14. *The Preparation of* iso*Butylenediamine.*

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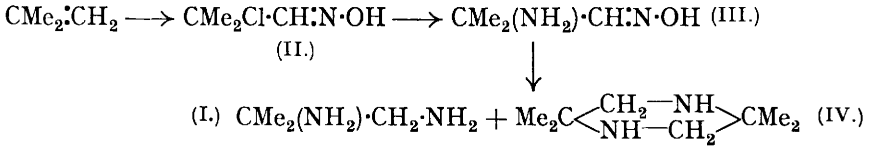
*iso*BUTYLENEDIAMINE (I) is a substance of special interest in connexion with stereochemical studies of the metals, because it is the simplest chelating diamine which is both unsymmetrical in structure and yet incapable of becoming a centre of optical activity in a co-ordination complex, even if the two amino-groups be regarded as united to the metal by links of different type. Reihlen and his collaborators (*Annalen*, 1932, **493**, 20) and Strack and Schwaneberg (*Ber.*, 1932, **65**, 710) have prepared it from α-amino*iso*butyronitrile or its acetyl derivative by reduction with hydrogen in presence of a platinum or palladium catalyst.

The alternative method now described depends on the conversion of *iso*butylene into α-chloro*iso*butyraldoxime (II), the reaction of this with alcoholic ammonia to give



$$\begin{array}{l} \mathrm{CMe_2{:}CH_2 \longrightarrow \underset{(II.)}{CMe_2Cl{\cdot}CH{:}N{\cdot}OH} \longrightarrow CMe_2(NH_2){\cdot}CH{:}N{\cdot}OH\ (III.)} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \mathrm{(I.)\ CMe_2(NH_2){\cdot}CH_2{\cdot}NH_2 + Me_2C{<}\begin{matrix} CH_2\text{—}NH \\ NH\text{—}CH_2 \end{matrix}{>}CMe_2\ (IV.)} \end{array}$$

α-*amino*iso*butyraldoxime* and its *hydrochloride*, and the reduction of either of these substances in alcoholic solution with sodium amalgam in presence of acetic acid, yielding a mixture of the diamine (I) with a tetramethylpiperazine (probably IV) (compare Reihlen, *loc. cit.*), from which the former is separated by means of the lower solubility of its hydrochloride in alcohol. The method is capable of giving the diamine in quantity from readily available materials, though the actual yield is only 15—20%, calculated on the amount of amino-oxime used.

α-Chloro*iso*butyraldoxime (II) separated as snow-white needles when *iso*butylene, prepared by the passage of *iso*butyl alcohol vapour over heated alumina (Ipatiev, *Ber.*, 1903, **36**, 2003), was passed into well-cooled amyl nitrite to which concentrated hydrochloric acid was gradually added (Ipatiev and Solonina, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 496); after being washed with water and with light petroleum and recrystallised from benzene, it melted at 104° (Ipatiev and Solonina give m. p. 96—97°).

α-*Amino*iso*butyraldoxime* (III).—A suspension of α-chloro*iso*butyraldoxime (100 g.) in saturated alcoholic ammonia (700 c.c.) reacted vigorously after 10 minutes, ammonium chloride being formed. After cooling, alcohol and ammonia were removed by distillation in a vacuum on the water-bath, and the residue was extracted with boiling benzene. The insoluble portion (23 g.) separated from alcohol in massive colourless crystals of α-*amino*iso*butyraldoxime hydrochloride*, m. p. 210° (decomp.) after darkening at about 200° (Found : C, 34·9; H, 8·1; Cl, 25·4. $C_4H_{10}ON_2$,HCl requires C, 34·65; H, 7·95; Cl, 25·6%). The benzene extracts on cooling deposited colourless crystals (50 g.) of α-*amino*iso*butyraldoxime*, m. p. 89° (with previous softening) after recrystallisation from alcohol and from benzene (Found : C, 47·0; H, 9·9. $C_4H_{10}ON_2$ requires C, 47·05; H, 9·8%). The oxime (total yield, 80%) is readily soluble in water and in alcohol and moderately easily soluble in benzene. It gives rise to strongly alkaline solutions and displaces ammonia from ammonium chloride.

The *benzylidene* derivative was obtained from alcoholic solution as massive colourless octahedra (sparingly soluble in water), m. p. 110° (Found : C, 69·5; H, 7·4. $C_{11}H_{14}ON_2$ requires C, 69·5; H, 7·4%).

iso*Butylenediamine Dihydrochloride.*—A solution of α-amino*iso*butyraldoxime or the hydrochloride (20 g.) in alcohol (200 c.c.) was acidified with glacial acetic acid and shaken, at about 30°, during the gradual addition of 2½% sodium amalgam (1500 g.), being meanwhile maintained slightly acid. After addition of a little water, the mercury was poured away, the semi-solid cake dissolved in aqueous sodium hydroxide (20 g. in 300 c.c. of water), and the solution distilled to dryness in a vacuum on the water-bath. The alkaline distillate was neutralised with hydrochloric acid and evaporated to dryness, and the crystalline residue, consisting of the dihydrochlorides of the diamine (I) and of a piperazine (IV), was extracted with alcohol. The portion which did not readily dissolve consisted of fairly pure *iso*butylenediamine dihydrochloride.

The extract was evaporated to dryness, and the residue again extracted with alcohol. In this manner a number of fractions of the less soluble portion were obtained; their compositions were checked by volumetric estimation of the chlorine and unsatisfactory fractions were resubmitted to fractionation. The dihydrochloride of the diamine crystallised from dilute alcohol in colourless rectangular plates (Found : C, 30·2; H, 8·9; Cl, 44·0. Calc. for $C_4H_{12}N_2,2HCl$: C, 29·8; H,8·7 ; Cl, 44·1%). The diacetamido-derivative had m. p. 100° after recrystallisation from ethylacetate (Reihlen and co-workers, *loc. cit.*, give m. p. 99—100°).

The *tetramethylpiperazine dihydrochloride* formed colourless needles from alcohol (Found : C, 44·6; H, 9·2; Cl, 32·8, 33·0. $C_8H_{18}N_2,2HCl$ requires C, 44·65; H, 9·3; Cl, 33·0%).

*Acetylation of α-Amino*iso*butyraldoxime.*—Acetylation of the oxime (1 g.) with acetic anhydride (3 c.c.) gave a mixture of substances separable by extraction with benzene, followed by ethyl acetate. Evaporation of the benzene extract gave α-acetamido*iso*butyronitrile (0·8 g.), which on recrystallisation from ethyl acetate formed colourless plates, m. p. 105—106° (alone or mixed with an authentic specimen; Hellsing, *Ber.*, 1904, **37**, 1921). The ethyl acetate extracts deposited a small quantity of N-*acetyl-α-amino*iso*butyraldoxime* as colourless needles, m. p. 198—199° (Found : C, 50·5; H, 8·3. $C_6H_{12}O_2N_2$ requires C, 50·0; H, 8·3%), very soluble in water and moderately easily soluble in ethyl acetate.

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