375. *Some Derivatives of Phenalene.**

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An attempt has been made to prepare alkyl derivatives of the little-investigated phenalene (I). 1-*Methyldihydrophenalen*-7-*one* has been synthesised. 7-*Hydroxy*-1-*methyldihydrophenalene* also has been prepared, but its dehydration has not been accomplished satisfactorily.

THE experiments herein described were completed before August, 1936, and are now placed on record in view of the publications of Koelsch (*J. Amer. Chem. Soc.*, 1936, **58**, 1326; Koelsch and Rosenwald, *ibid.*, 1937, **59**, 2167) dealing with similar topics.

The original object of the present work was the synthesis of an alkylphenalene. By analogy with the two tautomerides of an unsymmetrical indene, an alkylphenalene might exist in six forms, each of the three six-membered rings assuming the aromatic and the unsaturated character in turn.

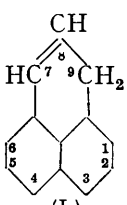
A possible method of testing the tautomerism of these hydrocarbons is the investigation

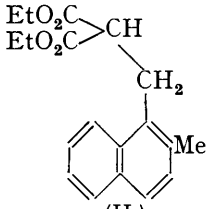
* The name "perinaphthindane" suggested by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1938, **60**, 1659) does not appear to be satisfactory in view of the fact that it suggests a tetracyclic compound, indane already containing a benzene nucleus.

of the oxidation products of an alkylphenalene. If six-fold tautomerism occurs, the oxidation might yield a mixture of three dicarboxylic acids.

The syntheses of 1-methylphenalene and 1 : 7-dimethylphenalene have been attempted with the above object in view, but difficulties were encountered in the final stages. 1-Chloromethyl-2-methylnaphthalene was obtained from 2-methylnaphthalene by the method of Anderson and Short (J., 1933, 485). This compound had been prepared by Ziegler and Tiemann (*Ber.*, 1922, **55**, 3410) from 1-bromo-2-methylnaphthalene and by Darzens and Lévy (*Compt. rend.*, 1936, **202**, 73). The prescription of the latter authors appears to be the most satisfactory and therefore we do not describe our modification of the method of Anderson and Short.

The condensation of 1-chloromethyl-2-methylnaphthalene with ethyl sodiomalonate to give (II), the hydrolysis and decarboxylation to β-2-*methyl*-1-*naphthylpropionic acid* (III), and the ring closure of the chloride of the acid (III) to 1-*methyldihydrophenalen*-7-*one* (IV) were carried out by methods similar to those used by Mayer and Sieglitz (*Ber.*, 1922, **55**, 1835) in the series 1-bromomethylnaphthalene to dihydrophenalen-7-one.


(I.)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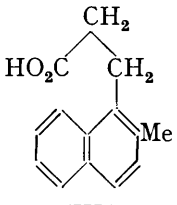
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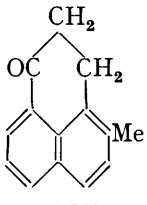
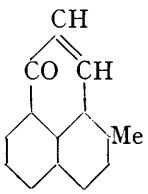

(IV.)

The dehydration of β-1-naphthylpropionic acid might occur in the alternative direction with formation of 4 : 5-benzindan-1-one, but such a ring closure is excluded in the case of β-2-methyl-1-naphthylpropionic acid.

The ketone, m. p. 49—50°, which we obtained and used for the preparation of derivatives was bright yellow. We suspected that it might be methylphenalenone (V), but the analyses of the substance and its oxime and the formation of the orange-coloured *methylperinaphthacridine* (VI) caused us to reject this view. Professor J. W. Cook has kindly drawn our attention to the work of Cook and Hewett (J., 1934, 365) and of Darzens and Lévy (*Compt. rend.*, 1935, **201**, 902), from which it appears that the ketone should be colourless. Application of the procedure of Cook and Hewett showed that this surmise is probably correct; the purified substance, m. p. 54—55°, is very faintly yellow and evaporation of the mother-liquor from the last crystallisation gave a few colourless crystals. It is probable, therefore, that the yellow ketone is substantially (IV) contaminated with a little (V).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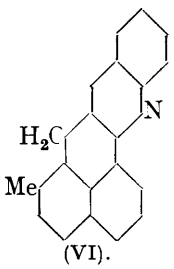
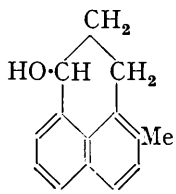

(VI).


(VII).

Two routes possibly leading to 1-methylphenalene from (IV) have been explored. The reduction to 7-*hydroxy*-1-*methyldihydrophenalene* (VII) was accomplished by the Pondorff method (*Z. angew. Chem.*, 1926, **39**, 138). The attempted dehydration of this by the Tschugaeff reaction gave a product the picrate of which afforded unsatisfactory analytical data.

The oxime of (IV) has been reduced to 7-*amino*-1-*methyldihydrophenalene*. The exhaustive methylation of this was attempted, but the results were again not promising.

Experimental.

Ethyl 2-Methyl-1-naphthylmethylmalonate (II).—A solution of 1-chloromethyl-2-methylnaphthalene (106 g.) in a little dry benzene was added slowly to a paste of ethyl sodiomalonate [prepared from ethyl malonate (180 g.) in dry benzene (225 c.c.) and powdered sodium (13·5 g.)]. The mixture was refluxed for 12 hours, cooled, and the sodium chloride removed by washing with water. The benzene solution was dried and distilled. The product (164 g.), b. p. 190—195°/2—3 mm., was a greenish-yellow liquid, which solidified on cooling to a low-melting crystalline mass (yield, 94%) (Found : C, 72·5; H, 7·3. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%).

2-Methyl-1-naphthylmethylmalonic Acid.—The above ester (148 g.) was boiled for 4 hours with a solution of potassium hydroxide (84 g.) in water (200 c.c.). The solution was cooled and acidified with dilute hydrochloric acid. A white solid separated; it crystallised from boiling water in colourless needles, m. p. 172° (decomp.) (Found : C, 70·5; H, 5·9. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·5%).

β-*2-Methyl-1-naphthylpropionic Acid* (III).—The malonic acid (89 g.) was heated at 170—180° until the evolution of carbon dioxide ceased (½ hour). The residue was distilled, b. p. 193—195°/3 mm. The distillate solidified (69 g.) and then crystallised from light petroleum (b. p. 60—80°) in white needles, m. p. 93° (Found : C, 78·5; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%), freely soluble in cold alcohol, ether and acetone and in hot benzene, light petroleum, and acetic acid, and moderately soluble in hot water. Its solution in concentrated sulphuric acid was red.

1-Methyldihydrophenalen-7-one (IV).—The acid chloride of β-2-methyl-1-naphthylpropionic acid was obtained by refluxing the acid (71 g.) with a large excess of thionyl chloride on the steam-bath until no more hydrogen chloride was evolved, and removing the excess of thionyl chloride at 100°/30 mm.

A suspension of powdered anhydrous aluminium chloride (93 g.) in dry light petroleum (b. p. 80—100°; free from unsaturated hydrocarbons) (220 c.c.) was cooled in ice and stirred while the above crude acid chloride, dissolved in dry light petroleum (b. p. 80—100°) (250 c.c.), was added dropwise. The mixture was heated on the steam-bath and stirred for 1¾ hours. It was then poured on ice, and the product extracted with ether. The extract was washed with dilute aqueous sodium hydroxide and water and dried. The dark brown residue after removal of the solvent was distilled and the yellow to orange-red distillate, b. p. 160—210°/3 mm., was collected and redistilled. The product (47 g.), b. p. 170—173°/1·5 mm., was a bright yellow oil, which quickly solidified to a pasty mass of yellow needles. It crystallised from light petroleum (b. p. 40—60°) in bright yellow needles, m. p. 49—50° (Found : C, 85·5; H, 6·2. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%), readily soluble in alcohol, ether, and benzene, and moderately soluble in aqueous alcohol and aqueous acetic acid. Its solution in concentrated sulphuric acid was bright orange.

The concentrated hydrochloric acid washings of a benzene solution were orange-coloured, but gave no precipitate on dilution with water. The ketone recovered from the benzene was crystallised from aqueous methyl alcohol and then from light petroleum and obtained in pale straw-coloured needles, m. p. 54—55° (Found : C, 85·5; H, 6·3%). The sulphuric acid solution was orange-yellow.

The *oxime* was prepared, following Cook, Hewett, and Lawrence (J., 1936, 79), by heating the ketone (3·8 g.), hydroxylamine hydrochloride (1·5 g.), and dry pyridine (20 c.c.) on the steam-bath for 4 hours. It crystallised from alcohol in yellowish leaflets, m. p. 147—149° (Found : C, 79·5; H, 6·2; N, 6·6. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2; N, 6·6%). The 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine in brownish-red needles, m. p. 250° (decomp.) (Found : C, 63·3; H, 4·5. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3%).

Methylperinaphthacridine (VI).—1-Methyldihydrophenalen-7-one (2·4 g.) and *o*-aminobenzaldehyde (1·5 g.) were dissolved in a little warm alcohol. A few drops of concentrated alcoholic potassium hydroxide were added, and the mixture kept overnight. The orange solid formed was recrystallised from alcohol and obtained in fine yellow needles, m. p. 134—137° (Found : C, 89·2; H, 5·5. $C_{21}H_{15}N$ requires C, 89·7; H, 5·4%). The orange solution in alcohol exhibits an intense violet-blue fluorescence; in concentrated sulphuric acid (VI) gives an intense crimson solution, and with dilute hydrochloric acid a red, sparingly soluble hydrochloride is formed. The latter is soluble in alcohol to an orange solution with a greenish-yellow fluorescence.

7-Hydroxy-1-methyldihydrophenalene.—1-Methyldihydrophenalen-7-one (26·2 g.), aluminium *iso*propoxide (31·5 g.), and anhydrous *iso*propyl alcohol (260 c.c.) were so heated at 110—115°

under a fractionating column that about 60 c.c. of liquid distilled in each hour. More *iso*-propyl alcohol was added from time to time to keep the volume of the reaction mixture constant. After 4 hours' heating, acetone could no longer be detected in the distillate and the bulk of the *iso*propyl alcohol was then distilled rapidly; the residue was treated with an excess of 25% aqueous potassium hydroxide. The product was taken up in ether, and the extract washed with dilute acid and with water and dried. The solvent was removed, and the solid residue distilled, b. p. 160—170°/0·8 mm. The substance crystallised from boiling light petroleum (300 c.c., b. p. 80—100°) in long colourless needles (12·6 g.), m. p. 126—127·5° (Found: C, 84·7; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

Attempted Tschugaeff Dehydration of 7-Hydroxy-1-methyldihydrophenalene.—A mixture of the methyldihydrophenalenol (12·5 g.), sodium (1·9 g.), and toluene (200 c.c.) was refluxed for 10 hours, carbon disulphide (10 c.c.) added slowly with shaking to the cooled mixture, and the whole left overnight. Methyl iodide (35 c.c.) was then added, and the mixture refluxed for 4 hours. The sodium iodide formed was removed by shaking with water, and the solvents were distilled from the reaction mixture. The residue was distilled at 40 mm., and the product was redistilled as a yellow oil smelling of sulphur compounds (7·1 g.). It was dissolved in warm alcohol (40 c.c.) and added to a solution of picric acid (10·9 g.) in warm alcohol (200 c.c.). The orange precipitate which separated on cooling was recrystallised twice from alcohol containing some picric acid. The product, orange-brown needles (4·8 g.), had m. p. 128—129·5° (Found: C, 58·8, 58·8; H, 5·0, 4·8; N, 10·7. $C_{14}H_{12},C_6H_3O_7N_3$ requires C, 58·7; H, 3·7; N, 10·3%. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2%. $C_{14}H_{18},C_6H_3O_7N_3$ requires C, 57·9; H, 5·1; N, 10·1%).

7-Amino-1-methyldihydrophenalene.—A mixture of 1-methyldihydrophenalen-7-one oxime (4·2 g.), absolute alcohol (150 c.c.), and glacial acetic acid (20 c.c.) was heated to 55°, and sodium amalgam (370 g. of 3%) added gradually. The mercury was removed, sufficient sulphuric acid added to retain the amine as sulphate, and the mixture steam-distilled to remove alcohol. The cooled acid liquid was extracted with ether to remove unchanged oxime, made alkaline, and extracted with ether three times. The extracts of the alkaline solution were shaken several times with dilute hydrochloric acid, and the combined acid solutions concentrated on the steam-bath; the residue (2·1 g.) was recrystallised twice from alcohol (charcoal). The product, m. p. 264—268° (decomp.), sintering at 258°, formed greyish-white leaflets (Found: C, 71·7; H, 7·1; N, 6·1; Cl, 15·2. $C_{14}H_{16}NCl$ requires C, 71·9; H, 6·9; N, 6·0; Cl, 15·2%).

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