415. *Investigations of the Olefinic Acids. Part XVI. The Synthesis of Δ^{10}-n-Undecenoic Acid.*

By PETER GAUBERT, R. P. LINSTEAD, and H. N. RYDON.

Syntheses of Δ^6-*n*-heptenoic, Δ^8-*n*-nonenoic, and Δ^{10}-*n*-undecenoic acids are described. The last-named product is identical with the material made from castor oil; thus, after sixty years, the constitution of this acid receives synthetic confirmation.

ALTHOUGH Δ^{10}-*n*-undecenoic acid was first obtained sixty years ago by the pyrolytic distillation of castor oil under reduced pressure (Krafft, *Ber.*, 1877, **10**, 2034) and is an intermediate in the perfume industry, no synthetic evidence as to its constitution has been put forward. Its accepted structure rests on the facts that it yields sebacic acid on oxidation (Becker, *Ber.*, 1878, **11**, 1414; Krafft and Seldis, *Ber.*, 1900, **33**, 3572; Chuit and co-workers, *Helv. Chim. Acta*, 1926, **9**, 1074), and *n*-undecoic acid on reduction (Krafft, *Ber.*, 1878, **11**, 2219; Fokin, *Z. angew. Chem.*, 1908, **22**, 1499). The other degradative evidence, *viz.*, the production of acetic and *n*-nonoic acids by alkali-fusion (Becker, *loc. cit.*), is anomalous and recalls the misleading alkali-fusion of oleic acid.

The starting material for our synthesis was Δ^4-*n*-pentenol (I; $n = 3$), which can be obtained in good yield by the action of sodium on the readily accessible tetrahydrofurfuryl chloride (Paul, *Bull. Soc. chim.*, 1935, **2**, 745). The synthesis was carried out by the straightforward but arduous process of repeating the following series of reactions three times, n being successively 3, 5, and 7 :

$$\begin{tikzcd}
\text{(I.)}\ CH_2{:}CH{\cdot}[CH_2]_n{\cdot}OH \arrow[r, "PBr_3", "C_5H_5N"'] & CH_2{:}CH{\cdot}[CH_2]_n{\cdot}Br\ \text{(II.)} \arrow[d, "CHNa(CO_2Et)_2"] \\
\text{(IV.)}\ CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH(CO_2H)_2 \arrow[d, "-CO_2"] & CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH(CO_2Et)_2\ \text{(III.)} \arrow[l, "\text{hydrolysis}"'] \\
\text{(V.)}\ CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}CO_2H \arrow[r, "\text{reduction}", "\text{of ester}"'] & CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}CH_2{\cdot}OH
\end{tikzcd}$$

Δ^6-*n*-Heptenoic acid (V; $n = 3$), obtained from the first series of reactions, had previously been prepared by Wallach (*Annalen*, 1900, **312**, 207) by the action of nitrous acid on 7-amino-*n*-heptoic acid, and by Fairweather (*Proc. Roy. Soc. Edin.*, 1926, **46**, 71) as a by-product in the electrolysis of the half-ester of suberic acid; the latter method did not appear suitable for the preparation of large quantities of material, and the purity of the product prepared by Wallach's method was uncertain (cf. Linstead and Rydon, J., 1934, 1996). The structure of our synthetic acid was proved by oxidation to adipic acid.

The second series of reactions, starting with Δ^6-n-*heptenol* (I; $n = 5$), obtained by reduction of ethyl Δ^6-*n*-heptenoate, yielded Δ^8-*n*-nonenoic acid (V; $n = 5$). This acid had previously also been prepared by an electrolytic method (Franke and Liebermann, *Monatsh.*, 1922, **43**, 4596; cf. Crum Brown and Walker, *Annalen*, 1893, **274**, 61). The structure of our material was confirmed by oxidation, by means of potassium permanganate in sodium bicarbonate solution, to suberic acid. A similar oxidation in potassium hydroxide solution gave a product containing much pimelic acid; this is another example of the type of abnormal oxidation discovered by Lapworth and Mottram (J., 1925, **127**, 1987; cf. Green and Hilditch, this vol., p. 764).

The third series of operations starting with Δ^8-*n*-nonenol (I; $n = 7$), prepared from ethyl Δ^8-*n*-nonenoate, yielded Δ^{10}-*n*-undecenoic acid (V; $n = 7$). The recrystallised synthetic material melted at 24—24·5°; a mixture of this with a purified specimen of the product from castor oil, m. p. 24·5—25° (for which we are much indebted to Dr. J. C. Smith), melted at 24—25°.

EXPERIMENTAL.

Δ^6-n-*Heptenoic Acid.*—The following is an improvement of the earlier methods for the preparation of Δ^4-*n*-pentenol (Paul, *loc. cit.*; *Bull. Soc. chim.*, 1933, **53**, 424; Robinson and L. H. Smith, J., 1936, 196). A mixture of 290 g. of tetrahydrofurfuryl chloride (Kirner, *J. Amer. Chem. Soc.*, 1930, **52**, 3251) and 300 c.c. of dry ether was added in drops during 5 hours to a stirred suspension of " molecular " sodium in 500 c.c. of dry ether. After refluxing for a further hour, much of the ether was distilled off and the residue was cautiously decomposed with ice. The ethereal layer was separated, dried over potassium carbonate, and distilled. The yield of Δ^4-*n*-pentenol, b. p. 134—137°/751 mm., was 82%.

A mixture of 200 g. of the pentenol and 50 g. of dry pyridine was added in drops during 5 hours to 252 g. of phosphorus tribromide, mechanically stirred and cooled in ice. The product was distilled (glycerol bath) with continued stirring until thick white fumes appeared.

The distillate was washed with 10% sodium hydroxide solution and water, dried and distilled, yielding 230 g. (67%) of Δ^4-*n*-pentenyl bromide (II; *n* = 3), b. p. 125—129°.

365 G. of the pentenyl bromide were cautiously added to ethyl sodiomalonate prepared from sodium (57 g.), absolute alcohol (570 g.), and ethyl malonate (480 g.). After refluxing overnight, the product was poured into calcium chloride solution and extracted with ether. Distillation of the dried extract yielded 415 g. (74%) of ethyl Δ^4-*n*-pentenylmalonate, b. p. 130—136°/14 mm. A similar experiment with pentenyl chloride (Paul, *Ann. Chim.*, 1932, **18**, 337) in place of the bromide gave only a 46% yield. 257 G. of the pentenylmalonic ester were hydrolysed overnight with a solution of 350 g. of potassium hydroxide in 400 c.c. of water and 50 c.c. of alcohol. The solution was concentrated in a vacuum, acidified, and thoroughly extracted with ether. Evaporation of the dried extract left an oil, which rapidly solidified in a vacuum desiccator; yield, 182 g. (94%). Crystallisation from benzene–light petroleum (b. p. 60—80°) yielded Δ^4-n-*pentenylmalonic acid* (IV; *n* = 3), m. p. 87° (Found: C, 55·6; H, 6·9. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%).

30 G. of the pentenylmalonic acid were decarboxylated at 150° for 24 hours. The cooled product was treated with an excess of aqueous sodium bicarbonate, and neutral by-products removed with ether; the residual solution was acidified and extracted with ether. Two distillations of the dried extract afforded 15 g. (67%) of Δ^6-*n*-heptenoic acid (V; *n* = 3), b. p. 125°/15 mm., m. p. − 6·5°, $n_D^{14·9°}$ 1·4404, $d_{4°}^{14·9°}$ 0·9515, $[R_L]_D$ 35·50 (calc., 35·60) (Found: C, 66·1; H, 9·6; equiv., 129. Calc.: C, 65·6; H, 9·4%; equiv., 128). The p-*toluidide* had m. p. 59·6° after crystallisation from light petroleum (b. p. 40—60°) (Found: C, 77·8; H, 8·9. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·7%).

To an ice-cooled, stirred solution of 3 g. of the acid in aqueous sodium bicarbonate, an excess of 3% potassium permanganate solution was added during 3 hours. After standing overnight, the product was decolourised with sulphur dioxide and thoroughly extracted with ether. Evaporation of the dried extract left a solid; crystallisation from benzene–light petroleum (b. p. 60—80°) yielded 2 g. of adipic acid, m. p. and mixed m. p. 150°.

Δ^8-n-*Nonenoic Acid.*—206 G. of Δ^6-*n*-heptenoic acid were treated with 250 c.c. of thionyl chloride, and the reaction completed by warming on the water-bath for an hour; distillation yielded 220 g. (93%) of Δ^6-*n*-heptenoyl chloride, b. p. 70°/20 mm. 33 G. of this were treated with 30 c.c. of absolute alcohol; after a week the mixture was poured into calcium chloride solution and extracted with ether, and the extract washed, first with sodium bicarbonate solution and then with water. Distillation of the dried extract yielded 33 g. (94%) of ethyl Δ^6-*n*-heptenoate, b. p. 89—91°/22 mm. (Found: C, 69·2; H, 10·3. Calc.: C, 69·2; H, 10·2%). When the mixture was refluxed overnight instead of being kept for a week, the yield was only 67%, much high-boiling material being formed.

A solution of 200 g. of ethyl heptenoate in 1000 c.c. of absolute alcohol was run, as rapidly as possible, on 300 g. of clean sodium contained in a 3 l. 3-necked flask fitted with dropping-funnel, mechanical stirrer, and reflux condenser. After the addition the mixture was heated to 140° and stirred overnight. The product was cooled to 100°, and a further 500 c.c. of alcohol were added; the condenser was then reversed and the heating continued, while water was added from the dropping-funnel, until the distillate was no longer unsaturated. Ethyl alcohol was removed from the first 1500 c.c. of distillate by distillation through a long column. The residue was added to the last runnings from the distillation, and the whole saturated with potassium carbonate and extracted with ether. The product was dried over potassium carbonate and yielded 105 g. (72%) of Δ^6-n-*heptenol* (I; *n* = 5), b. p. 105°/20 mm., $n_D^{20°}$ 1·4403, $d_{4°}^{20°}$ 0·8455, $[R_L]_D$ 35·76 (calc., 35·58) (Found: C, 73·0; H, 12·4. $C_7H_{14}O$ requires C, 73·7; H, 12·3%).

A mixture of 105 g. of the heptenol and 20 g. of pyridine was added dropwise, with ice-cooling and stirring, to 100 g. of phosphorus tribromide during 4 hours. The product was distilled under 10 mm. to a bath temperature of 145°. The distillate was washed thrice with 10% sodium hydroxide solution, twice with water, dried, and re-distilled, affording 94 g. (58%) of Δ^6-n-*heptenyl bromide* (II; *n* = 5), b. p. 77—81°/20 mm., which appeared to contain a little dibromoheptane (Found: Br, 46·2. $C_7H_{13}Br$ requires Br, 45·2%).

The condensation of the heptenyl bromide (92 g.) with the sodio-compound of ethyl malonate (95 g.) was carried out as in the case of the pentenyl bromide. Yield of ethyl Δ^6-*n*-heptenylmalonate (III; *n* = 5) 115 g. (86%), b. p. 138—144°/2 mm. This was hydrolysed overnight with a solution of 150 g. of potassium hydroxide in 200 c.c. of water and a little alcohol. The solution was concentrated under reduced pressure and then acidified. The precipitated acid was removed, and the filtrate extracted with ether; the solid obtained by evaporation of the dried extract was added to the rest of the acid, and the whole crystallised from benzene–light petroleum (b. p. 60—80°), yielding 78 g. (87%) of Δ^6-n-*heptenylmalonic acid* (IV; $n = 5$), m. p. 90—91° [Found: C, 60·0; H, 8·0; equiv., 99·8. $C_{10}H_{16}O_4$ (dibasic) requires C, 60·0; H, 8·0%; equiv., 100].

40 G. of pure heptenylmalonic acid after 4 hours' heating at 140° yielded 26 g. (83%) of Δ^8-n-*nonenoic* acid (V; $n = 5$), b. p. 116—118°/1 mm., m. p. 5°, $n_D^{15°}$ 1·4492, $d_{4°}^{15·8°}$ 0·9146, $[R_L]_D$ 45·77 (calc., 44·83) [Found: C, 68·9; H, 10·3; equiv. (by titration), 155·6. $C_9H_{16}O_2$ requires C, 69·2; H, 10·2%; equiv., 156·0]. This acid has a not unpleasant waxy odour, markedly different from the unpleasant rancid odour of its lower homologues. The p-*toluidide* had m. p. 68° after crystallisation from light petroleum (b. p. 60—80°) (Found: C, 78·0; H, 9·8. $C_{16}H_{23}ON$ requires C, 78·4; H, 9·4%).

Oxidation of 4 g. of the acid with potassium permanganate in sodium bicarbonate solution as before gave 3·2 g. of suberic acid, m. p. 135°, mixed m. p. 135—136°. 2 G. of the acid were similarly oxidised, 10% sodium hydroxide solution being used in place of the bicarbonate; the product (1·7 g.) had m. p. 78—82° and was shown by analysis to be a mixture of pimelic and suberic acids (Found: C, 53·9; H, 7·7; equiv., 84. Calc. for pimelic acid: C, 52·5; H, 7·5%; equiv., 80. Calc. for suberic acid: C, 55·1; H, 8·0%; equiv., 87).

25 G. of the nonenoic acid were treated with 25 c.c. of thionyl chloride, the reaction being completed on the water-bath. Distillation of the product yielded 24 g. (86%) of Δ^8-*n*-nonenoyl chloride, b. p. 110°/30 mm. This was added cautiously to 25 c.c. of absolute alcohol; the mixture was kept at room temperature overnight and then heated on the water-bath for an hour. Ethyl Δ^8-*n*-nonenoate (23 g.; 81%) had b. p. 114—116°/15 mm.

A solution of 23 g. of the ester in 100 c.c. of absolute alcohol was run rapidly on 30 g. of clean sodium under reflux. The product was heated at 140° for 4 hours with mechanical stirring, 100 c.c. of rectified spirit were then run in, followed by 100 c.c. of water, and the Δ^8-n-*nonenol* (I; $n = 7$) was isolated by the procedure described above for Δ^6-*n*-heptenol. Yield, 9 g. (51%), b. p. 135°/20 mm., $n_D^{23°}$ 1·4450, $d_{4°}^{23°}$ 0·8394, $[R_L]_D$ 45·02 (calc., 44·60) (Found: C, 75·6; H, 12·9. $C_9H_{18}O$ requires C, 76·0; H, 12·7%).

A mixture of 9 g. of the nonenol and 1·5 g. of pyridine was added dropwise during 30 minutes to 7 g. of phosphorus tribromide with stirring and ice-cooling. Stirring was continued for 4 hours and the product was then distilled under reduced pressure. The distillate was taken up in ether, washed with dilute sodium hydroxide solution, dried, and redistilled, yielding 8 g. of Δ^8-n-*nonenyl bromide* (II; $n = 7$), b. p. 110—115°/15 mm. (Found: Br, 38·8. $C_9H_{17}Br$ requires Br, 39·0%). The bromide was condensed with ethyl sodiomalonate (from 10·5 g. of ester) to give 9 g. (81%) of ethyl Δ^8-*n*-nonenylmalonate (III; $n = 7$), b. p. 136°/1 mm. On hydrolysis as before, a solid acid was obtained, which was dried on a porous tile and recrystallised from benzene–petroleum (b. p. 80—100°). Δ^8-n-*Nonenylmalonic acid* (IV; $n = 7$) had m. p. 107° (Found: C, 62·5; H, 9·1. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%).

Δ^{10}-n-*Undecenoic Acid.*—8 G. of the nonenylmalonic acid were heated at 140° for 3 hours. The residue, which solidified on cooling, was taken up in sodium bicarbonate solution and freed from neutral matter by ether extraction. The residual solution was acidified and extracted with ether. Distillation of the dried extract yielded 3·4 g. (53%) of Δ^{10}-*n*-undecenoic acid (V; $n = 7$), b. p. 131°/1 mm., m. p. 22—23°. This crystallised from *n*-hexane at − 18° in shining leaflets, m. p. 24—24·5° (compare Ashton and Smith, *loc. cit.*).

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, October 20th,* 1937.]