Polynuclear Heterocyclic Systems. Part VIII.† *Synthetic Applications of the Schmidt Reaction.*

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Although the Beckmann transformation of the chrysenequinone monooxime (V) leads to the two amido-acids (II and VI), the Schmidt reaction with chrysenequinone gives the amido-acid (II) exclusively. By treatment with hydrazoic acid the two amido-acids have been converted into 1 : 2- (III) and 7 : 8-benzophenanthridone (VII) respectively, and thence into the benzophenanthridines.

PHENANTHRIDONE has been prepared by the action of hydrazoic acid on phenanthraquinone (Caronna, *Gazzetta*, 1941, **71**, 481), but the general reaction has not been investigated in detail and little information exists which would enable one to predict the result for an unsymmetrical *o*-quinone (cf. Stephenson, *J.*, 1949, 2620; Badger, Howard, and Simons, *J.*, 1952, 2849).

Caronna (*loc. cit.*) found that treatment of the chrysenequinone (I) with excess of hydrazoic acid gave 1 : 2-benzophenanthridone (III) exclusively. This has now been confirmed, and it has also been shown that if only 1 mol. of hydrazoic acid is used, the amido-acid (II) is obtained, which on further treatment with hydrazoic acid yields 1 : 2-benzophenanthridone.

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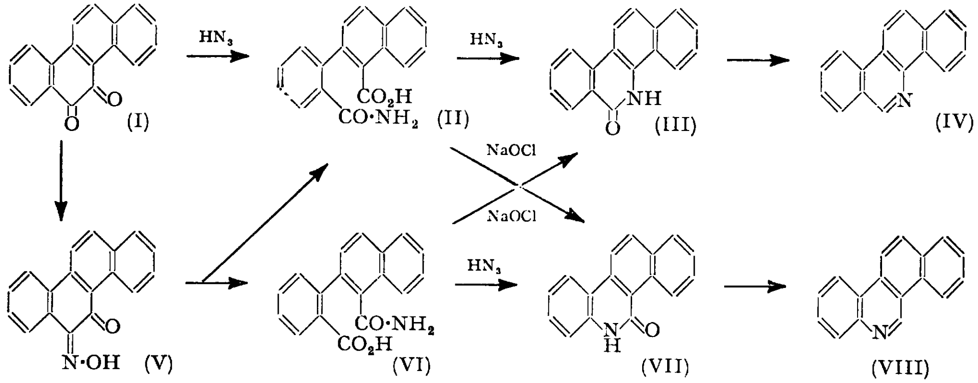
* The symbols $2p_z^2$, $3p_z^2$ beg the question as to the proper description of the lone-pair donor electrons on the N and Cl atoms.

† Part VII, *J.*, 1953, 2774.

On the other hand, Beckmann rearrangement of the chrysenequinone mono-oxime (probably V) has been shown (Graebe, *Annalen*, 1904, **335**, 122) to lead to the two amido-acids (II and VI). The acid (II) gives 1 : 2-benzophenanthridone (III) on treatment with hydrazoic acid (cf. above), and, as Graebe (*loc. cit.*) has shown, it gives 7 : 8-benzophenanthridone (VII) on treatment with sodium hypochlorite. Similarly, the acid (VI) has

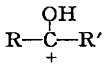


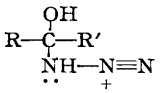
now been shown to give 7 : 8-benzophenanthridone (VII) with hydrazoic acid; and as Graebe (*loc. cit.*) has shown it gives 1 : 2-benzophenanthridone with sodium hypochlorite.

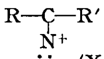
In each case the benzophenanthridones (III, VII) were converted into the chlorobenzophenanthridines, which were then reduced to the benzophenanthridines (IV and VIII). The same bases were obtained from the phenanthridones by reduction with lithium aluminium hydride, followed by dehydrogenation of the unstable dihydrides. The structures of these benzophenanthridines follow from the independent syntheses of the 1 : 2-benzo-compound by Kenner, Ritchie, and Statham (*J.*, 1937, 1169) and by Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1946, **78**, 173).

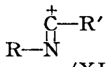
The absorption spectra (Figure) of both benzophenanthridines resembled that of chrysene very closely, except that the group III absorption bands are much more intense in the aza-hydrocarbons.

The mechanism of the Schmidt reaction with ketones seems to be fairly well established (Smith *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 320; 1950, **72**, 2503, 3718; Newman and Gildenhorn, *ibid.*, 1948, **70**, 317). The ketone is converted into the carbonium ion (IX) which with hydrazoic acid gives (X). Elimination of water and of nitrogen then gives the intermediate ion (XI) which immediately rearranges to the carbonium ion (XII). On the addition of water, this gives the amide. The Beckmann transformation of

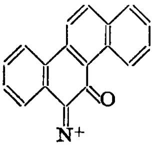

$$R{-}\overset{OH}{\underset{+}{C}}{-}R'$$
(IX)


$$R{-}\overset{OH}{\underset{\ddot{N}H-N\equiv \overset{+}{N}}{C}}{-}R'$$
(X)

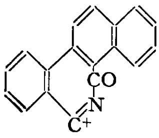

$$R{-}\underset{\ddot{N}^{+}}{C}{-}R'$$
(XI)


$$\begin{array}{l} \quad\overset{+}{C}{-}R' \\ \quad\| \\ R{-}N \end{array}$$
(XII)

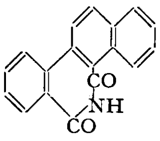
ketoximes is believed to be essentially similar, both reactions proceeding *via* the ion (XI). The Schmidt reaction with *o*-quinones, and the Beckmann transformation of quinone oximes are not so well understood. With chrysenequinone (I) the Schmidt reaction gives



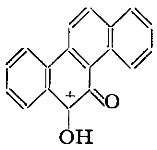
(XIII)



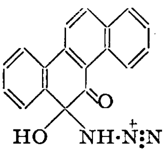
(XIV)



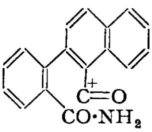
(XV)



(XVI)



(XVII)



(XVIII)

the amido-acid (II) and thence 1 : 2-benzophenanthridone (III) exclusively, but the Beckmann transformation of chrysenequinone oxime (V) yields both amido-acids. It is suggested that the Beckmann transformation proceeds normally to give the ion (XIII) which subsequently rearranges to the carbonium ion (XIV). Addition of 1 mol. of water would give the imide (XV), but addition of 2 mols. of water would give a mixture of both amido-acids.

On the other hand, as only one product is obtained in the Schmidt reaction with chrysenequinone it seems that the ion (XIII) is not then formed. The carbonium ion (XVI) is probably first formed, and this would react with hydrazoic acid to give (XVII). Subsequent elimination of nitrogen evidently leads to fission of the carbon–carbon bond and formation of the ion (XVIII). The latter would lead to the amido-acid (II) on addition of water, or to 1 : 2-benzophenanthridone (III) on treatment with a further mol. of hydrazoic acid.

Ultra-violet absorption spectra of chrysene (———) *and* 1 : 2- (— —) *and* 7 : 8-*benzophenanthridine* (. . . .), *all in ethanol.*

EXPERIMENTAL

2-o-*Benzamido*-1-*naphthoic Acid*.—A mechanically stirred solution of chrysenequinone (6 g.) in concentrated sulphuric acid (20 c.c.) was treated with sodium azide (1·7 g.) at such a rate that the temperature was maintained at 50° (40 min.). After a further 30 min. at 50°, the mixture was poured into water (300 c.c.). The precipitate was collected, washed with water, and freed from unchanged chrysenequinone and some 1 : 2-benzophenanthridone by treatment with 10% sodium carbonate solution. After acidification with hydrochloric acid, the product was collected (70% yield). Recrystallisation from alcohol gave 2-*o*-benzamido-1-naphthoic acid as colourless plates, m. p. 230° (Found : C, 74·3; H, 4·4; N, 4·5. Calc. for $C_{18}H_{13}O_3N$: C, 74·2; H, 4·5; N, 4·8%).

The same acid, m. p. 230°, was obtained together with 2-*o*-carboxyphenyl-1-naphthoamide, m. p. 275°, from chrysenequinone mono-oxime by the Beckmann rearrangement according to Graebe (*loc. cit.*) who gave m. p. 220° and 275° respectively.

1 : 2-*Benzophenanthridone*.—Powdered sodium azide (1 g.) was added gradually to a well-stirred solution of the above benzamidonaphthoic acid (3 g.) in concentrated sulphuric acid (15 c.c.) at 55—60°. The mixture was kept at 55—60° for a further hour, and then poured into water. The product was freed from unchanged acid by treatment with 10% sodium carbonate solution and washed with water. After one recrystallisation from glacial acetic acid the 1 : 2-benzophenanthridone was obtained as colourless prisms, m. p. 330°.

The same benzophenanthridone was obtained in almost quantitative yield by the addition of powdered sodium azide (3·5 g.) to chrysenequinone (6 g.) in concentrated sulphuric acid (20 c.c.) (cf. Caronna, *loc. cit.*). After crystallisation from glacial acetic acid and sublimation in a high vacuum 1 : 2-benzophenanthridone had m. p. 332° (Graebe, *loc. cit.*, gives m. p. 332·5°).

In agreement with Graebe, 1 : 2-benzophenanthridone was also obtained from 2-*o*-carboxyphenyl-1-naphthoamide by oxidation with sodium hypochlorite.

9-*Chloro*-1 : 2-*benzophenanthridine*.—1 : 2-Benzophenanthridone (2 g.), phosphorus oxychloride (18 c.c.), and dimethylaniline (0·6 c.c.) were refluxed for 4 hr. The excess of phosphorus oxychloride was then removed *in vacuo*, and the residue treated with iced water. The product was collected, washed with water, and extracted with benzene, and the solution was evaporated. Recrystallisation of the residue from alcohol gave 2-*chloro*-1 : 2-*benzophenanthridine* as colourless plates, m. p. 156·5° (90%). It was also obtained as colourless blades from benzene–light petroleum. For analysis it was purified by sublimation at 120°/5 × 10^{-5} mm. (Found : C, 77·5; H, 3·8. $C_{17}H_{10}NCl$ requires C, 77·4; H, 3·8%). It was recovered unchanged from refluxing alcohol or alcoholic hydrochloric acid after 2 hr.

2-*Anilino*-1 : 2-*benzophenanthridine*.—The foregoing chloro-base (0·1 g.) and aniline (0·2 g.) were heated on a steam-bath for 1 hr. A little 50% alcohol was then added, whereupon the product crystallised. Recrystallisation from aqueous alcohol (charcoal) gave the 2-*anilino*-derivative in almost quantitative yield as pale yellow needles, m. p. 152° (Found : C, 86·1; H, 4·7; N, 8·9. $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0; N, 8·7%).

1 : 2-*Benzophenanthridine*.—(i) 9-Chloro-1 : 2-benzophenanthridine (1 g.) and potassium hydroxide (0·5 g.) in alcohol (35 c.c.) were hydrogenated over Raney nickel (1 g.; *Org. Synth.*, **1941**, **21**, 15) at room temperature and pressure. After 4 hr., 2 mols. of hydrogen had been absorbed and hydrogenation ceased. The filtrate was concentrated to about 10 c.c., and on the addition of a little water the product separated. After recrystallisation from alcohol, 1 : 2-benzophenanthridine (86%) formed colourless prisms, m. p. 136°, alone or mixed with a specimen prepared by zinc dust distillation of 1 : 2-benzophenanthridone (Graebe, *loc. cit.*, gives m. p. 135·5°).

(ii) 1 : 2-Benzophenanthridone (0·5 g.) and lithium aluminium hydride (0·4 g.) in dry dioxan (15 c.c.) were refluxed for 10 hr., cooled, treated with a little water, and filtered. The inorganic residue was washed with hot dioxan, and the filtrate and washings were concentrated. Water was then added and the resulting bright yellow precipitate (presumably the dihydride) collected. After one recrystallisation from alcohol it had m. p. 213°, but further attempted purification in this manner reduced the m. p. considerably. It was dehydrogenated by heating it with 10% platinised asbestos (0·1 g.) in *p*-cymene for 2 hr. Recrystallisation of the product from alcohol gave 1 : 2-benzophenanthridine (95%), m. p. 136°, identical with the product obtained by the previous method.

(iii) 1 : 2-Benzophenanthridine was obtained almost quantitatively by reduction of the 9-chloro-derivative (0·5 g.) with lithium aluminium hydride (0·3 g.) in dry dioxan (15 c.c.) for 8 hr., and dehydrogenation as above.

7 : 8-*Benzophenanthridone*.—(i) Powdered sodium azide (1 g.) was added gradually to a well-stirred solution of 2-*o*-carboxyphenyl-1-naphthoamide (3 g.) in concentrated sulphuric acid (15 c.c.) at 55—60°, as above. After one recrystallisation from chlorobenzene, 7 : 8-benzophenanthridone formed colourless prisms, m. p. 332° (95%). Graebe, *loc. cit.*, gives m. p. 338°.

(ii) 7 : 8-Benzophenanthridone was obtained by oxidation of 2-*o*-benzamido-1-naphthoic acid with sodium hypochlorite according to Graebe (*loc. cit.*). After sublimation under reduced pressure it had m. p. 338°.

9-*Chloro*-7 : 8-*benzophenanthridine*.—7 : 8-Benzophenanthridone (1 g.) was refluxed with phosphorus oxychloride and a little dimethylaniline as described above. The excess of oxychloride was removed *in vacuo*. To facilitate removal of the last traces a little benzene was added and then removed *in vacuo*. The residue was extracted with light petroleum, the solvent evaporated, and the product (0·83 g.) crystallised from benzene and from pure dioxan. 9-*Chloro*-7 : 8-*benzophenanthridine* formed colourless plates, m. p. 163°, from benzene (Found : C, 77·3; H, 3·9; N, 5·0; Cl, 13·6. $C_{17}H_{10}NCl$ requires C, 77·4; H, 3·8; N, 5·3; Cl, 13·45%).

In a preliminary experiment in which no special care was taken to remove traces of phosphorus oxychloride, the residue was extracted with alcohol. The resulting crystalline compound, which contained no chlorine, formed colourless needles, m. p. 125·5°, from alcohol, and was identified as the 9-*ethoxy*-compound (Found : C, 83·8; H, 5·65; N, 5·25. $C_{19}H_{15}ON$ requires C, 83·5; H, 5·5; N, 5·1%). The m. p. was not depressed by admixture with a specimen prepared by refluxing the 9-chloro-compound with sodium ethoxide in alcohol.

Hydrolysis of the 9-chloro-compound to 7 : 8-benzophenanthridone was effected in quantitative yield by 1 hour's refluxing in 95% alcohol or in alcoholic hydrochloric acid. It was, however, recovered unchanged following 2 hours' refluxing with ammoniacal alcohol.

The 9-chloro-compound and aniline on the steam-bath (1 hr.) gave the 9-*anilino*-derivative (67%), in pale yellow needles, m. p. 155° (from alcohol) (Found: C, 85·9; H, 4·9; N, 8·9%).

7 : 8-*Benzophenanthridine*.—(i) The 9-chloro-compound was hydrogenated as above (3 hr.), giving 7 : 8-benzophenanthridine as colourless plates (78%), m. p. 183° (from alcohol). The m. p. was not depressed by admixture with a specimen prepared from 7 : 8-benzophenanthridone by zinc dust distillation (Graebe, *loc. cit.*, gave m. p. 182°).

(ii) 7 : 8-Benzophenanthridone and lithium aluminium hydride in dioxan, as above, gave a crude, yellow, unstable dihydride (?), m. p. 261°, dehydrogenated with 10% platinised asbestos in boiling *p*-cymene, to 7 : 8-benzophenanthridine, m. p. 183° (from alcohol), identical with the material obtained as above.

(iii) 7 : 8-Benzophenanthridine was obtained almost quantitatively on reduction of the 9-chloro-compound with lithium aluminium hydride and dehydrogenation of the product with platinised asbestos.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

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