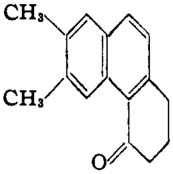
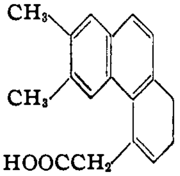
1-Keto-1,2,3,4,5,11-hexahydro-9,10-dimethyl-pyrene

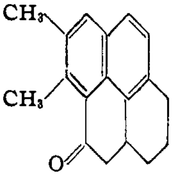
By condensation of 2,3-dimethylnaphthalene with succinic anhydride and subsequent reduction and cyclization, Haworth[1] has prepared 4-keto-1,2,3,4-tetrahydro-6,7-dimethylphenanthrene, m. p. 112° (I). By treatment with zinc and methyl bromoacetate and subsequent dehydration (with phosphorus pentoxide in benzene) and hydrolysis, 6,7-dimethyl-1,2-dihydro-4-phenanthrylacetic acid (II) was obtained.[2] By cyclization of the corresponding tetrahydrophenanthrene derivative 1-keto-1,2,3,4,5,11-hexahydro-9,10-dimethyl-pyrene (III) was prepared, which might be an interesting starting material for the synthesis of complex polycyclic hydrocarbons.



I



II



III

6,7-Dimethyl-1,2-dihydro-4-phenanthrylacetic acid (II). The ketone (I) (5 g.) was heated with zinc wool (2.4 g.) and methyl bromoacetate (4.5 cc.) in benzene (50 cc.) for twenty minutes on the water-bath. The reaction product was treated with dilute sulfuric acid and the solvent distilled off after washing with sodium carbonate solution and drying. The residue was boiled with phosphorus pentoxide (3 g.) and benzene (10 cc.) for one hour. The unsaturated ester of (II) was not purified but treated directly for six hours with boiling 20% methyl alcoholic potassium hydroxide solution. The methyl alcohol was removed with steam and the aqueous solution extracted with ether, filtered and acidified with dilute hydrochloric acid; from glacial acetic acid m. p. 186°; yield, 1.5 g.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.2; H, 7.0.

1-Keto-1,2,3,4,5,11-hexahydro-9,10-dimethyl-pyrene (III): The preceding acid (1.5 g.) was hydrogenated in glacial acetic acid (60 cc.) in presence of a palladium hydroxide–barium sulfate catalyst.[3] The theoretical quantity of hydrogen was quickly absorbed. The residue of the filtered solution, after the removal of the solvent *in vacuo*, was boiled for two hours with phosphorus pentoxide (10 g.) in toluene (20 cc.). Treatment of the product with ice, washing with water and removal of the solvent gave an oil which distilled under 5 mm. pressure between 190–200°. On trituration with alcohol, the distillate solidified; from isopropyl alcohol, m. p. 160°; yield, 1 g.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.4; H, 7.2. Found: C, 86.6; H, 7.6.

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[1] Haworth and co-workers, *J. Chem. Soc.*, 2250 (1932); 458 (1934).

[2] The isomeric formula with semicyclic double bond is, of course, not excluded.

[3] Kuhn and Stroebele, *Ber.*, **70**, 785 (1937).

DEPARTMENT OF ORGANIC CHEMISTRY
HEBREW UNIVERSITY
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RECEIVED JUNE 12, 1944

N-(*p*-Ethoxyphenyl)-4-acetamidoanthranilic Acid

A solution of 10.7 g. of 2-chloro-4-acetamidobenzoic acid in dilute potassium carbonate solution (6.9 g. in 25 cc. of water) was refluxed with efficient mechanical stirring for three hours with 7 cc. of *p*-phenetidine and 0.3 g. of copper powder. Then 40 cc. of water, 0.5 g. of sodium sulfide and 1.5 g. of Norite were added; the mixture was refluxed for fifteen minutes and filtered hot. The cooled filtrate was acidified with 7.5 cc. of concentrated hydrochloric acid. The gray solid that precipitated was filtered, washed with water and then dissolved in 70 cc. of 5% sodium hydroxide solution, boiled with 1.5 g. of Norite, filtered, cooled, and acidified. The product was almost colorless after washing with water until free of salts; yield, 10.8 g. (69%); m. p. 204–208°. After several recrystallizations from methanol-dioxane, white feathery needles, m. p. 213–214°, were obtained.

Anal. Calcd. for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; neut. equiv., 314. Found: C, 64.77; H, 5.80; neut. equiv., 320.

WINTHROP CHEMICAL COMPANY, INC. RICHARD CARROLL
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RECEIVED JUNE 27, 1944

Crotyl Malonate, Methylvinylcarbinyl Malonate and Cinnamyl Cyanoacetate

Crotyl Malonate.—Ethyl malonate (0.5 mole) was added to a solution of sodium (0.3 g.) in crotyl alcohol (1.5 moles) in a flask attached to an adiabatic, total-reflux, variable take-off type column with a 30 × 1.2 cm. section packed with glass helices. Ethyl alcohol (40 g.) was distilled from the mixture during three hours. Ether was added to the residue, and the solution was washed with dilute hydrochloric acid, dried over sodium sulfate, and concentrated *in vacuo*. Distillation through a Widmer column yielded 85 g. (80%) of crotyl malonate; b. p. 83–84° (0.1 mm.); $n^{25}D$ 1.4547; $d^{25}{}_{25}$ 1.0385; *M*D calcd. 55.38, found 55.57.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.29; H, 7.53.

Methylvinylcarbinyl Malonate.—This ester was obtained from methylvinylcarbinol and ethyl malonate by the procedure described above in 38% yield; b. p. 112–113° (7 mm.); $n^{25}D$ 1.4381; $d^{25}{}_{25}$ 1.0080; *M*D calcd. 55.38, found 55.44.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.18; H, 7.53.

The mixed ester, ethyl methylvinylcarbinyl malonate, was also isolated from the reaction mixture as a lower boiling fraction in 28% yield; b. p. 98–99° (7 mm.); $n^{25}D$ 1.4270; $d^{25}{}_{25}$ 1.0279; *M*D calcd. 46.61, found 46.64.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.06; H, 7.58. Found: C, 58.23; H, 7.51.

Cinnamyl Cyanoacetate.—Ethyl cyanoacetate (20 g.) and benzene (25 g.) were added to a solution of 0.1 g. of sodium in 25 g. of cinnamyl alcohol. The benzene–ethanol azeotrope was removed by distillation through the total-reflux type column during five hours. The product was washed and distilled, and yielded 14.3 g. of cinnamyl cyanoacetate, b. p. 163–166° (1.2 mm.). The ester solidified and was recrystallized from a mixture of ether and pentane; m. p. 56.5–57°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51. Found: C, 71.43; H, 5.38.

Pyrolysis of the Esters.—Previous work has shown that allyl-type esters of acetoacetic and benzoylacetic acid produce carbon dioxide and fair to good yields of pure γ,δ-unsaturated ketones on heating at 170–230°. In contrast to these results, crotyl malonate (35.4 g.), heated at 210–250° for seven hours, gave 2.54 liters (68%) of carbon dioxide and 12.3 g. of a mixture of esters, b. p. 93–107° (12 mm.), $n^{25}D$ 1.4400. This mixture was probably composed of the isomers $CH_2{=}CHCH(CH_3)CH_2COOCH_2\text{-}CH{=}CHCH_3$ and $CH_3CH{=}CHCH_2CH_2COOCH_2CH{=}CHCH_3$, for the middle fraction, b. p. 96–97.5° (15 mm.), $n^{25}D$ 1.4398, analyzed correctly (other isomers may be present but are less probable).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.45; H, 9.60.

Methylvinylcarbinyl malonate gave similar results on heating, while cinnamyl cyanoacetate gave 91% of the theoretical amount of carbon dioxide in one hour at 240° and was converted into a dark, solid resin.