149. *Oxidative Ring Closure in the Friedel–Crafts Reaction. Part II. Condensation of Aromatic Acid Chlorides with Naphthalene Derivatives.*

By Gerard D. Buckley.

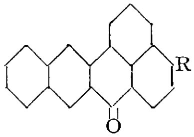
The formation of *meso*benzanthrone derivatives is shown to occur when a β-naphthoyl or 2-phenanthroyl chloride is condensed with an α-alkylnaphthalene in presence of at least 2 mols. of aluminium chloride in carbon disulphide solution. Use of benzoyl, α-naphthoyl, and 3-phenanthroyl chlorides led only to ketone formation. No *meso*benzanthrone was formed when the α-alkylnaphthalene was replaced by naphthalene, β-methylnaphthalene, α-bromonaphthalene, or 8-methylquinoline, but some indication of cyclisation was observed in the reaction of β-naphthoyl chloride with α-ethylanthracene.

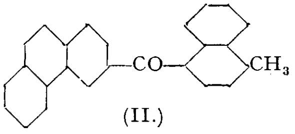
The formation of 4-methyl-9′ : 10′-benzo*meso*benzanthrone (I ; R = Me) by interaction of β-naphthoyl chloride and α-methylnaphthalene in carbon disulphide in presence of at least 2 mols. of aluminium chloride is described in the preceding paper. It is evident that *meso*benzanthrone formation under these conditions must be a specific reaction restricted to relatively unusual combinations of acid halide and hydrocarbon, since, although the Friedel–Crafts and allied reactions have been exhaustively investigated by many workers during the last 80 years, no other case of *meso*benzanthrone formation under Friedel–Crafts conditions has been recorded.

Experiments have now been carried out to determine the limits within which the constitution of the acid chloride and the hydrocarbon derivative may be varied without inhibiting the reaction.

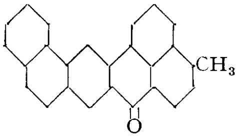
A series of acid chlorides was caused to react with α-methylnaphthalene by the aid of 2·5 mols. of aluminium chloride under the conditions previously described for the formation of (I ; R = Me). Benzoyl chloride gave only 4-benzoyl-1-methylnaphthalene, no 4-methyl*meso*benzanthrone being formed (cf. Mayer, Fleckenstein, and Gunther, *Ber.*, 1930, **63**, 1464), and α-naphthoyl chloride gave only 4-methyl-1 : 1′-dinaphthyl ketone (cf. Cook and Robinson, J., 1938, 505). 3-Phenanthroyl chloride gave a colourless product, $C_{26}H_{18}O$, m. p. 129°, which dissolved in sulphuric acid to give a red solution and was presumed to be 4-*methyl*-1-*naphthyl* 3′-*phenanthryl ketone* (II). Identical results were obtained when the above experiments were repeated with 5 mols. of aluminium chloride. Quinoline-6-carboxyl chloride gave no identifiable products.

(I.)





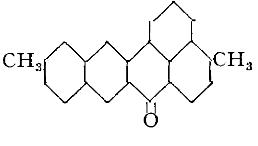
(II.)

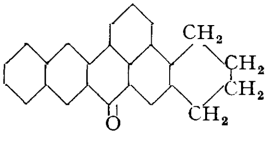


(III.)

2-Phenanthroyl chloride, however, condensed with α-methylnaphthalene in presence of 2·5 mols. of aluminium chloride to give a 20% yield of a yellow, crystalline substance, $C_{26}H_{16}O$, m. p. 268—269°, which dissolved in concentrated sulphuric acid to give a deep brown solution. This was clearly a cyclisation product and, by analogy with the product from β-naphthoyl chloride, is considered to be 4-*methyl*-9′ : 10′ : 2″ : 1″-*naphtho*-meso*benzanthrone* (III). Under similar conditions 6-methyl-2-naphthoyl chloride gave a yellow crystalline product, m. p. 244—245°, which dissolved in concentrated sulphuric acid to give the brilliant blue-green colour characteristic of the 9 : 10-benzo*meso*benzanthrone system, and must therefore be 4 : 11-*dimethyl*-9′ : 10′-*benzo*meso*benzanthrone* (IV).

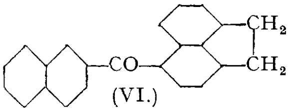
(IV.)

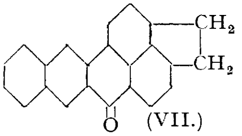


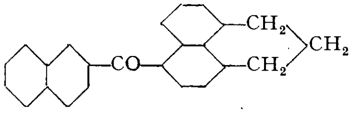


(V.)

The reaction of various derivatives of naphthalene and related compounds with β-naphthoyl chloride was next investigated under similar conditions. Naphthalene itself gave the usual mixture of α- and β-naphthyl ketones, and β-methylnaphthalene gave exclusively 2-methyl-1 : 2′-dinaphthyl ketone. α-Chloro- and α-bromonaphthalenes gave mixtures, from which no definite products were isolated but which did not give the characteristic colour reaction of the 9 : 10-benzo*meso*benzanthrones with sulphuric acid. α-Ethylnaphthalene and 1 : 2 : 3 : 4-tetrahydrophenanthrene gave products (I; R = Et) and (V), respectively, having the typical properties of the benzo*meso*benzanthrones. Acenaphthene with 2·5 mols. of aluminium chloride gave only 5-β-*naphthoylacenaphthene* (VI), but with 5 mols. of condensing agent a 10% yield of the cyclisation product, 3 : 4-*ace*-9′ : 10′-*benzo*meso*benzanthrone* (VII), was isolated.


(VI.)


(VII.)


(VIII.)

Under the conditions employed, acenaphthenone and 8-methylquinoline failed to react with β-naphthoyl chloride and were recovered unchanged. 1-Ethylanthracene gave only a tar, from which no crystalline product could be isolated, but the crude material gave a green colour with sulphuric acid; some ring closure may therefore have occurred in this case. Perinaphthane gave resinous products when 2·5 mols. of aluminium chloride were used, but 6-β-*naphthoylperinaphthane* (VIII) was isolated in good yield when only 1 mol. of condensing agent was used.

Finally, 4-methyl-1-naphthoyl chloride was condensed with naphthalene in presence of 2·5 mols. of aluminium chloride. This was expected to lead to the formation of a mixture of 4-methyl-1 : 1′-dinaphthyl ketone and 4-methyl-9′ : 10′-benzo*meso*benzanthrone (I; R = Me). The product, however, contained no trace of the *meso*benzanthrone but appeared to consist of a mixture of ketones, from which only 4-methyl-1 : 1′-dinaphthyl ketone was isolated in a pure state.

The above results make it clear that *meso*benzanthrone formation can occur in the Friedel–Crafts reaction when one of the reacting substances is a β-naphthoyl or 2-phenanthroyl chloride and the other is a naphthalene or anthracene derivative capable of undergoing condensation and having an alkyl substituent in the α-position. Knowledge of the reaction is at present too limited to warrant the formulation of theories to account for the occurrence of cyclisation in these cases or for its failure to occur more generally in the Friedel–Crafts reaction. Elucidation of these problems must await a clearer understanding of the course of the reaction and the nature of the intermediate complexes.

Experimental.

(Analyses are by Mr. E. S. Morton. M. p.'s are uncorrected.)

Condensation of Aromatic Acid Chlorides with Naphthalene and Anthracene Derivatives.—The following standard conditions were used: The naphthalene derivative (1·2 mols.), dissolved in carbon disulphide (5 vols.), was treated with powdered aluminium chloride (2·5 mols., except where otherwise stated), and the mixture stirred and cooled to 0°. The acid chloride (1 mol.) was added during 30 minutes at 0—10°, and the mixture was stirred at 20° for 18 hours, then poured into ice and dilute hydrochloric acid, and the solvent removed by steam-distillation. The residue was cooled, and the crude product collected on a filter or extracted with ether.

Benzoyl chloride and α-methylnaphthalene. Distillation of the crude product in a vacuum gave an 80% yield of 4-benzoyl-1-methylnaphthalene as a pale yellow oil, b. p. 235—240°/9 mm., which solidified on long standing, m. p. 67—69° (cf. Mayer, Fleckenstein, and Gunther, *loc. cit.*). A small tarry residue which remained appeared to contain no 4-methyl-*meso*benzanthrone.

α-Naphthoyl chloride and α-methylnaphthalene. The crude product was crystallised repeatedly from acetic acid, giving colourless plates of 4-methyl-1 : 1′-dinaphthyl ketone, m. p. 100° (cf. Cook and Robinson, *loc. cit.*).

3-*Phenanthroyl chloride and α-methylnaphthalene.* Crystallisation of the crude product from β-ethoxyethyl alcohol gave a 40% yield of 4-*methyl*-1-*naphthyl*-3′-*phenanthryl ketone* (II), colourless needles, m. p. 129°, soluble in concentrated sulphuric acid to give a red solution (Found: C, 89·45; H, 5·4. $C_{26}H_{18}O$ requires C, 90·15; H, 5·2%).

2-*Phenanthroyl chloride and α-methylnaphthalene.* Crystallisation of the crude product from chlorobenzene gave a 20% yield of golden-yellow needles of a polycyclic compound, probably 4-*methyl*-9′ : 10′ : 2″ : 1″-*naphtho*meso*benzanthrone* (III), m. p. 268—269°, soluble in concentrated sulphuric acid to give a brown solution (Found: C, 90·0; H 4·75. $C_{26}H_{16}O$ requires C, 90·7; H, 4·65%).

6-*Methyl*-2-*naphthoyl chloride and α-methylnaphthalene.* The crude product was crystallised from chlorobenzene and from β-ethoxyethyl alcohol, giving greenish-yellow needles of 4 : 11-*dimethyl*-9′ : 10′-*benzo*meso*benzanthrone* (IV), m. p. 244—245°, soluble in concentrated sulphuric acid to give a blue-green solution (Found: C, 89·05; H, 4·9. $C_{23}H_{16}O$ requires C, 89·6; H, 5·2%).

β-Naphthoyl chloride and β-methylnaphthalene. Crystallisation from acetic acid gave colourless crystals, m. p. 135—136°, in 60% yield, identical in properties with the 2-methyl-1 : 2′-dinaphthyl ketone of Fieser and Dietz (*Ber.*, 1929, **62**, 1829).

β-Naphthoyl chloride and α-ethylnaphthalene. Crystallisation of the crude product from acetic acid and from toluene gave a 10% yield of 4-*ethyl*-9′ : 10′-*benzo*meso*benzanthrone* (I; R = Et), golden-yellow plates, m. p. 192°, soluble in concentrated sulphuric acid to a blue-green solution (Found: C, 89·1; H, 5·25. $C_{23}H_{16}O$ requires C, 89·6; H, 5·2%).

β-Naphthoyl chloride and 1 : 2 : 3 : 4-*tetrahydrophenanthrene.* Crystallisation of the crude product from chlorobenzene gave a 45% yield of orange needles of 4 : 5 : 6 : 7-*tetrahydro*-4′ : 5′ : 9′ : 10′-*dibenzo*meso*benzanthrone* (V), m. p. 230°, soluble in concentrated sulphuric acid to a brilliant blue-green solution (Found: C, 89·4; H, 5·6. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

β-Naphthoyl Chloride and Acenaphthene.—(a) *With* 2·5 *mols. of aluminium chloride.* Crystallisation of the crude product from light petroleum (b. p. 60—80°) and from acetone gave a 30% yield of 5-*β-naphthoylacenaphthene* (VI), as pale yellow plates, m. p. 128°, which dissolved in concentrated sulphuric acid to give a red solution (Found : C, 89·85; H, 5·6. $C_{23}H_{16}O$ requires C, 89·6; H, 5·2%).

(b) *With* 5 *mols. of aluminium chloride.* The crude product was crystallised from acetic acid, sublimed at 200—220°/0·01 mm., and recrystallised from chlorobenzene to give a 10% yield of orange-yellow needles of 3 : 4-*ace*-9′ : 10′-*benzo*meso*benzanthrone* (VII), m. p. 204°, soluble in concentrated sulphuric acid to give a blue-green solution (Found: C, 90·3; H, 4·75. $C_{23}H_{14}O$ requires C, 90·2; H, 4·55%).

β-Naphthoyl Chloride and Perinaphthane.—Reaction under the usual conditions gave only resinous products. Therefore powdered aluminium chloride (0·75 g.) was added during 30 minutes to a stirred mixture of β-naphthoyl chloride (0·95 g.), perinaphthane (0·9 g.), and carbon disulphide (10 c.c.), at 0—5°. The mixture was stirred at 0—5° for 3 hours, poured into ice water, and the solvent removed by steam-distillation. After cooling, the residue was extracted with ether, and the extract washed with dilute sodium hydroxide solution and dried over potassium carbonate. After removal of the ether, the residue was crystallised from light petroleum (b. p. 60—80°) and from acetic acid, giving 6-*β-naphthoyl-perinaphthane* (VIII) as colourless plates, m. p. 122—123°, soluble in concentrated sulphuric acid to give an orange-red solution (Found : C, 89·6; H, 6·25. $C_{24}H_{18}O$ requires C, 89·45; H, 5·6%).

β-Naphthoyl Chloride and α-Ethylanthracene.—The product was a red tar which gave a dull green coloration with sulphuric acid. Attempts to isolate a pure compound were unsuccessful.

4-*Methyl*-1-*naphthoyl Chloride and Naphthalene.*—Distillation of the crude product in a vacuum gave a viscous yellow liquid, b. p. 250—255°/0·05 mm., which partly crystallised on standing. The crystals were collected, washed with a little acetone, and repeatedly recrystallised from acetic acid, giving 4-methyl-1 : 1′-dinaphthyl ketone, m. p. 99—100°.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
BLACKLEY, MANCHESTER, 9.

[*Received, May* 18*th*, 1945.]