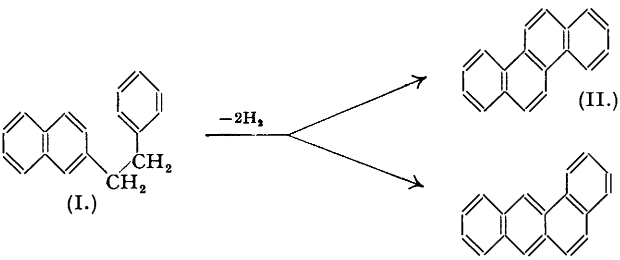
317. *The Phenanthrene Cyclisation of Dibenzyl-type Derivatives.*

By Ng. Ph. Buu-Hoï, Ng. Hoán, and Pierre Jacquignon.

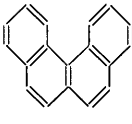
The limitations of the aluminium chloride-catalysed cyclodehydrogenation of dibenzyl compounds to phenanthrene derivatives have been investigated in a number of instances in the benzene, thiophen, and naphthalene series; in the naphthalene series, new examples of molecular rearrangements accompanying the cyclisation have been brought to light.

Ruzicka and Hösli (*Helv. Chim. Acta*, 1934, **17**, 470) found that treatment of dibenzyl with aluminium chloride in carbon disulphide solution gave phenanthrene in 15% yield, and later Ruzicka and Márkus (*ibid.*, 1940, **23**, 385) prepared 3-methylchrysene similarly from 1-methyl-5-2′-phenylethylnaphthalene. In spite of its potential practical interest for the preparation of phenanthrene derivatives and of its interesting theoretical implications, this cyclodehydrogenation reaction has not since been investigated, except for a recent synthesis of picene from 1 : 2-di-1′-naphthylethane (Buu-Hoï and Hoán, *J. Org. Chem.*, 1949, **14**, 1023).

The present work deals with a preliminary investigation of the possible use of this reaction for the preparation of phenanthrene derivatives in the aromatic and heterocyclic series. An attempt to prepare 3 : 4-benzophenanthrene (IV) by the aluminium chloride-catalysed cyclodehydrogenation of 2-2′-phenylethylnaphthalene (I) resulted in none of this hydrocarbon, but gave a mixture of chrysene (II) with some 1 : 2-benzanthracene (III) :



(I.) (II.) (III.)

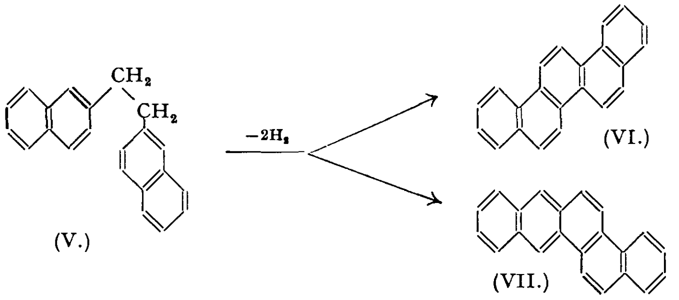


(IV.)

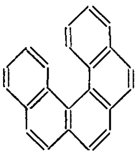
The formation of chrysene from (I) involved a shift of the substituent from the 2- to the 1-position on the naphthalene nucleus; this is a rather unusual feature, but some indications in the literature point to the likelihood of such β ⟶ α conversions. For instance, Chattaway and Lewis (*J.*, 1894, **65**, 869) observed that β-chloronaphthalene is partly converted into the α-isomer under the influence of small amounts of aluminium chloride; in the same conditions, β-bromonaphthalene is similarly converted into the α-isomer. More recently, Wibaut, Sixma, and Suyver (*Rec. Trav. chim.*, 1949, **68**, 526) observed that rearrangement anew, and found that an equilibrium is reached under the influence of aluminium chloride, starting from either α- or β-bromonaphthalene.

The concurrent formation of 1 : 2-benzanthracene is similar to the preferential Pschorr cyclisation of the diazo-compound from *o*-amino-α-2-naphthylcinnamic acid to 1 : 2-benzanthracene instead of to the expected 3 : 4-benzophenanthrene (Cook, *J.*, 1930, 1089; cf. Weitzenböck and Lieb, *Monatsh.*, 1912, **33**, 564).

Cyclodehydrogenation of 1 : 2-di-2′-naphthylethane (V) was also anomalous, for in place of the expected 3 : 4-5 : 6-dibenzophenanthrene (VIII), we obtained a mixture of picene (VI) with some naphtho(2′ : 1′-1 : 2)anthracene (1 : 2-6 : 7-dibenzophenanthrene) (VII) :

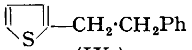


(V.) (VI.) (VII.)

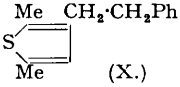

(VIII.)

2-2′-Phenylethylnaphthalene was prepared by Wolff–Kishner–Huang-Minlon reduction (*J. Amer. Chem. Soc.*, 1946, **68**, 2847) of 2-phenylacetylnaphthalene, which we obtained most easily by a Friedel–Crafts reaction between phenylacetyl chloride and naphthalene in nitrobenzene (cf. Buu-Hoï and Cagniant, *Bull. Soc. chim.*, 1945, **12**, 307). This was a marked improvement in the preparation of that ketone by the earlier procedures which necessitated a separation of the two isomers through their picrates (see, for instance, Ruggli and Reinert, *Helv. Chim. Acta*, 1926, **9**, 71). Similarly, 6-methyl-2- and 1-methyl-7-2′-phenylethylnaphthalene and 1-methyl-4-2′-phenylethylnaphthalene were prepared from the corresponding ketones (Buu-Hoï and Royer, *Rec. Trav. chim.*, 1946, **65**, 251; Cook and Galley, *J.*, 1931, 2012). In the case of 2 : 3-dimethylnaphthalene, phenylacetylation in nitrobenzene yielded a homogeneous ketone which should be 2 : 3-dimethyl-6-phenylacetylnaphthalene in view of the results of the Friedel–Crafts condensation of this hydrocarbon with succinic (Haworth and Bolam, *J.*, 1932, 2248) and phthalic anhydrides (Fieser and Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 3342; Fieser and Peters, *ibid.*, 1932, **54**, 3742). In agreement with this constitution was the Pfitzinger condensation with isatin to give the corresponding cinchoninic acid in high yield, a proof that no methyl group was present *ortho* to the carbonyl group (cf. Buu-Hoï *et al.*, *Bull. Soc. chim.*, 1946, **13**, 123, 134, 374). Wolff–Kishner–Huang-Minlon reduction of this ketone gave 2 : 3-dimethyl-6-2′-phenylethylnaphthalene (3-2′-phenylethylpyrene could similarly be obtained from 3-phenylacetylpyrene). Treated with aluminium chloride, the above naphthalene hydrocarbons yielded very impure cyclodehydrogenation products.

In the benzene group, an unsuccessful attempt was made to synthesise either picene or 1 : 2-5 : 6-dibenzanthracene by means of a double cyclodehydrogenation of 4-2′-phenylethyldibenzyl. Failure also attended a similar attempt to effect a triple cyclodehydrogenation of 4 : 4′-di-(2-phenylethyl)dibenzyl (obtained by reduction of 4 : 4′-bisphenylacetyldibenzyl, a by-product in the Friedel–Crafts reaction of phenylacetyl chloride with dibenzyl).



(IX.)



(X.)

In the thiophen series, 2-2′-phenylethylthiophen (IX) and 2 : 5-dimethyl-3-2′-phenylethylthiophen (X) were largely decomposed when heated with aluminium chloride in carbon disulphide.

EXPERIMENTAL.

2-*Phenylacetylnaphthalene.*—To a well-stirred, ice-cooled solution of phenylacetyl chloride (50 g.) and naphthalene (50 g.) in nitrobenzene (200 c.c.), powdered aluminium chloride (50 g,) was added in small portions. The mixture was kept overnight at room temperature, then poured on cracked ice, the nitrobenzene removed by steam-distillation, and the residue taken up in benzene. After drying (Na_2SO_4) and removal of the solvent, the residue was distilled *in vacuo*, to give 2-phenylacetylnaphthalene, b. p. *ca.* 238°/16 mm., crystallising from ethanol in prisms (25 g.), m. p. 100°. Ruggli and Reinert (*loc. cit.*) gave m. p. 99—99·5°.

2-2′-*Phenylethylnaphthalene.*—A mixture of pure 2-phenylacetylnaphthalene (22 g.), 85% hydrazine hydrate (22 g.), potassium hydroxide (22 g.), and diethylene glycol (125 c.c.) was gradually heated to 200° with removal of water, and then refluxed for 2 hours. After cooling, the reaction mixture was diluted with water, and the hydrocarbon formed taken up in benzene. The benzene solution was washed with dilute hydrochloric acid, then with water, and dried (Na_2SO_4). After removal of the solvent, the residue gave, on vacuum-distillation, a hydrocarbon (15 g.), b. p. 230—232°/25 mm., crystallising from ethanol in needles, m. p. 95°. Cook and Hewett (*J.*, 1934, 365) gave m. p. 99° for this hydrocarbon.

Cyclodehydrogenation of 2-2′-*Phenylethylnaphthalene.*—A mixture of the foregoing hydrocarbon (10 g.), powdered aluminium chloride (10·5 g.), and carbon disulphide (100 c.c.) was refluxed for 4 hours. The brown reaction mixture was poured on cracked ice, the carbon disulphide was removed by steam-distillation, and the hydrocarbons were taken up in benzene. The benzene solution was dried (Na_2SO_4), the solvent removed, and the residue purified by vacuum-distillation. The solid distillate (3 g.) gave, after two recrystallisations from ethanol, shiny leaflets, m. p. 247°, which showed no m. p. depression on admixture with chrysene. Further proof of constitution was the chromic oxidation to chrysenequinone, m. p. 240°. The mother-liquors from the separation of chrysene were evaporated, and the residue crystallised from ethanol, thus giving a further crop of chrysene. Repetition of this process yielded finally a residue crystallising from ethanol in shiny leaflets, m. p. 160°, giving no m. p. depression on admixture with authentic 1 : 2-benzanthracene. In the mother-liquors from the separation of 1 . 2-benzanthracene, no trace of 3 : 4-benzophenanthrene could be detected.

Cyclodehydrogenation of 1 : 2-*Di*-2′-*naphthylethane.*—This hydrocarbon was easily prepared by Buu-Hoï and Hoán's procedure (*loc. cit.*). 10 G. of this compound were treated with aluminium chloride (10 g.) in carbon disulphide (100 c.c.) as in the foregoing instance. After the usual treatment and vacuum-distillation of the reaction-product, the portion (4 g.) of b. p. >350°/15 mm. was recrystallised twice from xylene, giving colourless sublimable leaflets, m. p. 365°, identical with an authentic sample of picene prepared according to Buu-Hoï and Hoán (*loc. cit.*). The xylene mother-liquors from the purification of picene were heated with maleic anhydride (Clar and Lombardi, *Ber.*, 1932, **65**, 1418); sublimation of the adduct thus obtained yielded 1 : 2-6 : 7-dibenzophenanthrene, crystallising from xylene in pale yellow sublimable leaflets, m. p. 293°. Clar (*Ber.*, 1929, **62**, 1578) gave for this hydrocarbon m. p. 293—294°.

2-*Methyl*-6-2′-*phenylethylnaphthalene.*—A mixture of 2-methyl-6-phenylacetylnaphthalene (5 g.) (prepared according to Buu-Hoï and Royer, *loc. cit.*, from very pure β-methylnaphthalene), 85% hydrazine hydrate (5 g.), potassium hydroxide (5 g.), and diethylene glycol (100 c.c.) was slowly heated to 200° with removal of water, and then refluxed for 4 hours. After routine treatment of the reaction-product, the *hydrocarbon* was obtained as a solid, b. p. 255—257°/35 mm., crystallising from ethanol in leaflets (3·5 g.), m. p. 94° (Found : C, 92·4; H, 7·3. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%).

7-*Methyl*-1-2′-*phenylethylnaphthalene.*—This *hydrocarbon* (12 g.) was similarly obtained from 7-methyl-1-phenylacetylnaphthalene (Buu-Hoï and Royer, *loc. cit.*) (15 g.), 85% hydrazine hydrate (15 g.), potassium hydroxide (15 g.), and diethylene glycol (100 c.c.); it formed a pale yellow oil, b. p. 225—227°/19 mm. (Found : C, 92·5; H, 7·4. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%). The picrate crystallised from ethanol in needles, m. p. 107°.

Cyclodehydrogenation of these isomeric compounds yielded intractable mixtures of hydrocarbons.

2 : 3-*Dimethyl*-6-*phenylacetylnaphthalene.*—To an ice-cooled mixture of 2 : 3-dimethylnaphthalene (40 g.), phenylacetyl chloride (40 g.), and nitrobenzene (250 c.c.), powdered aluminium chloride (45 g.) was added in small portions with stirring. The reaction product was kept overnight and then treated in the usual way. After purification by vacuum-distillation and recrystallisation from ethanol, the *ketone* was obtained as needles, m. p. 138° (Found : C, 87·5; H, 6·7. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%). The *oxime* formed, from ethanol, shiny prisms, m. p. 169° (Found : C, 83·2; H, 6·6. $C_{20}H_{19}ON$ requires C, 83·4; H, 6·6%).

2-(2 : 3-*Dimethyl*-6-*naphthyl*)-3-*phenylcinchoninic Acid.*—A mixture of the foregoing ketone (2 g.), isatin (1·2 g.), potassium hydroxide (1·3 g. dissolved in 2 c.c. of water), and ethanol (8 c.c.) was refluxed for 24 hours. After dilution with water and removal of the neutral impurities by ether-extraction, the reaction product yielded on acidification with acetic acid the *cinchoninic acid* (2·5 g.) which crystallised from ethanol in yellowish needles, m. p. 287—288° (shrinking above 270°) (Found : C, 83·2; H, 5·3. $C_{28}H_{21}O_2N$ requires C, 83·4; H, 5·2%). Heating of this acid above its m. p. and vacuum-distillation of the residue gave 2-(2 : 3-*dimethyl*-6-*naphthyl*)-3-*phenylquinoline* which crystallised from ethanol as shiny needles, m. p. 158° (Found : C, 90·0; H, 5·7. $C_{27}H_{21}N$ requires C, 90·2; H, 5·8%). The picrate of this base formed, from xylene, prisms, m. p. 248—249° (decomp.).

2 : 3-*Dimethyl*-6-2′-*phenylethylnaphthalene.*—2 : 3-Dimethyl-6-phenylacetylnaphthalene (23 g.), 85% hydrazine hydrate (23 g.), and potassium hydroxide (23 g.) in diethylene glycol (180 c.c.) gave the expected *hydrocarbon*, b. p. 240—242°/14 mm., crystallising from ethanol in needles, m. p. 120° (Found : C, 92·2; H, 7·9. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%).

1-*Methyl*-4-2′-*phenylethylnaphthalene*.—The reduction of 1-methyl-4-phenylacetylnaphthalene (Cook and Galley, *loc. cit.*) gave a liquid *hydrocarbon*, b. p. 233—235°/14 mm. (Found: C, 92·8; H, 7·5. $C_{19}H_{18}$ requires C, 92·7; H, 7·3%), which formed a picrate, m. p. 114° (needles from ethanol).

3-2′-*Phenylethylpyrene*.—3-Phenylacetylpyrene was prepared according to Buu-Hoï and Royer (*Bull. Soc. chim.*, 1946, **13**, 659) and formed from ethanol–benzene needles, m. p. 115° (lit., m. p. 104°). Reduction of this ketone (8 g.) with 85% hydrazine hydrate (8 g.) and potassium hydroxide (8 g.) in diethylene glycol (100 c.c.) yielded a *hydrocarbon* crystallising from ethanol in prisms, m. p. 83° (Found: C, 94·3; H, 6·0. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%).

4-2′-*Phenylethyldibenzyl*.—4-Phenylacetyldibenzyl (Buu-Hoï and Royer, *Rec. Trav. chim.*, 1946, **65**, 251) (38 g.), hydrazine hydrate (40 g.), and potassium hydroxide (40 g.) in diethylene glycol (250 c.c.) yielded the expected *hydrocarbon* (26 g.), b. p. 245—250°/13 mm., crystallising from ethanol in leaflets, m. p. 91° (Found: C, 92·2; H, 7·8. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%). This compound yielded on cyclodehydrogenation a liquid product, possibly impure 3-2′-phenylethylphenanthrene.

4 : 4′-*Bisphenylacetyldibenzyl*.—This diketone was obtained in 50% yield in the Friedel–Crafts condensation of dibenzyl (50 g.) with phenylacetyl chloride (86 g.) in the presence of aluminium chloride (80 g.) in carbon disulphide (300 c.c.). It had b. p. 345—350°/13 mm. and crystallised from ethanol in needles, m. p. 179° (Found: C, 86·0; H, 6·5. $C_{30}H_{26}O_2$ requires C, 86·1; H, 6·2%).

4 : 4′-*Di*-(2-*phenylethyl*)*dibenzyl*.—This *hydrocarbon* crystallised from a mixture of ethanol–benzene in leaflets, m. p. 139° (Found: C, 90·0; H, 9·8. $C_{30}H_{30}$ requires C, 90·3; H, 9·7%).

2-2′-*Phenylethylthiophen*.—2-Phenylacetylthiophen (82 g.) was prepared from thiophen (42 g.), phenylacetyl chloride (80 g.), and aluminium chloride (68 g.) in carbon disulphide (250 c.c.) (30 minutes at room temperature). It gave on reduction with hydrazine hydrate (75 g.) and potassium hydroxide (70 g.) in diethylene glycol (400 c.c.) an 85% yield of 2-2′-*phenylethylthiophen*, b. p. 159—160°/13 mm., crystallising from methanol in leaflets, m. p. 109° (Found: C, 76·3; H, 6·5. $C_{12}H_{12}S$ requires C, 76·6; H, 6·4%). On treatment of this compound with aluminium chloride in carbon disulphide much hydrogen sulphide was evolved.

2 : 5-*Dimethyl*-3-2′-*phenylethylthiophen*.—2 : 5-Dimethyl-3-phenylacetylthiophen (Buu-Hoï and Hoán, *ibid.*, 1948, **67**, 309) gave on reduction a 70% yield of 2 : 5-*dimethyl*-3-2′-*phenylethylthiophen* as a pale yellow oil, b. p. 175—179°/13 mm. (Found: C, 77·5; H, 7·6. $C_{14}H_{16}S$ requires C, 77·8; H, 7·4%). Extensive evolution of hydrogen sulphide was also observed on treatment of this compound with aluminium chloride.

The Radium Institute, University of Paris.

[*Received, December 27th,* 1950.]