CCCLIII.—*A Synthesis of Behenolic Acid.*

By RAMAKANTA BHATTACHARYA, SHANKAR RAO SALETORE, and JOHN LIONEL SIMONSEN.

AN analytical investigation led Mirchandani and Simonsen (J., 1927, 371) to conclude that *iso*erucic acid is an inseparable mixture of Δ^{11}-*heneicosene*-1-*carboxylic acid* (I) and Δ^{13}-*heneicosene*-1-*carboxylic acid* (II).*

$$\underset{\text{(I.)}}{CH_3\cdot[CH_2]_8\cdot CH{:}CH\cdot[CH_2]_{10}\cdot CO_2H} \quad \underset{\text{(II.)}}{CH_3\cdot[CH_2]_6\cdot CH{:}CH\cdot[CH_2]_{12}\cdot CO_2H}$$

Syntheses of these two acids are desirable to establish this, but unfortunately the methods available for syntheses of this type are somewhat limited (compare Robinson and Robinson, J., 1925, **125**, 175). The most direct method would appear to be the preparation of the corresponding acetylenic acids, since the reduction of these to the ethylenic acids is readily performed, and we decided to explore first the synthesis of behenolic acid (III).

$$\underset{\text{(IV.)}}{C_8H_{17}\cdot C{\vdots}CNa} + \underset{\text{(V.)}}{CH_2Br\cdot[CH_2]_{10}\cdot CO_2Me} \longrightarrow CH_3\cdot[CH_2]_7\cdot C{\vdots}C\cdot[CH_2]_{11}\cdot CO_2H \text{ (III.)}$$

The method adopted was the condensation of the sodium derivative of decinene (IV) with *methyl* 11-*bromododecoate* (V). Decinene was prepared by Picon's method (*Compt. rend.*, 1919, **169**, 32) from octyl iodide and sodium acetylide : we have found that the reaction proceeds best at 180°. For the synthesis of the bromo-ester, decane-1 : 10-dicarboxylic acid was prepared in considerable quantity by Walker and Lumsden's method (J., 1901, **79**, 1191) : their methods for the preparation of 10-bromoundecoic acid and its conversion into the dibasic acid have both been improved.

Methyl hydrogen decane-1 : 10-*dicarboxylate*, obtained by the partial hydrolysis of the dimethyl ester, was reduced to 11-*hydroxydodecoic acid*, m. p. 78—79°, by the method of Grün and Wirth (*Ber.*, 1922, **55**, 2216). This acid does not appear to be identical with any of the hydroxydodecoic acids previously described. It was thought that it might be identical with the acid isolated by Power and Rogerson from *Ipomœa purpurea* (*Amer. J. Pharm.*, 1908, **80**, 251), but direct comparison with a specimen of this acid, for which we are much indebted to Dr. T. A. Henry, showed this not to be the case. The hydroxy-acid, when treated with hydrogen bromide in methyl-alcoholic solution, was converted into the

---

* In the paper referred to (p. 373), the acids (I) and (II) are wrongly named as derivatives of docosene.

required bromo-ester. Although this crystallised well, we have not succeeded in obtaining it quite pure. Condensation of sodiodecinene and methyl 11-bromododecoate in xylene at 160° resulted in the formation of a liquid ester which, on hydrolysis, gave an acid crystallising from methyl alcohol in needles, m. p. 57°, identical in all respects with a specimen of behenolic acid prepared from erucic acid.

EXPERIMENTAL.

10-*Bromoundecoic Acid.*—To a mechanically stirred and well-cooled solution of hydrogen bromide in toluene (HBr, 10—15%) the requisite amount of undecylenic acid was gradually added. After 2—3 hours, the bromo-acid, which had crystallised (m. p. 51°), was collected; a further quantity could be obtained by cooling the filtrate in a freezing mixture. The bromo-methyl ester, b. p. 165°/10 mm., prepared by the action of methyl alcohol and sulphuric acid (Found: Br, 28·2. Calc.: Br, 28·7%), was converted into the cyano-ester (b. p. 180°/10 mm.) by digestion for 2 hours with an alcoholic solution of potassium cyanide. On hydrolysis, the cyano-ester gave an excellent yield of decane-1 : 10-dicarboxylic acid: this is a more convenient method than that described by Walker and Lumsden (*loc. cit.*) for the preparation of this acid.

Methyl Hydrogen Decane-1 : 10-*dicarboxylate.*—Methyl decane-1 : 10-dicarboxylate, b. p. 170°/10 mm. (Found: C, 65·5; H, 10·0. Calc.: C, 65·1; H, 10·1%) (compare Chuit, *Helv. Chim. Acta*, 1926, **9**, 264), was converted into the hydrogen ester by the method of Grün and Wirth (*loc. cit.*, p. 2215) or by partial hydrolysis with cold alkali. The yield was in both reactions poor. The dibasic acid and the hydrogen ester were separated by treatment with light petroleum, in which the former was very sparingly soluble. *Methyl hydrogen decane*-1 : 10-*dicarboxylate* crystallised from methyl alcohol in prisms, m. p. 51° (Found: C, 63·5; H, 10·0. $C_{13}H_{24}O_4$ requires C, 63·9; H, 9·8%).

11-*Hydroxydodecoic Acid.*—To a mechanically stirred suspension of finely divided potassium methyl decane-1 : 10-dicarboxylate (dried over phosphoric oxide) in boiling absolute alcohol (10—12 parts), sodium (4 times the theoretical quantity) was added as rapidly as possible. After 1 hour, dilute alcohol and water were added and the mixture was heated to hydrolyse the ester. The excess of alcohol was removed with steam, and hydrochloric acid added until the solution was faintly alkaline. After extraction with ether to remove neutral reduction products, magnesium sulphate was added; the magnesium salt of the hydroxy-acid was then precipitated. This was collected and decomposed with hydrochloric acid and the hydroxy-acid obtained was converted once more into the magnesium salt. The acid now regenerated from the magnesium salt still contained an appreciable quantity of the dibasic acid which could not be readily separated by crystallisation. The crude acid was therefore boiled with acetyl chloride, the excess of acetyl chloride removed on the water-bath, and the mixture of 11-acetoxydodecoic acid and decane-1 : 10-dicarboxylic acid separated by treatment with light petroleum, in which the former was readily soluble. The acetylated acid was a wax which did not lend itself to purification. It was hydrolysed with alkali and the *hydroxy-acid* was repeatedly crystallised from light petroleum (b. p. 60—80°) and finally from dilute methyl alcohol; it was then obtained in needles, m. p. 78—79° (Found: C, 66·4; H, 10·9. $C_{12}H_{24}O_3$ requires C, 66·7; H, 11·1%).

The *magnesium* salt, which was very sparingly soluble in water, was an amorphous, white solid (Found: Mg, 5·0. $C_{24}H_{46}O_6Mg$ requires Mg, 5·3%). The methyl ester had b. p. 160°/7 mm. and the anilide crystallised from light petroleum in small prisms, m. p. 87°.

Methyl 11-*Bromododecoate*.—The hydroxy-acid, dissolved in four parts of methyl alcohol, was saturated with hydrogen bromide and after digestion on the water-bath for 3 hours the methyl alcohol was removed in a current of hydrogen bromide. The residue, which crystallised, was dissolved in ether, and the ethereal solution was washed with sodium carbonate solution to remove any acid present, dried, and evaporated. The *bromo-ester* crystallised from methyl alcohol in fatty needles, m. p. about 50°, which was not altered by recrystallisation. Analysis showed the ester to be still somewhat impure (Found: Br, 23·3. $C_{13}H_{25}O_2Br$ requires Br, 27·3%).

Decinene.—Into a suspension of sodamide (from 5 g. of sodium) in liquid ammonia (Hess and Munderloh, *Ber*., 1918, **51**, 377), acetylene was passed until complete conversion into sodium acetylide had taken place, the temperature being maintained at —60° to —45° by means of liquid air. Octyl iodide (50 g.) having been added, the mixture was allowed gradually to attain room temperature, the ammonia evaporating. After 12 hours, the temperature was maintained at 180° for 8—10 hours. Water was added to the cooled mixture, and the decinene separated by distillation in steam. The hydrocarbon was washed with dilute sulphuric acid to remove basic impurities and distilled; the greater portion passed over at 175—180°/685 mm. ($d_{30^\circ}^{30^\circ}$ 0·799, $n_{D}^{30^\circ}$ 1·44) and was sufficiently pure for conversion into the sodium derivative.

Condensation of Sodiodecinene and Methyl 11-*Bromododecoate*.—To finely divided sodium (0·25 g.), in an atmosphere of hydrogen, decinene (3 g.) was gradually added, the formation of the sodium compound being hastened by gentle heating. After the addition of the bromo-ester (3·4 g.) in xylene the mixture was heated at 160° for 8 hours. Water was added to the cooled solution, and the xylene and the excess of decinene were removed in steam; the residual oil was dissolved in ether, the ethereal solution washed with sodium carbonate solution, and the solvent evaporated. The thick, oily residue was hydrolysed with methyl-alcoholic potassium hydroxide; the acid, isolated in the usual manner, partly crystallised on keeping. After draining on porous porcelain, it was recrystallised from methyl alcohol, behenolic acid being obtained in glistening needles, m. p. 57°. It was carefully compared with a specimen of behenolic acid prepared from erucic acid, and a mixture of the two acids had m. p. 56·8—57° (Found: C, 78·3; H, 11·6. Calc.: C, 78·5; H, 11·9%). The barium salt also was analysed (Found: Ba, 17·2. Calc.: Ba, 17·0%).

One of us (J. L. S.) wishes to thank Professor C. S. Gibson, O.B.E., for the provision of facilities in his laboratory for carrying out some of the experiments detailed above.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

GUY'S HOSPITAL MEDICAL SCHOOL,
(UNIVERSITY OF LONDON), S.E. 1.

[*Received, August 27th,* 1928.]