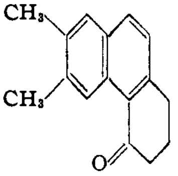
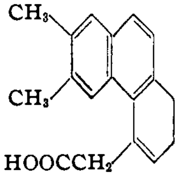
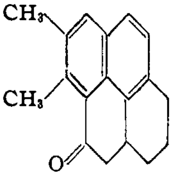
1-Keto-1,2,3,4,5,11-hexahydro-9,10-dimethyl-pyrene

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
JERUSALEM, PALESTINE ELIAHU BOGRACHOV

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
RENSSELAER, NEW YORK WARREN D. MCPHEE

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 $CH_2{=}CHCH(CH_3)CH_2COOCH_2{-}CH{=}CHCH_3$ 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.

Allyl-type esters of β-keto acids may be represented as rearranging through chelated enol forms.[1] It may be significant that in these cases in which enol forms exist either not at all or to a very small extent, the rearrangement does not proceed smoothly. The results could also be interpreted as resulting from weaker activation of the central methylene group by CN and COOR groups than by COR groups.

Carroll has heated ethyl malonate with allyl, crotyl and cinnamyl alcohols and phenylvinylcarbinol, in the presence of a small amount of sodium acetate, and observed that unsaturated acids are formed when the reaction mixtures are saponified.[2]

We are indebted to Mr. Saul Gottlieb for microanalyses.

DEPARTMENT OF CHEMISTRY
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WALTER KIMEL
ARTHUR C. COPE

RECEIVED NOVEMBER 12, 1943

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[1] Kimel and Cope, THIS JOURNAL, **65**, 1992 (1943).

[2] Carroll, *J. Chem. Soc.*, 507 (1941). See ref. 1 concerning the elation of Carroll's work to this investigation.

NEW BOOK

Lectures on the Inorganic Nutrition of Plants. (Prather Lectures at Harvard University.) By D. R. HOAGLAND, Professor of Plant Nutrition, University of California. The Chronica Botanica Co., Waltham, Mass.; G. E. Stechert and Co., 31 East 10th Street, New York, N. Y., 1944. 226 pp. Illustrated, 15.5 × 23.5 cm. Price, $4.00.

The seven lectures included in this volume comprise five Prather Lectures delivered at Harvard University and two supplementary lectures on allied topics. The introductory lecture deals with the main problems of plant nutrition, and with the trends of present-day research upon the relationship between the plant and the soil in which it normally grows. In the second lecture, the so-called micronutrient elements are considered. These include the ions of copper, zinc, manganese, boron, and possibly molybdenum, now fairly generally recognized as being essential, although only in minute amounts, for plant nutrition. Particular attention is devoted to zinc.

In the third lecture the absorption and accumulation of salts by plants is described with especial emphasis on the intimate relationship of these processes to the metabolism of the cells of the root tissue; in the fourth, the movement of inorganic ions within the plant, again with emphasis upon the essential share taken by the metabolism of the living cells. The fifth lecture describes the conditions that have been found to be necessary for the successful growth of plants in artificial culture media.

In the first of the two supplementary lectures, various problems having to do with the chemical composition of plant tissues, and with current hypotheses that have been advanced to account for the behavior of some of the more important components, are discussed, while the last lecture deals with the fundamentally important but little understood question of potassium nutrition in plants.

The numerous experiments mentioned are comprehensively illustrated by text figures and plates. Much of the material is derived from the wide experience of the Berkeley group, and, as might be anticipated, full advantage has been taken of the unique opportunities at the University of California for the use of radioactive isotopes to detect and follow the behavior of individual inorganic ions in plants. Although brief and, for the most part, nontechnical, the treatment is stimulating and suggestive, and great stress is laid upon the fact that our present-day knowledge is far from satisfactory and by no means comprehensive. To quote the distinguished author: "Plant nutrition is not of itself a science. Its study rests on the application of other sciences to a vastly complex system. Progress is slow and laborious. There does not usually exist the possibility of setting down in the precise and elegant terms of the physical scientist the course of events in the growing plant."

Students of the plant sciences and biochemists in general have reason to be grateful for this concise summary of the work of Professor Hoagland and his associates, and it is to be hoped that it may serve to attract attention to the innumerable problems awaiting solution and description in the "precise terms of the physical scientist."

H. B. VICKERY

BOOKS RECEIVED

July 10, 1944–August 10, 1944

JEROME ALEXANDER, Editor. "Colloid Chemistry, Theoretical and Applied." Volume V. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y. 1256 pp. $20.00.

LOUIS F. FIESER and MARY FIESER. "Organic Chemistry." D. C. Heath and Company, 285 Columbus Avenue, Boston, Mass. 1112 pp. $8.00 (College edition, $6.00).

SAMUEL GLASSTONE. "Theoretical Chemistry." D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y. 515 pp. $5.00.

PASCUAL JORDAN. "Physics of the 20th Century." Philosophical Library, Inc., 15 East 40th Street, New York (16), N. Y. 185 pp. $4.00.

F. F. NORD and C. H. WERKMAN, Editors. "Advances in Enzymology." Volume IV. Interscience Publishers, Inc., 215 Fourth Avenue, New York (3), N. Y. 332 pp. $5.50.