

the rate of the alkaline hydrolysis. In this figure the abscissas are the logarithms of Kindler's³ rate constants for the hydrolysis of the three

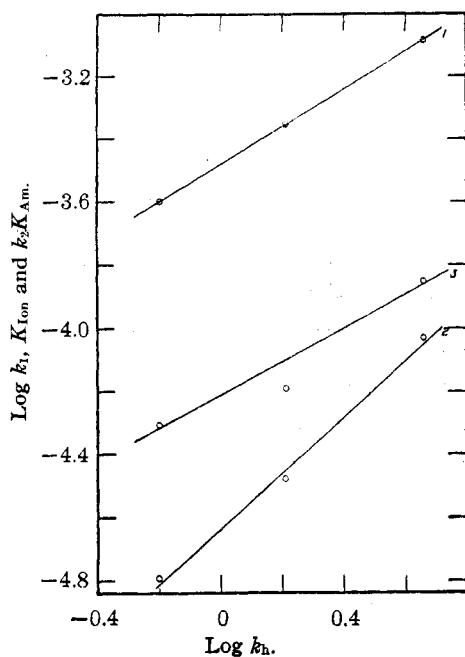


Fig. 3.

phenylacetic esters. In curve 1 the ordinates are the logarithms of our k_1 , in the curve 2 they are the logarithms of our $k_2 K_{Am}$. It is especially worthy of note that the correlation exists for the reaction

of electrically neutral ammonia (k_1) with the ester as well as for the reaction of negatively charged amide ion ($k_2 K_{Am}$).

That the existence of this correlation may be taken as serious evidence for a similarity in mechanism is shown by curve 3 in Fig. 3 in which the ordinates are the ionization constants of the corresponding phenylacetic acids. The constants for this reaction, whose mechanism is of necessity fundamentally different from the others, do show a parallel trend with the other constants, but the deviations from linearity are unmistakably larger.

Summary

The rate of reaction of methyl phenylacetate and of its *p*-chloro and *p*-nitro derivatives with ammonia in methanol solution has been measured at 25°. The reaction shows considerable deviation from second order course, the source of which is not clear. It is markedly retarded by ammonium chloride and strongly accelerated by sodium methylate. The quantitative study of these effects indicates that there is an uncatalyzed reaction of ester with ammonia and a parallel base catalyzed reaction, presumably a reaction of ester with amide ion. There exist linear relationships between the logarithms of the rates of both catalyzed and uncatalyzed reactions and the rates of hydrolysis of the same esters.

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NOTES

Synthesis of 2,3-Cyclopentenophenanthrene

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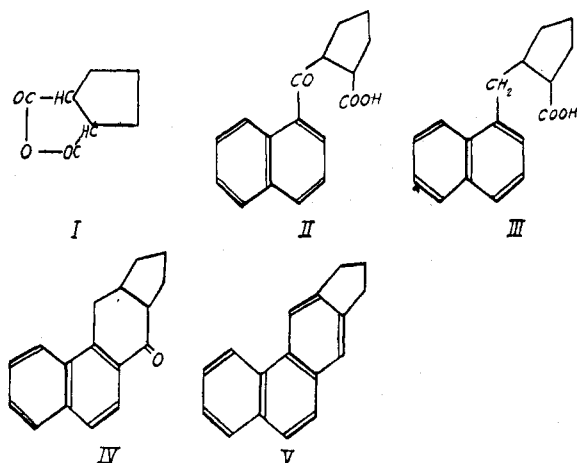
While the synthesis of 1,2-cyclopentenophenanthrenes can be effected by various methods, no way is known so far, leading to the series of 2,3-cyclopentenophenanthrene (V). In order to determine its physical properties (spectrum, formation of mixed crystals with similar phenanthrene derivatives, especially of the cyclopentenophenanthrene type), we prepared (V) by an unambiguous method.

The starting material for our synthesis was the anhydride of cyclopentane-1,2-dicarboxylic

acid (I), which was reacted upon with α -naphthylmagnesium bromide, using the method of Weizmann and co-workers.¹ The resulting 1-(α -naphthoyl)-cyclopentane-2-carboxylic acid (II) was reduced with amalgamated zinc wool and gave 1-(α -naphthyl-methyl)-cyclopentane-2-carboxylic acid (III). Its cyclization to give 2,3-cyclopentano-1-keto-1,2,3,4-tetrahydrophenanthrene (IV) was effected with difficulty, the best reagent proving to be phosphoric oxide in boiling benzene. Clemmensen reduction of the ketone (IV) and dehydrogenation with selenium gave the desired hydrocarbon (V).

(1) Weizmann and co-workers, *J. Chem. Soc.*, 1370 (1935).

While this work was in progress, Bachmann² reported some preliminary experiments on the cyclization of (3-phenanthryl)-propionic acid. The cyclization product was assumed to be 1'-keto-2,3-cyclopentenophenanthrene, the isomeric formula of 1'-keto-3,4-cyclopentenophenanthrene being assumed to be less likely. According to the evidence presented by Hillemann³ the latter formula should be preferred. It will be interesting to compare our substance (V) with 2,3-dimethylphenanthrene which is available by two independent methods.⁴



Experimental

Cyclopentane-1,2-dicarboxylic acid anhydride (I) was prepared according to Wassermann⁵ from the acid with boiling acetic anhydride.

1-(α -Naphthoyl)-cyclopentane-2-carboxylic Acid (II).—The Grignard solution prepared from bromonaphthalene (8.5 cc.) and magnesium (1.4 g.) was added to an ethereal solution of the above anhydride (7.2 g.). The violent interaction produced a white crystalline precipitate, which after three hours of boiling was decomposed with cold dilute sulfuric acid. Most of the keto acid (7.1 g.) separated spontaneously; a second crop (1.25 g.) was extracted from the ethereal layer with soda solution, acidified and triturated with methanol and ether. The keto acid contains water of crystallization. (Found at 80° *in vacuo*: H₂O, 9.1. Calcd. for C₁₇H₁₆O₃ + 1.5 H₂O: H₂O, 9.1). By recrystallization from methyl alcohol, it is obtained in prismatic hexagons, which give perfect analytical figures, but melt at 169–170° after prolonged sintering. We ascribe this fact to spontaneous conversion into the hydroxylactone form. (Calcd. for C₁₇H₁₆O₃: C, 76.1; H, 6.0. Found: C, 75.7; H, 6.0.)

1-(α -Naphthyl-methyl)-cyclopentane-2-carboxylic Acid (III).—The keto acid (II) (12 g.) and amalgamated

zinc wool (120 g.) were heated with a mixture of concentrated hydrochloric acid and water (1:1), until the metal had completely disappeared, from time to time some more concentrated acid being added. The acid (III) was extracted with ether and crystallized spontaneously, on evaporation of the solvent, yield, 9.2 g. It was triturated with petroleum ether, collected and recrystallized from a small quantity of ethyl acetate to rhombic crystals, m. p. 99–101°. (Calcd. for C₁₇H₁₈O₂: C, 80.3; H, 7.1. Found: C, 80.0; H, 7.2.)

1-Keto-2,3-cyclopentano-1,2,3,4-tetrahydrophenanthrene (IV).—(a) The acid (III) (2 g.) was heated at 115–120° for two hours (oil-bath) with tin chloride (3 cc.) and toluene (4 cc.) and poured out into ice-cold concentrated hydrochloric acid. The toluene solution, addition with ether, was washed with hydrochloric acid of decreasing concentration, then with soda solution and water. On evaporation of the solvent, the residue crystallized spontaneously. Triturated with methanol, it gave the ketone in a nearly pure condition (0.25 g.). It was recrystallized from propyl alcohol; needles, m. p. 163–164°. (Calcd. for C₁₇H₁₆O: C, 86.4; H, 6.8. Found: C, 86.3, 85.7; H, 6.5, 6.5.)

(b) The acid (III) (0.5 g.) in benzene (7.5 cc.) was heated on the water-bath for three hours with phosphoric oxide (3 g.). The mass was decomposed with ice, ether was added and the organic layer extracted with soda solution. On evaporation of the ether and the benzene, the ketone remained in pure, crystalline state (0.05 g.). This method proved to be the most convenient one.

(c) Cyclization with sulfuric acid gave variable results.

2,3-Cyclopentano-1,2,3,4-tetrahydrophenanthrene.—The above ketone (IV) (0.7 g.) was reduced with zinc wool (7 g.) according to the method described above. The hydrocarbon crystallized spontaneously (0.5 g.) and was recrystallized from petroleum ether; broad needles, m. p. 119–121°. (Calcd. for C₁₇H₁₈: C, 91.9; H, 8.1. Found: C, 92.0, 92.2; H, 8.2, 8.3.)

2,3-Cyclopentenophenanthrene (V).—The tetrahydro compound (0.5 g.) was heated to 320–340° with selenium (2 g.) for twenty-four hours (sealed tube). The product was extracted with boiling mixture of ether and acetone and the solvent evaporated. The residue was distilled at 0.05 mm., whereupon it crystallized spontaneously; yield 0.38 g. Recrystallization from ethyl alcohol, diluted with some propyl alcohol, gave prismatic plates, m. p. 85–85.5°. (Calcd. for C₁₇H₁₄: C, 93.5; H, 6.5. Found: C, 93.1, 93.0; H, 6.8, 6.8.)

THE DANIEL SIEFF RESEARCH INSTITUTE
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Synthesis of Methylcholanthrene

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Among the aromatic degradation products of sterols, bile acids and similar substances two are of special interest, since they contain nearly all the carbon atoms of the starting materials: the hydrocarbon C₂₂H₂₀ from cholic acid and its

(2) Bachmann, *THIS JOURNAL*, **57**, 1381 (1935).

(3) Hillemann, *Ber.*, **69**, 2610 (1936).

(4) Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934); Fieser and Hershberg, *THIS JOURNAL*, **57**, 1508 (1935).

(5) Wassermann, *Helv. Chim. Acta*, **13**, 207, 228 (1930); see there for references.