216. *Polycyclic Aromatic Hydrocarbons. Part XXV. 1- and 2-Alkyl Derivatives of* 3 : 4-*Benzphenanthrene.*

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1- and 2-Alkyl derivatives of 3 : 4-benzphenanthrene have been obtained by reduction of the *ketones* arising by the action of alkylmagnesium halides on the corresponding 3 : 4-*benzphenanthramides.* 1-iso*Propyl*- 3 : 4-*benzphenanthrene* has been obtained from *methyl* 3 : 4-*benz*-1-*phenanthroate* by treatment with methylmagnesium iodide and subsequent dehydration and hydrogenation.

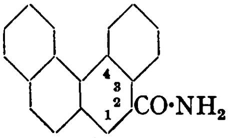
IN Part XXII (Hewett, this vol., p. 293) the carcinogenic activity of several derivatives of 3 : 4-benzphenanthrene was discussed and it was indicated that the greatest activity was obtained by substitution in the 1- and the 2-position. The present paper deals with the preparation of further 1- and 2-alkyl derivatives in order to study the influence on carcinogenic activity of the size of the substituent.

The condensation of alkylmagnesium halides with amides has usually given poor yields of the ketones, although Béis (*Compt. rend.*, 1903, **137**, 575) claims that the yield increases with increase of carbon content of the amide. The condensation of a large excess of methylmagnesium iodide and ethylmagnesium bromide with 3 : 4-*benz*-1- and -2-*phenanthramide* (I) gave the corresponding 1- and 2-*alkyl ketones* in yields of 75%. In one experiment the amide (I) and a small excess of methylmagnesium iodide yielded 3 : 4-*benz*-2-*phenanthronitrile* as the sole product to be isolated, and in another experiment the nitrile, prepared by dehydration of the amide (I) with phthalic anhydride, was recovered unchanged after boiling with a slight excess of methylmagnesium iodide. Ramart, Laclôtre, and Anagnostopoulos (*Compt. rend.*, 1927, **185**, 282) also have obtained nitriles by the action of Grignard reagents on acid amides.

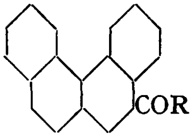
The ketones on reduction by the Kishner–Wolff method gave 1-*ethyl*-, 1-n-*propyl*-, 2-*ethyl*- (III; R = Me) and 2-n-*propyl*-3 : 4-*benzphenanthrene* (III; R = Et).

Since this work was completed, Newman and Joshel (*J. Amer. Chem. Soc.*, 1940, **62**, 972) have prepared 2-*ethyl*-3 : 4-*benzphenanthrene*, but, although the m. p. of the picrate of their product is in general agreement with that described here, the m. p. of their hydrocarbon is considerably lower.

Methyl 3 : 4-*benz*-1-*phenanthroate* reacted with methylmagnesium iodide to give, after dehydration with picric acid, 1-*iso*propenyl-3 : 4-benzphenanthrene, isolated as the *picrate*, which was readily hydrogenated over palladium to 1-iso*propyl*-3 : 4-*benzphenanthrene*.



(I.)



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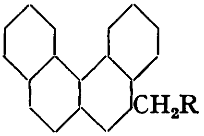

(III.)

EXPERIMENTAL.

3 : 4-*Benz*-1-*phenanthramide*.—3 : 4-Benz-1-phenanthroyl chloride (25 g.) (Hewett, this vol., p. 297) was dissolved in benzene (100 c.c.) and shaken with aqueous ammonia (*d* 0·880). The *amide* crystallised from acetic acid in colourless needles, m. p. 238—239° (Found : C, 83·6; H, 5·0. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%).

1-*Acetyl*-3 : 4-*benzphenanthrene*.—The above amide (6·0 g.) was finely powdered and added, with ice-cooling, to a Grignard solution prepared from methyl iodide (17·8 g.), magnesium (3·0 g.), and ether (100 c.c.). After the evolution of gas had ceased, the ether was distilled off, the residual syrupy liquid dissolved in benzene (50 c.c.), and the solution refluxed for 1 hour, cooled, and decomposed with ice and hydrochloric acid. The benzene was distilled with steam, the residue of ketone and imide dissolved in acetic acid (30 c.c.) and concentrated hydrochloric acid (10 c.c.), and the solution heated for 1 hour on the steam-bath, diluted with water, and extracted with benzene. The washed and dried benzene layer was distilled; the fraction, b. p. 227°/0·5 mm., on crystallisation from alcohol, gave the *ketone* (4·3 g.) in almost colourless needles, m. p. 95—96° (Found : C, 89·1; H, 5·4. $C_{20}H_{14}O$ requires C, 88·8; H, 5·2%). The *semicarbazone* separated from alcohol after several days in the cold; recrystallised from dioxan, it formed plates, m. p. 180° (decomp.) (Found : C, 76·6; H, 5·3. $C_{21}H_{17}ON_3$ requires C, 77·05; H, 5·2%).

1-*Ethyl*-3 : 4-*benzphenanthrene*.—The foregoing semicarbazone (2·2 g.) and sodium ethoxide (from 2·2 g. of sodium and 30 c.c. of ethyl alcohol) were heated at 180° for 18 hours. After dilution with water and extraction in ether, the neutral material was purified through its picrate. The regenerated hydrocarbon, obtained by passage of a benzene solution of the picrate through a column of alumina, distilled from an air-bath at 200°/0·5 mm. 1-*Ethyl*-3 : 4-*benzphenanthrene* separated from alcohol in colourless plates, m. p. 66—67° (Found : C, 93·55; H, 6·4. $C_{20}H_{16}$

requires C, 93·7; H, 6·3%). The pure *picrate* separated from alcohol in vermilion needles, m. p. 116—117° (Found : C, 64·8; H, 4·2. $C_{20}H_{16},C_6H_3O_7N_3$ requires C, 64·3; H, 3·9%).

1-*Propionyl*-3 : 4-*benzphenanthrene* was prepared from the amide and ethylmagnesium bromide as described for the 1-acetyl derivative (yield, 5·9 g. from 7·0 g. of the amide). It crystallised from alcohol in colourless plates, m. p. 94·5—95° (Found : C, 88·5; H, 5·8. $C_{21}H_{16}O$ requires C, 88·7; H, 5·65%). The *semicarbazone* formed very slowly in alcoholic solution and crystallised from dioxan; m. p. 229—230° (Found : C, 77·4; H, 5·8. $C_{22}H_{19}ON_3$ requires C, 77·4; H, 5·6%).

1-n-*Propyl*-3 : 4-*benzphenanthrene*, prepared by the action of sodium ethoxide on the above semicarbazone, separated from methyl alcohol–benzene in colourless tablets, m. p. 67—68° (Found : C, 93·2; H, 6·7. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%). The *picrate* formed deep orange needles from alcohol, m. p. 93—94° (Found : C, 65·3; H, 4·1. $C_{21}H_{18},C_6H_3O_7N_3$ requires C, 64·9; H, 4·3%).

1-iso*Propyl*-3 : 4-*benzphenanthrene*.—*Methyl* 3 : 4-*benz*-1-*phenanthroate* (10·5 g.), prepared by heating the acid (12 g.) in methyl alcohol (100 c.c.) saturated with hydrogen chloride, separated from benzene–methyl alcohol in colourless plates, m. p. 96·5—97·5° (Found : C, 84·05; H, 5·2. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%). It was added in benzene (50 c.c.) to methylmagnesium iodide (from magnesium, 3·7 g., methyl iodide, 21 g., and ether, 70 c.c.), cooled in ice. After ½ hour the mixture was boiled for 2 hours, the product decomposed with ice and ammonium chloride, and the washed and dried benzene layer evaporated. The residue was dissolved in alcohol and boiled with an equal weight of picric acid for 1 hour in order to ensure complete dehydration. On cooling, the *picrate* of 1-*iso*propenyl-3 : 4-benzphenanthrene separated in vermilion needles (14 g.), m. p. 94—95° (Found : C, 65·6; H, 4·2. $C_{21}H_{16},C_6H_3O_7N_3$ requires C, 65·15; H, 3·9%). The *iso*propenyl-3 : 4-benzphenanthrene (6·5 g.) recovered from the picrate was hydrogenated in alcohol with a palladium catalyst. The resulting 1-iso*propyl*-3 : 4-*benzphenanthrene* (4·3 g.) crystallised from alcohol in colourless tablets, m. p. 76—77°, after sublimation in a high vacuum at 100° (Found : C, 93·3; H, 6·75. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%). The *picrate* formed fine orange needles from alcohol, m. p. 105—106° (Found : C, 58·8; H, 3·9. $C_{21}H_{18},1\frac{1}{2}C_6H_3O_7N_3$ requires C, 58·7; H, 3·7%), and the *trinitrobenzene* complex formed pale yellow plates, m. p. 112·5—113° (Found : C, 67·4; H, 4·7. $C_{21}H_{18},C_6H_3O_6N_3$ requires C, 67·2; H, 4·4%).

Ethyl 3 : 4-*benz*-1-*phenanthroate*, m. p. 81—82° (Found : C, 84·2; H, 5·5. $C_{21}H_{16}O_2$ requires C, 84·1; H, 5·3%), gave poor results in the Grignard condensation.

3 : 4-*Benz*-2-*phenanthramide* (I).—3 : 4-Benz-2-phenanthroic acid (10 g.) (Hewett, this vol., p. 293) and thionyl chloride (30 c.c.) were boiled under reflux for 1 hour, and the excess of thionyl chloride removed under reduced pressure. The residual 3 : 4-*benz*-2-*phenanthroyl chloride* (9·5 g.) separated from light petroleum (b. p. 80—100°) in yellow needles, m. p. 110—111° (Found : C, 78·5; H, 4·0. $C_{19}H_{11}OCl$ requires C, 78·45; H, 3·8%). The acid chloride (8·7 g.), dissolved in benzene (50 c.c.), was shaken with aqueous ammonia (*d* 0·880); the *amide* crystallised from acetic acid in colourless plates, m. p. 228—229° (Found : C, 83·7; H, 5·0. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%).

3 : 4-*Benz*-2-*phenanthronitrile*.—(a) The foregoing amide (2·5 g.) and phthalic anhydride (5 g.) were boiled, in an oil-bath, for 1 hour (compare Waldmann, *Ber.*, 1938, **71**, 366). The melt was extracted with water and dilute ammonia solution, and the *nitrile* (0·6 g.) sublimed at 150°/0·7 mm. and crystallised from alcohol; m. p. 128—129° (Found : C, 90·0; H, 4·9. $C_{19}H_{11}N$ requires C, 90·1; H, 4·4%). (b) The amide (0·5 g.) was treated with methylmagnesium iodide (3 mols.) in ether. After the evolution of gas had ceased, benzene (7·5 c.c.) was added, the ether distilled off, the solution heated for ½ hour and diluted with ether, and the solid precipitate filtered off and boiled with 2N-sulphuric acid. The product, crystallised from alcohol, had m. p. 120—122°. It was recovered after an unsuccessful attempt to prepare a semicarbazone and then crystallised in needles, m. p. 128—129°, not depressed by the nitrile obtained under (a) (Found : C, 89·9; H, 4·7%).

2-*Acetyl*-3 : 4-*benzphenanthrene* (II; R = Me), prepared from the amide (I) and methylmagnesium iodide as described for the 1-series, in 78% yield, formed pale lemon needles, m. p. 111·5—112·5°, from alcohol (Found : C, 89·0; H, 5·2. $C_{20}H_{14}O$ required C, 88·8; H, 5·2%). The *semicarbazone* was obtained, after several days at room temperature, from alcoholic solution and crystallised from dioxan; m. p. 235—236° (Found : C, 77·55; H, 5·25. $C_{21}H_{17}ON_3$ requires C, 77·5; H, 5·2%).

2-*Ethyl*-3 : 4-*benzphenanthrene* (III; R = Me), obtained from the semicarbazone by Kishner–Wolff reduction, distilled from an oil-bath at 200°/0·3 mm. and, after purification through its picrate, separated from alcohol in colourless plates, m. p. 67—68° (Found : C, 93·8;

H, 6·3. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%). The *picrate* separated from alcohol in orange needles, m. p. 83—84° (Found: C, 64·45; H, 4·2. $C_{20}H_{16},C_6H_3O_7N_3$ requires C, 64·3; H, 3·9%). Newman and Joshel (*loc. cit.*) give the m. p. of the hydrocarbon as 50·4—51·2° and of the picrate as 80—81°.

2-*Propionyl*-3 : 4-*benzphenanthrene* (II; R = Et) was prepared in 74% yield from (I) and ethylmagnesium bromide and distilled at 230—234°/0·4 mm. It separated from benzene–methyl alcohol in colourless needles, m. p. 115·5—116·5° (Found: C, 88·7; H, 5·8. $C_{21}H_{16}O$ requires C, 88·7, H, 5·65%). The *semicarbazone*, obtained after several days' refluxing in alcoholic solution, had m. p. 211—212° after crystallisation from dioxan (Found: N, 11·5. $C_{22}H_{19}ON_3$ requires N, 12·3%).

2-n-*Propyl*-3 : 4-*benzphenanthrene* (III; R = Et), obtained by reduction of the foregoing semicarbazone, had b. p. 190—192°/0·3 mm.; it crystallised from alcohol in colourless plates, m. p. 71·5—72·5° (Found: C, 93·2; H, 6·7. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%). The *picrate* formed orange needles, m. p. 103·5—104° (Found: C, 65·2; H, 4·9. $C_{21}H_{18},C_6H_3O_7N_3$ requires C, 64·9; H, 4·3%).

3 : 4-*Benz*-2-*phenanthraldehyde* (II; R = H).—3 : 4-*Benz*-2-*phenanthranilide*, prepared from the acid chloride and aniline (2 mols.) in chloroform, crystallised from acetic acid in colourless needles, m. p. 214—215° (Found: C, 86·6; H, 5·1. $C_{25}H_{17}ON$ requires C, 86·4; H, 4·9%). The anilide (52 g.) in tetrachloroethane (200 c.c.) was heated with phosphorus pentachloride (40·5 g.) at 135° for ½ hour, and the phosphorus oxychloride and solvent distilled off under reduced pressure. The residue, in fresh tetrachloroethane, was slowly added to a solution of stannous chloride (160 g.) in ether (750 c.c.) saturated with hydrogen chloride. After 18 hours at 0° the solvent was distilled with steam, and the residue extracted with benzene, leaving 10 g. of recovered anilide. The benzene layer was washed, dried, and evaporated, and the residue distilled from an oil-bath at 260°/0·4 mm. The *aldehyde* (24·8 g.) crystallised from benzene–methyl alcohol in pale yellow needles, m. p. 130·5—131·5° (Found: C, 88·4; H, 4·7. $C_{19}H_{18}O$ requires C, 89·0; H, 4·7%). The *semicarbazone* crystallised from dioxan in lemon-yellow plates, m. p. 240—241° (Found: N, 12·7. $C_{20}H_{15}ON_3$ requires N, 13·4%). Reduction by the Kishner–Wolff method gave 2-methyl-3 : 4-benzphenanthrene, identical with that described in Part XIV (J., 1936, 596).

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