chromatogram was developed with 100 ml. of 50:1 petroleum ether (65–110°)–ethanol. The column was extruded and streaked with the reagents as shown in Table I, using capillary-tipped pipets which were drawn from about 10-cm. lengths of thick-walled 8-mm. (o.d.) Pyrex tubing. The tips were ground with emery until an orifice of approximately 0.1 mm. was formed, and the pipets were operated with 1-ml. medicine dropper bulbs.

Syringaldehyde occupied a well-defined zone between 39 and 65 mm. from the top of the chromatographic column, and vanillin an equally well-defined zone at 97 to 124 mm. Each zone was eluted with 50 ml. of acetone, the solvent was evaporated under a current of air on a steam-bath, and the recovered crystalline substances were air dried and weighed. Vanillin melting at 76–79° and syringaldehyde melting at 108–110.5° were recovered in yields of 99 and 98%, respectively. Single recrystallizations from water of these recovered aldehydes yielded vanillin melting at 81–82° and syringaldehyde melting at 111–112°, which were identical with those of the original materials.

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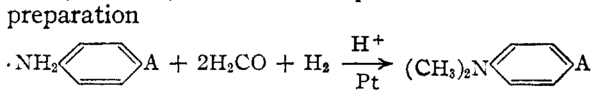
Reductive Methylation of Amines

BY D. E. PEARSON AND J. D. BRUTON

Reductive methylation is seldom used as a means of preparation of tertiary aromatic amines because of facile nuclear condensation.[1] However, it has been possible in this Laboratory to accomplish the following reductive methylations of which the first two (I and II) are much the preferred methods of preparation



$A = COCH_3$, yield 70% I
$A = COOH$, yield 87% II
$A = H$, yield 74% III (as picrate)

Also, the reductive methylation of glycine yielded 79% N,N-dimethylglycine.

The essential feature of the first two preparations was the avoidance of an excess of formaldehyde. The essential feature of the third preparation was the use of a slowly-generating source of formaldehyde, trioxane, as well as a limited concentration of the same.

It is interesting to note that previous attempts to prepare *p*-dimethylaminoacetophenone (I) have been quite frustrating,[2] the best yield reported being 3%.[3]

Experimental[4]

***p*-Dimethylaminoacetophenone (I).**—*p*-Aminoacetophenone (0.1 mole, Eastman Kodak Co. White Label) was dissolved in a mixture of 80 ml. of 95% ethyl alcohol and 5 ml. of concd. hydrochloric acid and cooled to 5°. In another flask, 15 ml. of formalin (40%, W. H. Curtin Co., 0.2 mole) was similarly cooled. The contents of both flasks were mixed in a Burgess–Parr reduction container with 0.15 g. of pre-reduced Adams catalyst and reduced at 45 lb. total hydrogen pressure in the usual manner. About 88 to 95% of the theoretical hydrogen was absorbed in 45 minutes; the ketone group was apparently not subject to hydrogenation under these conditions. The solution was then filtered, neutralized to color change,[5] and diluted with water to incipient cloudiness. After refrigeration, I was removed by filtration. Further dilution of the filtrate yielded more I. After air-drying, I was recrystallized from petroleum ether (b.p. 69–70°); 11.5 g., 70%; m.p. 102–104°; reported,[3] m.p. 105.5°; mixed m.p. with *p*-aminoacetophenone, 67–73°. The following variations lowered the yield: (1) delay in reducing after mixing all components,[6] (2) increase in molar ratio of formalin, (3) decrease in acid concentration, (4) re-use of Adams catalyst.

***p*-Dimethylaminobenzoic Acid (II).**—*p*-Aminobenzoic acid (recrystallized, 0.1 mole) was reductively methylated exactly as above. Despite the fact that the mixture was heterogeneous, the reduction went smoothly to completion in 1 hour. The solution was then made slightly basic with ammonium hydroxide, filtered to remove the catalyst, concentrated to one-third its volume and acidified while still hot. Refrigeration, filtration and air-drying yielded II, 14.4 g., 87%; m.p. 236.5–237.5°; reported, m.p. 233°. The above preparation is mentioned in the patent literature.[7]

Dimethylaniline (III).—Though of no preparative value in this specific case, reductive methylation of aniline revealed no evidence of nuclear condensation products under the following conditions. Aniline hydrochloride (Baker and Adamson, 13 g., 0.1 mole) was dissolved in a solution of water (50 ml.), sulfuric acid (50 ml.) and alcohol (50 ml.). The solution was cooled to 0° and poured into the container of a Burgess–Parr hydrogenation apparatus over pre-reduced Adams catalyst (0.15 g.). Trioxane (6.5 g., 0.072 mole, Eastman Kodak Co. Practical) was added and reduction at 45 lb. total pressure of hydrogen was begun. After an initial lag until the solution had warmed, the reduction proceeded at a slow rate and was discontinued after 7 hours when 88% of the theoretical amount of hydrogen had been absorbed. The solution was then filtered, made alkaline and extracted with ether. The ether was removed by distillation and the residue dissolved in 100 ml. of methyl alcohol containing 0.1 mole of picric acid. Refrigeration and filtration yielded dimethylaniline picrate (26.1 g., 74%; m.p. 156–158°). This included crops from the mother liquor.

N,N-Dimethylglycine.—Glycine (7.5 g., 0.1 mole) was dissolved in 40 ml. of water, 5 ml. of concentrated hydrochloric acid and 20 ml. of formalin (40%, 0.26 mole) and reduced as described. The solution was filtered to remove the catalyst, treated with 30 ml. of concd. hydrochloric acid and concentrated to a thick sirup. On cooling, the resultant crystals were filtered and recrystallized from glacial acetic acid. Yield of N,N-dimethylglycine hydrochloride was 22.2 g., 79%; m.p. 185–187°; reported, m.p. 183–184°. A similar preparation is reported but no yield given.[8]

(1) W. S. Emerson in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 194.

(2) C. D. Hurd and C. N. Webb, THIS JOURNAL, **49**, 551 (1927); J. Klingel, *Ber.*, **18**, 2694 (1885).

(3) H. Staudinger and N. Kon, *Ann.*, **384**, 111 (1911).

(4) All melting points were taken with partial immersion thermometer, A. S. T. M. specification.

(5) The mixture serves as its own indicator: red in acid; yellow in basic solution.

(6) F. C. Wagner, THIS JOURNAL, **55**, 724 (1933).

(7) A. Skita and W. Stuhmer, German Patent 716,668; *C. A.*, **38**, 2345 (1945).

(8) R. E. Bowman and H. H. Stroud, *J. Chem. Soc.*, 1342 (1950).

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Preparation of α,α-Diphenylpropionitrile[1]

BY P. L. PICKARD AND E. F. ENGLES[2]

While the literature contains several references[3,4,5,6,7] to the preparation of α,α-diphenylpropionic acid, no method suitable for the synthesis of large quantities of the corresponding nitrile are given. The ease of methylation of phenylace-

(1) This work was done with the support of the Office of Naval Research.

(2) Presented as a portion of a dissertation in partial satisfaction of the requirements for the Ph.D. in chemistry at the University of Oklahoma.

(3) C. Bottinger, *Ber.*, **14**, 1595 (1881).

(4) H. Meerwein, *Ann.*, **396**, 260 (1913).

(5) W. Thorner and Th. Zincke, *Ber.*, **11**, 1993 (1878).

(6) H. Staudinger and P. Meyer, *Helv. Chim. Acta*, **5**, 670 (1922).

(7) D. E. Bateman and C. S. Marvel, THIS JOURNAL, **49**, 2917 (1927).