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.

INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN
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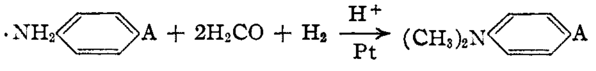
Reductive Methylation of Amines

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]

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[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).

DEPARTMENT OF CHEMISTRY
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RECEIVED SEPTEMBER 5, 1950

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-

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[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).

tonitrile using sodamide[8] suggested a similar preparation from diphenylacetonitrile. The proposed alkylation was carried out with methyl iodide, using sodium hydride as the alkylating catalyst. The yield on several preparations varied between 80–90%. The product was identified by its physical constants, by analysis, and by hydrolysis to the corresponding amide and acid.

Experimental.—To 32.5 g. (1.35 moles) of sodium hydride and 175 ml. of anhydrous diethyl ether in a three-necked round-bottom flask was added 262 g. (1.35 moles) of diphenylacetonitrile dissolved in 375 ml. of dry benzene and 100 ml. of diethyl ether. Addition was dropwise over a period of 3 hours. The mixture was refluxed for 30 hours. To the cooled reaction mixture was added 192 g. (1.35 moles) of methyl iodide in 100 ml. of benzene dropwise over a period of 6 hours. Sodium iodide was precipitated immediately. After cooling, the mixture was washed with cold 10% acetic acid to destroy any unreacted sodium hydride. The product was extracted with benzene and ether and dried over calcium chloride. Distillation yielded a highly colored fraction boiling constantly at 135° at 1 mm. pressure. This fraction was dissolved in 500 ml. of ether and treated with 80 g. of adsorption alumina, filtered and redistilled. The product boiling constantly at 142° at 2 mm. pressure weighed 227 g. (1.096 moles, 80.7%); $n^{20}{}_{\mathrm{D}}$ 1.5744, $d^{20}{}_{4}$ 1.0671; MR_{D} 64.13 (calcd. MR_{D} 64.03).

Anal. Calcd. for $C_{15}H_{13}N$: N, 6.76. Found: N, 6.94.

To 14 g. of potassium hydroxide in sufficient absolute ethanol to effect solution was added 5 g. of α,α-diphenylpropionitrile, and the solution refluxed for 168 hours. Slight evolution of ammonia was detected during the hydrolysis. The reaction mixture was poured into 200 ml. of water and 4 g. of crude amide recovered. Recrystallization from *n*-heptane produced a material melting at 103–104°.[9] Acidification of the filtrate from the crude product produced a small amount of α,α-diphenylpropionic acid melting at 173–174°.[10]

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[8] H. Adkins and G. M. Whitman, THIS JOURNAL, **64**, 150 (1942).

[9] H. Wieland and E. Dorrer, *Ber.*, **63B**, 407 (1930), report the m.p. as 103–104°. Bateman (ref. 7) gives m.p. as 149°.

[10] Thorner and Zincke (ref. No. 7) report the m.p. as 173–174°.

DEPARTMENT OF CHEMISTRY AND THE RESEARCH INSTITUTE
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NORMAN, OKLAHOMA
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Studies in Silico-organic Compounds. XI. Products Resulting from the Action of Benzylmagnesium Chloride on Triethoxysilane[1]

BY ALBERT L. REILLY AND HOWARD W. POST

Incidental to the study of certain other reactions, benzylmagnesium chloride was allowed to react with triethoxysilane in different molar ratios. Benzyldiethoxysilane, dibenzylethoxysilane and tribenzylsilane were formed.

Triethoxysilane (25 g., 0.15 mole) in 150 cc. of anhydrous ether was treated, with stirring, with 147 cc. of a 1.02 *M* solution of benzylmagnesium chloride in anhydrous ether (0.15 mole). After standing overnight at reflux temperature, the solid residue was separated and the ethereal layer was fractionated. Benzyldiethoxysilane was isolated, 3.9 g., 12% yield, b.p. 108–109° (5 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4666, $d^{25}{}_{25}$ 0.9782.

Anal. Calcd. for $C_{11}H_{18}SiO_2$: Si, 13.3; silane hydrogen (caustic treatment), 0.477; *MR*, 61.06. Found: Si, 12.9; silane hydrogen, 0.454; *MR*, 59.63.

Using double the relative amount of benzylmagnesium chloride, dibenzylethoxysilane was formed, 8 g., 20% yield, b.p. 141–143° (5 mm.), $n^{25}{}_{\mathrm{D}}$ 1.5370, $d^{25}{}_{25}$ 0.9945.

Anal. Calcd. for $C_{16}H_{20}SiO$: Si, 11.9: silane hydrogen, 0.390; *MR*, 80.08. Found: Si, 11.6; silane hydrogen, 0.380; *MR*, 80.38.

When 0.042 mole of triethoxysilane was allowed to react with 0.153 mole of benzylmagnesium chloride as above, tribenzylsilane was formed, 3 g., 23% yield, m.p. found 90–91°, literature[2,3] 91°.

Anal. Calcd. for $C_{21}H_{22}Si$: Si, 9.3; silane hydrogen, 0.331. Found: Si, 9.1; silane hydrogen, 0.320.

A greater degree of purity could not be attained for benzyldiethoxysilane in spite of careful fractionation and careful attention to the purity of reagents. Triethoxysilane was prepared in accordance with a method already in use.[4]

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[1] This work was made possible by a grant from the Office of Naval Research, under contract.

[2] Evison and Kipping, *J. Chem. Soc.*, 2830 (1931).

[3] Jenkins and Post, *J. Org. Chem.*, **15**, 552 (1950).

[4] Havill, Joffe and Post, *ibid.*, **13**, 280 (1948).

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RECEIVED AUGUST 4, 1950

1,1-Bis-(*p*-methoxyphenyl)-1-propene

BY KURT RORIG

From the aluminum chloride catalyzed reaction of propionyl chloride with anisole in carbon disulfide solvent, Gattermann[1,2] has isolated a by-product melting at 100 to 101° in addition to the expected *p*-methoxypropiophenone. Because this by-product gave *p*,*p*′-dimethoxybenzophenone upon chromic oxide oxidation, Gattermann considered it to be 1,1-bis-(*p*-methoxyphenyl)-1-propene. Gattermann rationalized its formation by assuming that the first-formed *p*-methoxypropiophenone condensed with a second molecule of anisole to give 1,1-bis-(*p*-methoxyphenyl)-1-propene and a molecule of water.

Much later, Skraup and Freundlich[3] prepared 1,1-bis-(*p*-methoxyphenyl)-1-propene by an unequivocal synthesis from *p*,*p*′-dimethoxybenzophenone and ethylmagnesium bromide. They found that the propene so prepared also melted at 101. However this propene differed in all other respects from the product they obtained by a repetition of Gattermann's experiment. Therefore they concluded that Gattermann had been in error.

By a repetition of Gattermann's work we were able to show that he was indeed correct in formulating the Friedel–Crafts product $C_{17}H_{18}O_2$, m. p. 100–101°, as 1,1-bis-(*p*-methoxyphenyl)-1-propene.

Experimental

Sixty grams of anhydrous aluminum chloride was added, as rapidly as the exothermic reaction allowed, to a solution of 50 g. of anisole and 50 g. of propionyl chloride in 100 ml. of carbon disulfide. After allowing the mixture to stand one-half hour it was carefully decomposed with water and extracted with ether. Upon evaporation of the dried ether extract 62 g. of yellow, semi-crystalline material remained. After two crystallizations from 95% ethanol this gave 23.5 g. of faintly yellowish plates melting 99.5–100.5°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OCH_3, 24.41. Found: C, 80.40; H, 7.22; OCH_3, 24.50.

This product gave a deep-red color when dissolved in concentrated sulfuric acid. The melting point of a mixture of this product, m.p. 99.5–100.5°, with some of the 1,1-bis-(*p*-methoxyphenyl)-1-propene, m.p. 99–100°, prepared by Skraup's Grignard synthesis[3] was 99.5–100.5°.

RESEARCH LABORATORIES
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RECEIVED SEPTEMBER 5, 1950

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[1] L. Gattermann, *Ber.*, **22**, 1129 (1889).

[2] L. Gattermann, R. Ehrhardt and H. Maisch, *ibid.*, **23**, 1199 (1890).

[3] S. Skraup and L. Freundlich, *Ann.*, **431**, 269 (1923).