790. 2 : 4′-*Dipiperidyl: Its Structure and Derivatives.*

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The structure of 2 : 4′-dipiperidyl, obtained as a by-product in the electrolytic reduction of pyridine, has been proved by dehydrogenation, followed by oxidation to picolinic and *iso*nicotinic acids. 2 : 4′- and 4 : 4′-Dipiperidyl, the two major constituents of the electrolysis residues, have been further characterised.

Of the six possible isomeric dipiperidyls, five have been prepared by the catalytic hydrogenation of the corresponding dipyridyls (Smith, *J. Amer. Chem. Soc.*, 1928, **50**, 1936). The sixth, 2 : 4′-dipiperidyl, was not obtained by this author. 2 : 4′-Dipyridyl is formed in only very small amounts in the preparation of mixed dipyridyls (*idem, ibid.*, 1924, **46**, 416; Morgan and Burstall, *J.*, 1932, 27), hence the preparation of 2 : 4′-dipiperidyl by this route does not warrant further investigation.

Evans and Parkes (*J. Soc. Chem. Ind.*, 1938, **57**, 302) investigated, as a possible absorbent for carbon dioxide, the mixture of dipiperidyls obtained as a by-product in the electrolytic reduction of pyridine to piperidine. They reported a hitherto unknown crystalline base, m. p. 53—54°, which they suggested might be 2 : 4′-dipiperidyl. The present work was undertaken to establish the structure of this base, and characterise it further. 4 : 4′-Dipiperidyl was found to be the other major constituent of the mixture. The low solubility of 2 : 4′-dipiperidyl carbonate was used for purification of the base after removal of most of the 4 : 4′-dipiperidyl by distillation with light petroleum. The free base was obtained by distillation of an aqueous solution of the carbonate under reduced pressure.

Dehydrogenation of 2 : 4′-dipiperidyl with palladised charcoal at 300° afforded 2 : 4′-dipyridyl. Oxidation with neutral permanganate then give a mixture of acids separated by adsorption on alumina into picolinic and *iso*nicotinic acid.

The benzoyl derivatives of 2 : 4'- and 4 : 4'-dipiperidyl were oils, but the ditoluene-*p*-sulphonates and three other derivatives crystallised. *s*-Trinitrobenzene gave red addition products, which however were unstable and of indefinite melting point.

Experimental

The material used was the residue from the electrolytic reduction of technically pure pyridine, and was a semi-solid syrup containing approx. 50% of water. Distillation up to 170° removed the water.

4 : 4'-*Dipiperidyl.*—Equal weights of the dried mixture of dipiperidyls and light petroleum (b. p. 100—120°) were distilled to 240°. The distillate, on cooling, deposited crude 4 : 4'-dipiperidyl. This was removed by filtration, and the filtrate redistilled to 300°, to remove any remaining 4 : 4'-dipiperidyl. Recrystallisation from benzene gave 4 : 4'-dipiperidyl as colourless needles, m. p. 171—172° (Found : N, 16·1. Calc. for $C_{10}H_{12}N_2$: N, 16·7%). On exposure to air these crystals gradually form a solid carbonate.

The *ditoluene*-p-*sulphonate*, prepared in pyridine, crystallised from acetone as colourless needles, m. p. 309—310° (Found : C, 60·4; H, 6·9; N, 5·7. $C_{24}H_{32}O_4N_2S_2$ requires C, 60·5; H, 6·8; N, 5·9%). The *bis-α-naphthylurea* separated from light petroleum as pinkish prisms, m. p. 239—240° (Found : C, 75·5; H, 6·5; N, 10·8. $C_{32}H_{34}O_2N_4$ requires C, 75·9; H, 6·8; N, 11·1%). The *bis*-2 : 4-*dinitrophenyl* derivative, prepared by the interaction of the base and 1-chloro-2 : 4-dinitrobenzene in alcohol, crystallised from alcohol as yellow prisms, m. p. 255—256° (decomp.) (Found : C, 53·0; H, 5·0; N, 16·5. $C_{22}H_{24}O_8N_6$ requires C, 52·8; H, 4·8; N, 16·8%).

2 : 4'-*Dipiperidyl.*—The filtrate from the extraction of 4 : 4'-dipiperidyl was evaporated to dryness, and the residue diluted with an equal weight of water. The resultant mixture was saturated with carbon dioxide, whereupon crude 2 : 4'-dipiperidyl carbonate was precipitated. Recrystallisation from a small volume of water gave the carbonate as colourless prisms, m. p. 144—145° (decomp.) (Found : C, 57·8; H, 8·9; N, 11·9. Calc. for $C_{11}H_{20}O_3N_2$: C, 57·7; H, 8·8; N, 12·3%). The base was obtained by boiling the carbonate with water under reduced pressure. 2 : 4'-Dipiperidyl, recrystallised from acetone, formed colourless crystals, m. p. 54°, b. p. 285—286° [Found : C, 71·1; H, 12·2; N, 16·9%; *M* (Rast), 162. Calc. for $C_{10}H_{20}N_2$: C, 71·4; H, 11·9; N, 16·7%; *M*, 168]. These were extremely hygroscopic, and absorbed carbon dioxide very rapidly in air.

The *ditoluene*-p-*sulphonate*, needles, m. p. 189—190° (Found : C, 60·6; H, 6·5; N, 6·0%), *bis-α-naphthylurea*, prisms, m. p. 285—286° (Found : C, 76·0; H, 6·2; N, 10·8%), and *bis*-2 : 4-*dinitrophenyl* derivative, yellow prisms, m. p. 247—248° (decomp.) (Found : C, 52·5; H, 4·6; N, 16·7%), were obtained and recrystallised as above. The *bisphenylthiourea*, prepared in alcohol, crystallised from alcohol as colourless prisms, m. p. 172° (Found : C, 65·4; H, 7·3; N, 12·4. $C_{24}H_{30}N_4S_2$ requires C, 65·6; H, 6·9; N, 12·8%).

Dehydrogenations.—(*a*) 2 : 4'-Dipiperidyl (2 g.) was intimately mixed with 20% palladised charcoal (1 g.) and heated to 300° (metal-bath). Brisk evolution of hydrogen ensued, and ceased after 30 min. Extraction with alcohol–acetone, followed by removal of solvent, gave 2 : 4'-dipyridyl (1·5 g.), b. p. 279°. Aqueous picric acid gave the picrate, m. p. 205° (Found : N, 18·0. Calc. for $C_{16}H_{11}O_7N_5$: N, 18·2%). Heating the dipiperidyl with selenium powder at 200—250° also brought about dehydrogenation, but the dipyridyl was difficult to obtain pure.

(*b*) 4 : 4'-Dipiperidyl similarly afforded 4 : 4'-dipyridyl, needles, m. p. 112° (picrate, m. p. and mixed m. p. 255°).

Oxidations.—(*a*) 2 : 4'-Dipyridyl (0·2 g.) was added to 4% potassium permanganate solution (10 c.c.), and the mixture warmed on the water-bath (20 min.). Manganese dioxide was filtered off, and the solution evaporated to dryness. The residue was extracted with boiling alcohol, and the extract evaporated to dryness. This residue was chromatographed in water (10 c.c.) on alumina. Picolinic acid was located by ferrous sulphate solution, with which it gave a reddish-yellow colour. Elution of the column gave *iso*nicotinic acid, m. p. 303°, and picolinic acid, m. p. 130°.

(*b*) 4 : 4'-Dipyridyl, on oxidation in a similar manner, gave *iso*nicotinic acid, m. p. 303°.

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