CCCXXII.—*The Reduction of* p-*Dimethylaminobenzaldehyde, and the Preparation of* p-*Dimethylaminobenzyl Alcohol.*

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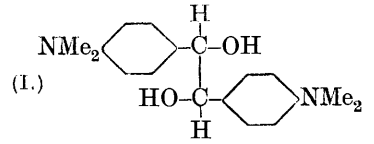
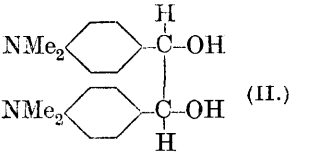
IN the course of the experiments described in the preceding paper, *p*-dimethylaminobenzyl alcohol was needed, but it was found that there is some confusion in the literature dealing with this compound, and that no satisfactory method is recorded for its preparation. Thus, Rousset (*Bull. Soc. chim.*, 1894, **11**, 318) claimed to have prepared the alcohol, colourless needles, m. p. 63°, by refluxing the corresponding aldehyde with caustic potash. Braun and Kruber (*Ber.*, 1912, **45**, 2978), however, could not repeat this work, and the present authors have also failed to obtain the alcohol by this means. Geigy and Co. (D.R.-P., 105,105) state that *p*-dimethylaminobenzyl alcohol can be isolated from the action of formaldehyde on dimethylaniline, but Cohn (*Chem.-Ztg.*, 1900, **24**, 564) contradicts the claim. Braun and Kruber, however, uphold Geigy and state that they have thus isolated the alcohol in a 2% yield as an oil which gave an oily benzoyl derivative; a *m*-nitrobenzoyl derivative, m. p. 51°; a methiodide, m. p. 126°; a picrate, m. p. 130°; and a chloroplatinate, m. p. 181°.

Rousset (*loc. cit.*) investigated the reduction of the aldehyde by sodium amalgam in alcohol, but instead of the alcohol obtained a solid, m. p. 155°. It has now been found that this solid is a mixture of two stereoisomeric s-*bis*(p-*dimethylaminophenyl*)*ethylene glycols* (I and II), one constituting about two-thirds; and that p-*dimethylaminobenzyl alcohol* can also be isolated from the reaction mixture in a 20% yield of the theoretical. The derivatives of *p*-dimethylaminobenzyl alcohol given by Braun and Kruber do not correspond in a single instance with those now obtained. Thus, it is found that the *benzoyl* derivative has m. p. 91°, the m-*nitrobenzoyl* derivative m. p. 76°, the *methiodide* 232°, and that the *chloroplatinate*, which these authors state to be insoluble in alcohol, crystallises from this medium with solvent of crystallisation, m. p. 100° (decomp.). It has not been found possible to prepare a crystalline picrate from the alcohol, but it is significant (see below) that dimethyl-*p*-toluidine gives a picrate corresponding in properties and m. p. to that given by Braun and Kruber for *p*-dimethylaminobenzyl alcohol.

The action of acids on the stereoisomeric glycols is of a complex nature and the pinacolin transformation has not yet been effected. Further, it has not been possible to prepare acetyl or benzoyl derivatives from (I) and (II). The glycol produced in greater

amount, m. p. 113°, gives a *dimethiodide*, whilst the other, m. p. 178°, under similar conditions, gives only a *monomethiodide*. No resolution experiments, however, have been attempted with a view to settling which glycol has the racemic and which the *meso*-structure.





The electrolytic reduction of *p*-dimethylaminobenzaldehyde has been described by Schepss (*Ber.*, 1913, **46**, 2574), who claims to have thus obtained a 41% yield of *p*-dimethylaminobenzyl alcohol as an oil which solidifies on cooling. It has now been found that in this reduction a mixture of at least the four following compounds is formed: dimethyl-*p*-toluidine, 15% of the theoretical; *p*-dimethylaminobenzyl alcohol, 20%; 4 : 4′-tetramethyldiaminodiphenylmethane; and the glycol, m. p. 178°. In all probability the glycol of m. p. 113° is also formed, but it has not been possible to isolate it from the reaction mixture.

Experimental.

p-*Dimethylaminobenzyl Alcohol.*—*p*-Dimethylaminobenzaldehyde (10 g.) was dissolved in ethyl alcohol (50 c.c.), sodium amalgam (150 g.; 4% Na) added, and the mixture refluxed for 4 hours on the water-bath. The colourless alcoholic solution was decanted into ice and water (250 g.), and the resulting colourless solid (A) was then collected, washed with water, and dried in a vacuum (7·8 g.). The filtrate was saturated with sodium chloride, extracted with ether, and after separation, drying, and fractionation, gave an almost colourless oil (1·6—1·8 g.), b. p. 123°/1 mm. (Found: C, 71·2; H, 8·65; N, 9·4. $C_9H_{13}ON$ requires C, 71·5; H, 8·6; N, 9·3%). p-*Dimethylaminobenzyl alcohol* is somewhat soluble in water, and when treated with benzoyl chloride in presence of caustic soda gives a *benzoate*, colourless prisms from ligroin, m. p. 91° (Found: C, 75·3; H, 6·9; N, 5·7. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). The m-*nitrobenzoate*, on the other hand, can only be prepared by reaction in pyridine, and is obtained as pale yellow plates, m. p. 76°, by crystallising rapidly from ligroin (80°) (Found: C, 64·1; H, 5·6. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·3%); it is easily soluble in dilute acids, but when its ligroin solution is heated for a short time decomposition occurs. The *methiodide* is easily formed by treating an acetone solution of the alcohol with methyl iodide, and crystallises from ethyl alcohol, in which it is sparingly

soluble, in colourless plates, m. p. 232° (decomp.) (Found : C, 41·4; H, 5·6; I, 43·4. $C_{10}H_{16}ONI$ requires C, 40·9; H, 5·5; I, 43·3%). The *chloroplatinate* forms pale brown leaflets from alcohol, containing solvent of crystallisation, m. p. 100° (decomp.) (Found : Pt, 24·8. $C_{18}H_{28}O_2N_2Cl_6Pt,2C_2H_5{\cdot}OH$ requires Pt, 24·3%).

Solid A. The combined material from three experiments (23·4 g.) was extracted with ether, leaving a solid (8 g.) which crystallised from alcohol in colourless prisms, m. p. 178° (Found : C, 72·1; H, 8·2; N, 9·2. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%). This *glycol* is sparingly soluble in alcohol, and both its alcoholic and acetic acid solutions show a blue fluorescence, whilst it gives a blood-red solution in sulphuric acid. When a hot acetone solution of the compound is treated with methyl iodide, a *monomethiodide* crystallises, and after recrystallisation from aqueous alcohol (1 : 5) gives colourless prisms, m. p. 232° (decomp.) (Found : C, 51·9; H, 6·3; I, 28·6. $C_{19}H_{27}O_2N_2I$ requires C, 51·7; H, 6·12; I, 28·8%).

On evaporation of the above ethereal extract, a colourless crystalline solid resulted (15 g.), which crystallised from alcohol–ligroin (80°) (1 : 9) in colourless needles, m. p. 113° (Found : C, 72·5; H, 8·0; N, 9·0. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%). This *glycol* is easily soluble in most organic solvents, giving blue fluorescent solutions, and a blood-red solution in sulphuric acid. When its acetone solution is treated with methyl iodide, the *dimethiodide* separates, which crystallises from alcohol in colourless plates with one molecule of alcohol of crystallisation, m. p. 97° (decomp.) (Found : I, 40·4; 40·0. $C_{20}H_{30}O_2N_2I_2,C_2H_5{\cdot}OH$ requires I, 40·3%).

Electrolytic Reduction of p-*Dimethylaminobenzaldehyde.*—A solution of *p*-dimethylaminobenzaldehyde (10 g.) in sulphuric acid (100 c.c., 20% H_2SO_4) was subjected to a current of 3 amps. in the electrolytic cell described in J., 1918, **113**, 764. The resulting colourless acid solution was made strongly alkaline, extracted with ether, and the extract left over-night, whereupon the glycol, m. p. 178° (0·5 g.), crystallised. When the ether was removed from the filtrate, and the residual oil steam-distilled, an oil rapidly passed over. This was extracted with ether, and the solution dried and fractionated, a colourless, strongly basic oil (1·3 g.) distilling at 70°/1 mm. (*p*-Dimethylaminobenzyl alcohol is but slightly volatile in steam.) The compound forms a picrate, yellow needles from alcohol, m. p. 130°, and a methiodide, colourless prisms from alcohol, m. p. 222°, and the melting points are not depressed when mixed with authentic specimens of the corresponding dimethyl-*p*-toluidine derivatives. The aqueous solution in the steam-distillation flask was decanted from the viscid oil, which was again extracted with water, the combined extract being saturated with sodium chloride and extracted

with ether. On fractionation, *p*-dimethylaminobenzyl alcohol (2·0 g.) passed over at 123°/1 mm. On cooling the viscid oil in ice for some time, a solid crystallised out and was collected and recrystallised from ligroin, forming colourless plates, m. p. 88°, not depressed by admixture with 4 : 4′-tetramethyldiaminodiphenylmethane.

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