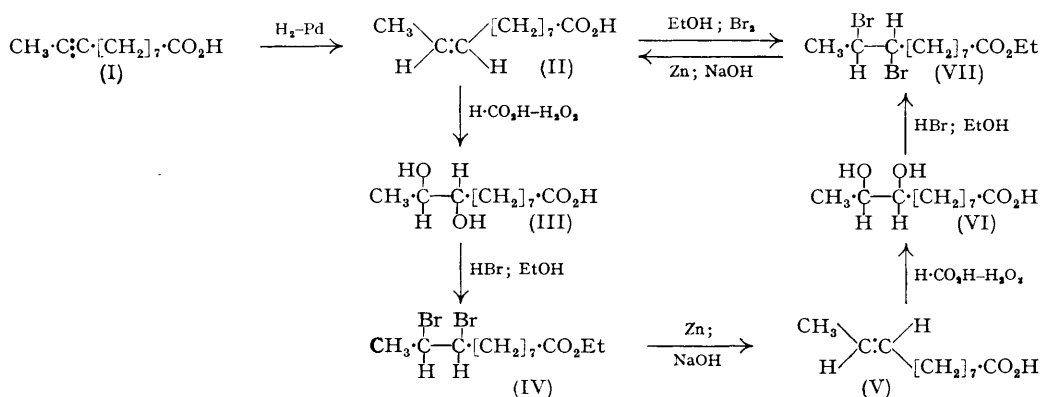


122. Synthetic Long-chain Aliphatic Compounds. Part VIII.*
The Preparation of cis- and trans-Undec-9-enoic Acids.†

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The acids named in the title have been prepared in a high state of purity *via* the crystalline dihydroxy-acids (III and VI). The *cis*-acid thus obtained differs from that obtained by semi-hydrogenation of the acetylenic acid (I), and this point is discussed.

COLLAUD (*Helv. Chim. Acta*, 1943, **26**, 1064) has described the semi-hydrogenation of undec-9-ynoic acid † (I) and the isolation of *cis*-undec-9-enoic acid (II) by fractional distillation. The required acetylenic acid (I) can be obtained from commercial undecylenic (undec-10-enoic) acid by addition of bromine and reaction of the resulting dibromo-acid with potassium hydroxide at 180° (Krafft, *Ber.*, 1896, **29**, 2234). *trans*-Undec-9-enoic acid (V) has been prepared from the acetylenic acid (I) by addition of hydrogen halide followed by



[The compounds being optically inactive, (III), (IV), (VI), and (VII) are accompanied by their enantiomorphs. These substances are represented above by the conventional projection formulæ; evidence concerning the spatial positions in $\alpha\beta$ -glycols has been summarised by Bader (*J. Amer. Chem. Soc.*, 1948, **70**, 3938).]

* Part VII, preceding paper.

† Geneva nomenclature (CO₂H = 1), throughout.

reduction of the unsaturated halogeno-acid (Krafft and Seldis, *Ber.*, 1900, **33**, 3572; Harris and Smith, *J.*, 1935, 1108) but purification of the product is difficult. We have now prepared the *cis*- and the *trans*-olefinic acid from the corresponding dihydroxy-acids; this procedure is known to furnish products of high purity (Ames and Bowman, *J.*, 1951, 1079, where the stereochemical course of these reactions is discussed).

Undec-9-ynoic acid (I) was hydrogenated until 1.08 mols. of hydrogen had been taken up and the product, isolated by distillation, was found to contain 92% of olefinic acid (II) by determination of the iodine value. Treatment of the crude acid with performic acid (Swern, Billen, Findley, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 1786) and hydrolysis of the resulting formoxy-hydroxy-acids furnished *threo*-9:10-dihydroxyundecanoic acid (III), readily purified by recrystallisation. This product was heated with hydrogen bromide in acetic-sulphuric acids and the resulting dibromo-acid esterified to give ethyl *erythro*-9:10-dibromoundecanoate (IV) which, on debromination and hydrolysis, furnished *trans*-undec-9-enoic acid (V), m. p. 17—18°, I.V. 138.4 (calc., 137.7). Krafft and Seldis (*loc. cit.*) gave m.p. approximately 19° but from their experimental data it seems doubtful if the material was homogeneous; Harris and Smith (*loc. cit.*) used an essentially similar method of preparation but, although the product was purified more rigorously and melted at 20°, it contained some saturated compounds (I.V., 134).

The *trans*-olefinic acid was similarly converted into the crystalline *erythro*-9:10-dihydroxyundecanoic acid (VI) and thence into ethyl *threo*-9:10-dibromoundecanoate (VII). Debromination and hydrolysis of the latter yielded the pure *cis*-undec-9-enoic acid, m. p. 1—2°, I.V. 138.2. Collaud (*loc. cit.*) gave m. p. 3—3.5° but did not report the iodine value of his material. It is of interest that the crude semihydrogenation product, containing only 92% of olefinic acid, also melted at 1—2°. Thus the presence of significant amounts of saturated acid has only a slight effect on the melting point of the unsaturated acid and this fact illustrates the importance of the iodine value (cf. Smith, *J.*, 1939, 974).

Purification of the crude semihydrogenation product through the dibromo-ester (VII) was also investigated; this was expected to provide the pure *cis*-olefinic acid more conveniently. The crude unsaturated ester in carbon tetrachloride solution was brominated at -10° and the dibromo-ester (VII) separated from saturated contaminants, and from excess of olefinic ester, by fractional distillation. Debromination of (VII) and hydrolysis of the resulting olefinic ester furnished an impure sample of *cis*-undec-9-enoic acid (II), m. p. -3° to -2°, I.V. 138.2. The iodine value indicates that the impurity present is not a saturated compound and is most probably the isomeric *trans*-acid. *trans*-Olefins are known to be formed to some extent during semihydrogenation of acetylenes; e.g., Sondheimer (*J.*, 1950, 879) showed that *cis*-hex-3-enol obtained by semihydrogenation of hex-3-ynol contained a significant proportion of the *trans*-isomer. Although the evidence is not yet conclusive, we consider that on account of these results and those of Sondheimer (*loc. cit.*), particular care should be taken in the purification of olefinic acids obtained by semihydrogenation of acetylenic acids (Strong and his collaborators, *J. Amer. Chem. Soc.*, 1948, **70**, 1699, 3391; 1950, **72**, 2116, 4263); indeed, it is our experience that even in the higher series where both the *trans*-olefinic and the saturated acids are solids their removal requires much effort with consequent loss of material.

EXPERIMENTAL

Undec-9-ynoic Acid.—Commercial undecylenic (undec-10-enoic) acid (60 g.) was dissolved in carbon tetrachloride (200 c.c.) and bromine (42 g.) added gradually, the temperature of the mass being kept below 30°. After removal of the solvent by distillation *in vacuo*, the crude dibromo-acid was added to a solution of potassium hydroxide (135 g.) in water (80 c.c.), and the mixture was heated in an open flask so that the internal temperature rose slowly to 180° and remained there for 30 minutes (cf. Harris and Smith, *loc. cit.*). Water (400 c.c.) was added and the solution acidified, the product being extracted with ethyl acetate. Distillation furnished a colourless oil, b. p. 134—138°/0.7 mm., which rapidly solidified. This procedure consistently yielded 43—47 g. of material, f. p. between 42° and 46°. Crystallisation of it (46 g.) from light petroleum (150 c.c.; b. p. 40—60°) furnished undec-9-ynoic acid (I) (21 g.), m. p. 58—59°. A second crop (7 g.) was obtained at 0° (total yield: 28 g., 47% calc. on the undecylenic acid).

The pure acid, m. p. 61°, was isolated by two further recrystallisations from light petroleum (b. p. 40—60°).

Semihydrogenation of Undec-9-ynoic Acid.—The acid (32 g.) in ethyl acetate (180 c.c.) was hydrogenated in the presence of palladised calcium carbonate (1 g.; 0.5% of Pd) until 4.3 l. (1.08 mols.) had been taken up. Distillation of the filtered solution yielded crude *cis*-undec-9-enoic acid (30 g.) as a colourless oil, b. p. 123—124°/0.8 mm., m. p. 1—2° (capillary) (Found: I.V., 127.1. Calc. for $\text{C}_{11}\text{H}_{20}\text{O}_2$: I.V., 137.7. Thus the material contains 92% of undecenoic acid).

threo-9:10-Dihydroxyundecanoic Acid.—The foregoing acid (29 g.) was treated with formic acid (90 c.c.) and hydrogen peroxide (20 c.c.; 100-vol.) under the conditions described by Swern *et al.* (*loc. cit.*). The residue, obtained after evaporation of volatile material, was refluxed with excess of sodium hydroxide solution (2N) and poured into dilute sulphuric acid (2N), the product being extracted with warm ethyl acetate. The extracts were washed twice with water, dried (Na_2SO_4), and concentrated to 100 c.c. *threo-9:10-Dihydroxyundecanoic acid*, which separated on cooling, recrystallised from ethyl acetate as plates, m. p. 82—83° (9.5 g.) (Found: C, 60.8; H, 9.9. $\text{C}_{11}\text{H}_{22}\text{O}_4$ requires C, 60.5; H, 10.2%).

trans-Undec-9-enoic Acid.—The foregoing dihydroxy-acid (12.7 g.) was treated with hydrogen bromide in acetic-sulphuric acids, and the product esterified with ethanol by the method previously described (Ames and Bowman, *loc. cit.*). *Ethyl erythro-9:10-dibromoundecanoate* (19.0 g.) distilled as an almost colourless oil, b. p. 149—152°/0.5 mm., n_D^{20} 1.4926 (Found: C, 41.9; H, 6.5. $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Br}_2$ requires C, 42.0; H, 6.5%). Debromination of this product by the standard method (*idem, ibid.*) furnished *ethyl trans-undec-9-enoate* (9.9 g.) as a colourless oil, b. p. 87—89°/0.5 mm., n_D^{20} 1.4406 (Found: C, 73.6; H, 11.5%; I.V., 118.8. $\text{C}_{13}\text{H}_{24}\text{O}_2$ requires C, 73.5; H, 11.4%; I.V., 119.6).

The olefinic ester (9.8 g.) was hydrolysed by ethanolic potassium hydroxide solution in an atmosphere of nitrogen, and the resulting *trans*-undec-9-enoic acid (7.8 g.) distilled as a colourless oil, b. p. 121—123°/0.7 mm., n_D^{20} 1.4519, m. p. 17—18° (capillary) (Found: I.V., 138.4).

erythro-9:10-Dihydroxyundecanoic Acid.—The *trans*-olefinic acid (7.5 g.) was converted into the corresponding dihydroxy-acid as in the previous case. *erythro-9:10-Dihydroxyundecanoic acid* (4.6 g.) separated from ethyl acetate in large, lustrous plates, m. p. 82—83° (Found: C, 60.5; H, 10.2. $\text{C}_{11}\text{H}_{22}\text{O}_4$ requires C, 60.5; H, 10.2%). This product was less soluble in ethyl acetate than the *threo*-isomer, which also melted at 82—83°; a mixture of the two isomers melted at 71—72°. An attempt to prepare the *erythro*-dihydroxy-acid directly from the crude *cis*-undec-9-enoic acid by hydrogen peroxide-osmic acid in acetic acid (Dorée and Pepper, *J.*, 1942, 477) was unsuccessful, giving only a small yield of a heterogeneous product.

cis-Undec-9-enoic Acid.—Treatment of the *erythro*-dihydroxy-acid (4.0 g.) with hydrogen bromide in acetic-sulphuric acids and esterification of the product with ethanol in the usual manner furnished *ethyl threo-9:10-dibromoundecanoate* (5.6 g.) as a pale yellow oil, b. p. 149—152°/0.6 mm., n_D^{20} 1.4937 (Found: C, 42.1; H, 6.8. $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Br}_2$ requires C, 42.0; H, 6.5%). The latter was debrominated by the general procedure to give *ethyl cis-undec-9-enoate* (2.6 g.), a colourless oil, b. p. 88—90°/0.6 mm., n_D^{20} 1.4418 (Found: C, 74.0; H, 11.9%; I.V., 118.4. $\text{C}_{13}\text{H}_{24}\text{O}_2$ requires C, 73.5; H, 11.4%; I.V., 119.6). Hydrolysis of this ester, as in the previous case, afforded pure *cis*-undec-9-enoic acid (1.8 g.) as a colourless oil, b. p. 118—120°/0.8 mm., n_D^{20} 1.4530, m. p. 1—2° (capillary) (Found: I.V., 138.2). The *p*-phenylphenacyl ester crystallised from ethanol in plates, m. p. 64.5—65°, unchanged by recrystallisation. Collaud (*loc. cit.*) gave m. p. 65—66°.

Attempted Purification of Crude cis-Undec-9-enoic Acid through the Dibromide.—A sample of the crude acid (3.8 g.) obtained by semihydrogenation was esterified azeotropically with ethanol (60 c.c.), benzene (60 c.c.), and concentrated sulphuric acid (0.5 c.c.). Isolated in the usual manner, the ester was dissolved in carbon tetrachloride (50 c.c.), and the solution was cooled to -10° while bromine (2.5 g.; 80% of the amount calculated for the undecenoic acid present) in carbon tetrachloride (50 c.c.) was added in small portions with shaking. The mixture was allowed to warm to room temperature, washed with potassium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated. The residue was repeatedly fractionated under reduced pressure until no further purification could be effected, as shown by *n*. *Ethyl threo-9:10-dibromoundecanoate*, b. p. 147—148°/0.5 mm., was thus obtained as a colourless oil, n_D^{20} 1.4925. Debromination of this material (17 g.) by the general procedure yielded *ethyl cis-undec-9-enoate* which distilled as a colourless oil, b. p. 92—94°/0.4 mm., n_D^{20} 1.4417 (8.5 g.) (Found: I.V., 119.6. Calc. for $\text{C}_{13}\text{H}_{24}\text{O}_2$: I.V., 119.6). The *cis*-undec-9-enoic acid (7 g.) obtained by hydrolysis was slightly impure (b. p. 117—119°/0.5 mm., n_D^{20} 1.4530, m. p. -3°

to -2° in a capillary tube) (Found : C, 71.9; H, 11.0%; I.V., 137.6. Calc. for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9%; I.V., 137.7). The *p*-phenylphenacyl ester prepared from this product was also slightly impure (m. p. 61°), but could not be purified further by recrystallisation (Found : C, 79.1; H, 8.1. Calc. for $C_{25}H_{30}O_3$: C, 79.3; H, 8.0%).

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