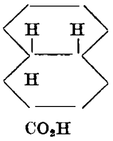
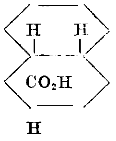
CCCCV.—*The Stereochemistry of the Hydronaphthalenes. Part I. Decahydro-β-naphthamides.*

By FRANCIS WILLIAM KAY and NOEL STUART.

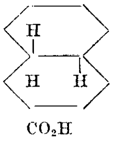
MOHR's theory of the isomerism of the decahydronaphthalenes, based on the views of Sachse on the strainless character of the *cyclo*hexane ring (*J. pr. Chem.*, 1918, **98**, 315), indicates that a monosubstituted decahydronaphthalene should exist in four distinct racemic forms. Decahydro-β-naphthoic acid, for example, should exist on this theory in the four racemic modifications represented diagrammatically by the formulæ I—IV, which show one of the two enantiomeric components of each form. I and II are derivatives of *cis*-, III and IV of *trans*-decahydronaphthalene.



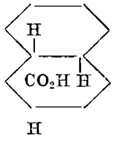
(I.)



(II.)



(III.)



(IV.)

Borsche and Lange (*Annalen*, 1923, **434**, 219), by fractionally crystallising the amide, isolated two of the four racemic forms of decahydro-β-naphthoic acid, melting respectively at 165—166° and 195°. In a footnote, they hinted at the possible existence of a third racemic form, but they apparently failed to realise the stereochemical significance of their results.

The re-examination of decahydro-β-naphthoic acid by the present authors revealed the existence of a third isomeride in the form of an amide melting at 139—140° and indicated the occurrence of a fourth.

Decahydro-β-naphthamide was prepared by reducing *ar*-tetrahydro-β-naphthoic acid and applying the usual technique to the crude decahydro-acid thus obtained—fractional crystallisation of the amidic mixture was preferred, as the corresponding mixture of acids was oily. Reduction with amyl alcohol and sodium at 150° yielded almost solely a *trans*-decahydro-β-naphthamide, contrary to the effect of catalytic hydrogenation, which produces *cis*-decahydronaphthalene to the extent of 90% (Willstätter and Seitz, *Ber.*, 1924, **57**, 683). The hydrogenation of the naphthalene nucleus is in fact conditioned by temperature and other physical factors, for the use of ethyl alcohol in the reduction of the tetrahydro-acid gave a totally different result, exhaustive fractional crystallisation of the mixed amides yielding a sparingly soluble component with a maximum melting point of 169—171° and a more soluble one, m. p. 139—140°, constituting 66% of the mixture. Neither of these two amides has been previously isolated, and their existence must be regarded as confirming the stereochemical ideas elaborated above.

EXPERIMENTAL.

Decahydro-β-naphthoic Acids.—(1) *ar*-Tetrahydro-β-naphthoic acid (5 g.), dissolved in 150 c.c. of amyl alcohol, was dropped on to 20 g. of sodium (five times the theoretical quantity) heated at 150°; towards the end of the reaction 150 c.c. of amyl alcohol were added to dissolve the remaining sodium. The product was poured into water, and the amyl alcohol removed by steam distillation. (It is not sufficient merely to distil the aqueous layer, as the sodium salt of the decahydro-acid is appreciably soluble in amyl alcohol.) The alkaline solution was acidified with dilute hydrochloric acid, the decahydro-acid separating as an oil which solidified to a waxy solid, m. p. 65—75°. (2) The above procedure was repeated, 100 c.c. of ethyl alcohol being used in place of the amyl alcohol and a further 50 c.c. added to dissolve all the sodium. The product solidified more rapidly than the preceding one and melted at 80—90°.

Decahydro-β-naphthamides.—A solution of 5 g. of the decahydro-acid in 50 c.c. of chloroform was dried over calcium chloride and treated with 7 g. of phosphorus pentachloride in the cold. When the evolution of hydrogen chloride ceased, the chloroform was distilled in a vacuum, and the residue evaporated several times with fresh chloroform to remove phosphorus oxychloride. The product was maintained for some time at 100° in a vacuum and was then slowly poured into 150 c.c. of concentrated aqueous ammonia; the crude amide, thus obtained in white flakes, melted, when dry, at 105—120° or 110—122° according as the initial acid had been prepared by reduction with amyl alcohol or with ethyl alcohol.

Fractionation of the Decahydro-β-naphthamides.—A solution of the crude amide in cold 50% aqueous alcohol was treated with successive small quantities of water; after each addition the solution was warmed slightly to dissolve the precipitated amide and then allowed to cool slowly and the crystals deposited were removed. In order to obtain the final, lower-melting and more water-soluble portions of the amide it was necessary to concentrate the solution. The fractions so obtained were further sub-divided in the same manner. Fractions having approximately the same m. p. were now combined and again fractionated. As a rule, the first crop obtained from any fraction had a higher m. p. than the last crop from the preceding fraction.

(1) *Amides from the acid obtained by reduction with amyl alcohol.* After four operations, an amide, m. p. 195—196°, and a small quantity of another, m. p. 171—174°, were obtained. By systematically working up the mother-liquors, almost all the 195°-amide was fractionated out in about twenty operations, leaving vanishingly small fractions with melting points between 100° and 195°.

(2) *Amides from the acid obtained by reduction with ethyl alcohol.* After eight operations, an amide of m. p. 169—171° was obtained (Found: N, 7·4. $C_{11}H_{19}ON$ requires N, 7·7%); exhaustive fractionation gave also, in twenty-four operations, an amide of m. p. 139—140° (Found: N, 7·5%) and scarcely anything else.

We desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of us (N.S.) which enabled this research to be carried out.

UNIVERSITY OF LIVERPOOL. [*Received, February* 23*rd*, 1925.]