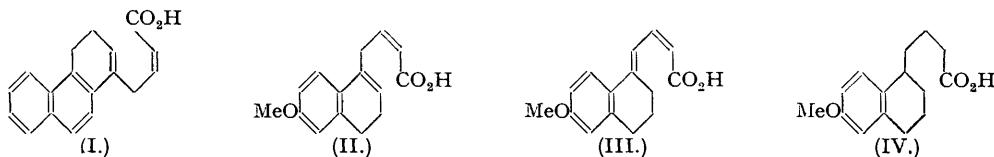


252. γ -6-Methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylidenecrotonic Acid.

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γ -6-Methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylidenecrotonic acid has been prepared and its structure elucidated by oxidative degradation and by measurement of its ultra-violet absorption spectrum. The acid can be used in a convenient new synthesis of 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene.

It has been shown that γ -bromocrotonic esters can be used in the Reformatsky reaction in the same way as α -bromo-esters (Fuson, Arnold, and Cooke, *J. Amer. Chem. Soc.*, 1938, **60**, 2272; Ziegler, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 120) and this method has recently been applied by Cook and Schoental (*J.*, 1945, 288), who suggested the formula (I) for the compound obtained from 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene.



The reaction has now been applied to 6-methoxy-1-tetralone, an acid, $C_{15}H_{16}O_3$, m. p. 189—190°, being obtained after the hydrolysis of the ester first formed. By analogy it was regarded as having structure (II). However, the acid exhibits absorption maxima (in chloroform solution) at 2490 Å. and 3480 Å., $\epsilon = 10,300$ and 30,000 respectively. These figures are in much better agreement with a structure such as (III), since this contains a more extended system of conjugation, though the wave-length of the primary maximum is rather higher than would be expected for even this system—this fact could possibly be ascribed to the “exocyclic” of one of the double bonds. Structure (III) is also supported by the fact that when the acid is oxidised by alkaline potassium permanganate an 80% yield of 6-methoxy-1-tetralone is obtained. Rearrangement of the double bonds is very unlikely under the mild conditions of the oxidation and so the new acid is regarded as γ -6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylidenecrotonic acid (III).

When the acid is heated at 280—300° with palladium-black, a 55% yield of γ -6-methoxy-1-naphthylbutyric acid is obtained. If the *methyl* ester of (III) is similarly heated and the product is hydrolysed, an almost quantitative yield of the naphthalenic acid is obtained. Cyclisation of the acid thus formed yields 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (Bachmann, Cole, and Wilds, *J. Amer. Chem. Soc.*, 1940, **62**, 284) which is a useful intermediate in the production of synthetic hormones, particularly those of the doisyonic acid series (Heer, Billeter, and Miescher, *Helv. Chim. Acta*, 1945, **28**, 1342); the method now described is a very convenient one for the preparation of this ketone.

Reduction of the acid (III) in acetic acid-ethanol solution using a palladium catalyst, or in aqueous alkaline solution using a Raney nickel catalyst, gives a high yield of γ -6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylbutyric acid (IV), and when heated with sulphur at 200° this is converted into γ -6-methoxy-1-naphthylbutyric acid (compare Haberland, *Ber.*, 1936 **69**, 1380). These reactions provide an alternative route for the conversion of the acid (III) into 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene.

EXPERIMENTAL.

(M. ps. were determined in sealed capillaries and are uncorrected.)

γ-6-Methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylidenecrotonic Acid (III).—Zinc wool (35 g.) was placed in a large flask, dry benzene (400 c.c.) containing mercuric chloride (100 mg.) added, and the mixture warmed for 15 minutes. 6-Methoxy-1-tetralone (94 g.) was added and then ethyl *γ*-bromocrotonate (114 g., b. p. 80—85°/2 mm., prepared essentially by the method of Ziegler *et al.*, *Annalen*, 1942, 551, 80) was run in at such a rate that the reaction proceeded at a vigorous but controllable pace. The mixture was heated under reflux for a further hour after all the ester had been added, and by this time a deep red complex had separated and most of the zinc had dissolved. The mixture was cooled and decomposed by shaking it with 2*N*-hydrochloric acid (500 c.c.). The product was extracted with ether, and the extract was washed with water, evaporated, and heated under reflux for 2 hours with potassium hydroxide (50 g.) in methanol (500 c.c.) and water (100 c.c.). The mixture was diluted with water and extracted with ether—this extract contained unchanged ketone (50 g.)—and then the aqueous layer was acidified, a yellow precipitate of the unsaturated acid being formed. The solid (28 g.) was collected and recrystallised from acetone or methanol; it formed hard prisms, m. p. 189—190° (Found : C, 73.2; H, 6.8. C₁₅H₁₆O₃ requires C, 73.7; H, 6.6%).

The methyl ester was prepared by the action of an ethereal solution of diazomethane on the acid or by refluxing the acid (10 g.) with methanol (80 c.c.) containing acetyl chloride (10 c.c.) for one hour (compare Riegel and Moffat, *J. Amer. Chem. Soc.*, 1943, 65, 1971). In each case the crystalline residue obtained after evaporating off the solvents was recrystallised from methanol, giving lemon-yellow prismatic plates of the ester, m. p. 85—86° (Found : C, 74.2; H, 7.2. C₁₆H₁₈O₃ requires C, 74.4; H, 7.0%).

Oxidation of Acid (III).—The acid (2 g.) was dissolved in excess of 2*N*-sodium carbonate, and finely powdered potassium permanganate was added to the stirred solution until the supernatant liquid remained coloured. The product was extracted with ether, and the extract dried (Na₂SO₄) and evaporated. 6-Methoxy-1-tetralone (1.15 g., 80%), m. p. 78—79° (undepressed by admixture with an authentic specimen of m. p. 79°), was obtained.

γ-6-Methoxy-1-naphthylbutyric Acid.—The methyl ester of (III) (10 g.) was heated at 280—300° for 1 hour in a metal-bath with palladium-black (700 mg.). The product was dissolved in methanol (60 c.c.), potassium hydroxide (10 g. in 10 c.c. of water) added, and the mixture heated under reflux for 2 hours. The cooled solution was filtered and then acidified with dilute hydrochloric acid; the naphthalenic acid (9.7 g.), m. p. 149—151°, was thus precipitated (Cohen, Cook, and Hewett, *J.*, 1936, 52, give m. p. 150—151°).

Reduction of Acid (III).—(a) The acid (1.0 g.) was dissolved in ethanol (75 c.c.) and acetic acid (10 c.c.), and after addition of palladium-strontium carbonate (500 mg. containing 5% palladium) the solution was shaken in an atmosphere of hydrogen. Hydrogen was rapidly absorbed, and after $\frac{1}{2}$ hour the theoretical volume of gas (calculated for the reduction of two double bonds) had been taken up. The solvents were evaporated, and the oily residue was crystallised from light petroleum (b. p. 60—80°), giving the required acid, m. p. 76—78° (900 mg.) (Haberland, *loc. cit.*, gives m. p. 79°).

(b) The acid (2.5 g.) was dissolved in water (25 c.c.) containing sodium hydroxide (6 c.c. 2*N*), Raney nickel catalyst (1 g.) added, and the mixture shaken in an atmosphere of hydrogen. The theoretical volume of hydrogen was absorbed in 3 hours. After filtration, the solution was acidified, and the oily precipitate crystallised from light petroleum. In this way 2.1 g. of the required acid, m. p. 77°, were obtained.

When the acid prepared by either method was heated at 200° for 3 hours with $\frac{1}{2}$ its weight of sulphur, *γ*-6-methoxy-1-naphthylbutyric acid, m. p. 149—150°, was obtained.

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