xylene was suspended in 100 cc. of acetone and the air displaced with carbon dioxide; 96 g. of a 20% solution of titanous chloride containing 17 cc. of concd. hydrochloric acid was added slowly. The reaction was vigorously exothermic. When the reaction ceased, 100 cc. of water was added, the acetone distilled off in an atmos-

(5) E. Lieber and G. B. L. Smith, THIS JOURNAL, **58**, 1417 (1936).
(6) J. Marshal, *Ind. Eng. Chem.*, **12**, 249 (1920).

phere of carbon dioxide, and the solution filtered. It was then extracted several times with ether and the ethereal extracts evaporated: yield, 0.5 g. of 2,4-dinitro-6-amino-*m*-xylene; m. p. 191°.

The water solution remaining after the ether extraction was neutralized and a slight excess of sodium hydroxide added, the brick-red precipitate formed was filtered off, washed and recrystallized from hot water: yield, 2.1 g. of brick red, needle-shaped crystals of 2-nitro-4,6-diamino-*m*-xylene; m. p. 213°. The diamine is soluble in alcohol, ether, dioxane, dilute acid and hot water but insoluble in cold water. *Anal.* Calcd.: N, 19.0. Found: N, 18.7.

The white crystalline dihydrochloride was prepared in the same way as the monoamine hydrochloride. *Anal.* Calcd.: Cl, 27.9. Found: Cl (Parr method), 27.6.

One and three-tenths grams of unreduced 2,4,6-trinitro-*m*-xylene was recovered from the filter residue.

Reduction by Catalytic Hydrogenation.—Six and three-hundredths grams of 2,4,6-trinitro-*m*-xylene was dissolved in 120 cc. of dioxane and 13.5 g. of Raney nickel with 0.125 g. of platinic chloride promoter. Hydrogen was introduced at 1 atm. absolute pressure. The hydrogenation proceeded very slowly at room temperature but at 60–70° went smoothly. The addition of $6H_2$ required forty-five minutes at which point the reaction became much slower, requiring two hundred and twenty minutes for the absorption of the next $3H_2$. The solution at this point was faint yellow in color, but darkened somewhat on filtering off the nickel and became very dark brown on standing overnight.

The reduction was repeated at 90° and 3 atm. absolute pressure. At this temperature the reaction was slightly exothermic and required only forty-five minutes for the addition of $9H_2$. After filtering off the nickel the dioxane solution was cooled, and saturated with dry hydrogen chloride. The violet precipitate of 2,4,6-triamino-*m*-xylene hydrochloride was filtered off, washed with dioxane, then dry ether and dried; yield, 99%. *Anal.* Calcd.: N, 18.8. Found: N, 18.3; Cl, 32.0 (indicating 2HCl).

The authors wish to acknowledge the assistance given by Mr. Julian Reasenberg in carrying out the hydrogenation experiment.

Summary

2,4,6-Trinitro-*m*-xylene was reduced with (1) ammonium sulfide giving better yields of 2,6-dinitro-4-amino-*m*-xylene than previously reported; (2) titanous chloride yielding the monoamino and diamino compounds; (3) hydrogen and Raney nickel giving 99% of the theoretical yield of 2,4,6-triamino-*m*-xylene.

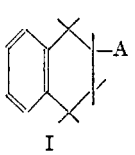
BROOKLYN, N. Y. RECEIVED FEBRUARY 25, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

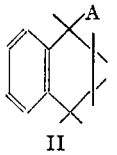
Substituted Tetrahydronaphthalenes. I. 1-Keto- and 1-Hydroxy-2-(*p*-dialkylaminobenzyl)-tetrahydronaphthalenes

BY R. L. SHRINER AND W. O. TEETERS

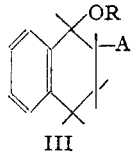
Tetrahydronaphthalene derivatives containing an hydroxyl and an amino group in the alicyclic portion represent a series of compounds containing one ring system and some of the functional groups present in morphine. A considerable number of basic tetrahydronaphthalene derivatives have been synthesized[1] and their pharmacological properties studied. About six different types of molecules, represented by formulas I–VI, have been prepared.



I

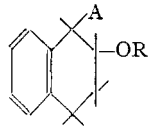


II

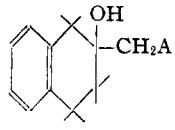


III

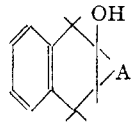
(1) (a) Bamberger and Müller, *Ber.*, **21B**, 1112 (1888); (b) Bamberger and Filehne, *ibid.*, **22B**, 777 (1889); (c) von Braun, Braunsdorf and Kirschbaum, *ibid.*, **55B**, 3648 (1922); (d) von Braun, Gruber and Kirschbaum, *ibid.*, **55B**, 3664 (1922); (e) von Braun and Weissbach, *ibid.*, **63B**, 3052 (1930); (f) Straus and Rohrbacher, *ibid.*, **54B**, 40 (1921); (g) Mosettig and Burger, THIS JOURNAL, **53**, 2295 (1931); (h) Gonzalez and Compoy, *Anales soc. espan. fis. quim.*, **20**, 534 (1922).



IV



V



VI

Where A is amino, alkylamino, dialkylamino, piperidino; R is hydrogen, alkyl.

The pharmacological data reported are quite interesting since the compounds may exhibit local anesthetic, mydriatic, hypnotic or pressor action. However, none of them had the analgesic action of morphine. In the present work tetrahydronaphthalene derivatives corresponding to formulas VII and VIII were prepared. The condensation of α-tetralone with *p*-dimethyl-, *p*-diethyl- and *p*-di-*n*-propylaminobenzaldehyde produced the *p*-dialkylaminobenzal derivatives (VII) which were reduced catalytically with hydrogen and platinum to the corresponding benzyl compounds (VIII). The reduction stopped at this stage even though the benzyl ketones (VIII)