530. *The Ring-expansion of 3 : 4-Benzofluorenone by Hydrazoic Acid.*

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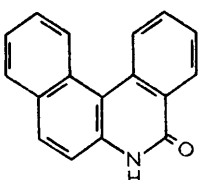
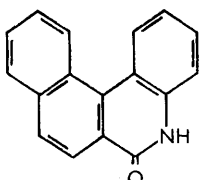
3 : 4-Benzofluorenone is converted by hydrazoic acid into a mixture of 3 : 4- and 5 : 6-benzophenanthridone in which the former predominates. The derived *N*-methyl-3 : 4- and -5 : 6-benzophenanthridone differ from products, derived from Pschorr reactions, to which these structures were formerly attributed.

RING expansion of 3 : 4-benzofluorenone by means of the Schmidt reaction would be expected to give a mixture of 3 : 4- (I) and 5 : 6-benzophenanthridone (II). Available data [1] do not make possible a reliable prediction as to which of these products would predominate, and the reaction has now been examined since it might have provided a not too difficult means of obtaining 5 : 6-benzophenanthridine.[2]

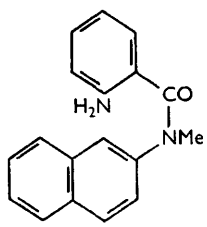
When treated in cold concentrated sulphuric acid with sodium azide, 3 : 4-benzofluorenone appeared to suffer little change apart from some sulphonation. However, ring-expansion occurred in warm trichloroacetic acid containing a small amount of sulphuric acid,[3] the best yield [35—40% of a mixture of (I) and (II)] being obtained with



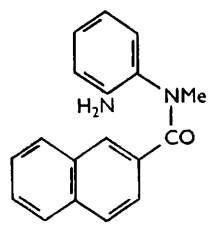
(I)



(II)



(III)



(IV)

two equivalents of sodium azide. Separation of the isomers (I) and (II) proved difficult, but fractional dissolution in benzene left (II) undissolved and it could then be purified by recrystallisation. The isomer (I) was not obtained pure; sharp-melting specimens from recrystallisation always contained 5—10% of (II). Consequently, only a rough estimate of the ratio (2 : 1) of (I) to (II) in the product could be made. (On attempted chromatography on alumina the products could not be eluted.)

The structure of 5 : 6-benzophenanthridone (II) was proved by reduction with a considerable excess of lithium aluminium hydride [4] followed by dehydrogenation, which

[1] Arcus, Coombs, and Evans, *J.*, 1956, 1498.
[2] Mills and Schofield, *J.*, 1956, 4213.
[3] Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 320.
[4] de Mayo and Rigby, *Nature*, 1950, **166**, 1075; Badger, Seidler, and Thomson, *J.*, 1951, 3207.

gave 5 : 6-benzophenanthridine, identified as its picrate.[2] With dimethyl sulphate in acetone and aqueous sodium hydroxide, the amide (II) gave *N*-methyl-5 : 6-benzophenanthridone. That *N*-methylation had occurred was demonstrated by converting 5 : 6-benzophenanthridone into 9-chloro-5 : 6-benzophenanthridine, and thence into 9-methoxy-5 : 6-benzophenanthridine, which differed from the methylation product.

Attempts to convert the crude 3 : 4-benzophenanthridone (contaminated with a small proportion of the isomer) into 3 : 4-benzophenanthridine by the method described above gave a mixture of inseparable picrates. However, methylation of the impure 3 : 4-benzophenanthridone and fractional crystallisation of the product did give pure *N*-methyl-3 : 4-benzophenanthridone. This was identical with a specimen prepared by oxidising *N*-methyl-3 : 4-benzophenanthridinium iodide with alkaline potassium ferricyanide in aqueous dioxan.

Compounds thought to be *N*-methyl-3 : 4- and *N*-methyl-5 : 6-benzophenanthridone, m. p. 198—199° and 158—159° respectively, have been described in the literature. The first resulted [5] from the decomposition of the diazonium salt from *N*-*o*-aminobenzoyl-*N*-methyl-2-naphthylamine (III), and the second was obtained similarly [6] from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine (IV). Evidence for the structure of the compound, m. p. 198—199°, was its identity with a product obtained by oxidising *N*-methyl-3 : 4-benzophenanthridinium iodide with aqueous-methanolic alkaline potassium ferricyanide. The m. p. seems rather high for a compound of the supposed structure, and in carrying out the ferricyanide oxidation under slightly different conditions we isolated a product (m. p. 120—121°), mentioned above, which is clearly different from that described by the earlier workers. We cannot account for this discrepancy.

Evidence for the structure of the compound, m. p. 158—159°, formerly [6] taken to be *N*-methyl-5 : 6-benzophenanthridone, was the fact that it differed from the product obtained when 3-amino-*N*-methyl-2-naphthanilide was submitted to the Pschorr reaction. Abramovitch, Hey, and Long [6] found that decomposition of the diazonium salt from 1-amino-*N*-methyl-2-naphthanilide gave mainly 2-naphthanilide, together with two by-products, m. p. 137° and 185°, both differing from the compound, m. p. 158—159°, which they believed to be *N*-methyl-5 : 6-benzophenanthridone. The by-product, m. p. 137°, has now been found (infrared spectra) to be *N*-methyl-5 : 6-benzophenanthridone (m. p. 140—141°).

It is clear that the Pschorr-reaction products from the amides (III) and (IV) need to be re-formulated. Such reactions with naphthalene derivatives are clearly complex, and can be misleading in producing substances isomeric with, but different from, the expected phenanthridones. These Pschorr reactions are being re-investigated at King's College, London.

Experimental

The Schmidt Reaction with 3 : 4-*Benzofluorenone.*—3 : 4-Benzofluorenone (5·0 g.), trichloroacetic acid (100 g.), and concentrated sulphuric acid (5·0 g.) were kept at 55—65° and treated with powdered sodium azide (1·5 g.), added all at once. After the vigorous evolution of nitrogen had ceased (20 min.) more sodium azide (0·75 g.) was added, followed after 10 min. by a further quantity (0·5 g.). The reaction mixture was kept at 55—65° for 1 hr. more, then poured into iced water. After thorough extraction with chloroform, the organic layer was washed with dilute aqueous sodium carbonate and dried (Na_2SO_4). Evaporation left a dark brown tar which on trituration with benzene gave a buff powder (2·1 g., 39%); m. p. *ca.* 220—250°. This (2·1 g.) was heated under reflux with benzene (200 ml.) for 5 min. and the resulting suspension was filtered whilst hot. The insoluble portion (0·70 g.; m. p. 264—275°) was treated in the same way with a further quantity (50 ml.) of benzene, and the residue (0·65 g.) was crystallised from xylene, whence 5 : 6-*benzophenanthridone* formed yellow-bronze needles, m. p. 275—276° (Found: C, 83·6; H, 4·6. $C_{17}H_{11}ON$ requires C, 83·2; H, 4·5%). This

[5] Hey and Turpin, *J.*, 1954, 2471.
[6] Abramovitch, Hey, and Long, *J.*, 1957, 1781.

compound existed in two crystalline modifications. Slow crystallisation from a relatively large volume of xylene yielded clusters of yellow-bronze needles, whilst from a small volume of solvent the compound formed matted buff fibres. The two forms had identical m. p.s and by crystallisation from an intermediate volume of solvent mixtures of both were obtained.

The benzene-soluble fraction was isolated as a brown solid, m. p. 236—240° (1·23 g.). Two crystallisations from xylene yielded buff needles, m. p. 241—243°, consisting mainly of 3 : 4-benzophenanthridone (Found: C, 83·7; H, 4·0%).

5 : 6-*Benzophenanthridine.*—5 : 6-Benzophenanthridone (0·10 g.) in a Soxhlet thimble was extracted slowly into a boiling suspension of lithium aluminium hydride (0·10 g.) in tetrahydrofuran (50 ml.). When all the material had been removed from the thimble the mixture was heated under reflux for a further 1½ hr. After cooling, the excess of lithium aluminium hydride was decomposed by the addition of aqueous tetrahydrofuran. Most of the solvent was distilled off, and the residue was made alkaline with 10% aqueous sodium hydroxide (100 ml.) and thoroughly extracted with benzene. Evaporation of the dried ($MgSO_4$) extract left a yellow gum which was heated with 30% palladium–charcoal (0·10 g.) for 3 hr. at 280° in a stream of nitrogen. The cooled mixture was extracted with hot ethanol, and the filtered solution treated with picric acid (0·10 g.) in ethanol. The bright yellow picrate [(0·085 g.; m. p. 252—254° (decomp.)] so formed, crystallised from 2-ethoxyethanol as yellow fibres (Found: C, 60·5; H, 3·25; N, 11·9. Calc. for $C_{17}H_{11}N,C_6H_3O_7N_3$: C, 60·3; H, 3·1; N, 12·1%), m. p. 253—254° alone or mixed with 5 : 6-benzophenanthridine picrate.[2]

N-*Methyl*-5 : 6-*benzophenanthridone.*—5 : 6-Benzophenanthridone (0·20 g.), acetone (50 ml.), and 10% aqueous sodium hydroxide (5 ml.) were heated under reflux and treated slowly with dimethyl sulphate (0·50 g.). The solution (kept alkaline with dilute aqueous sodium hydroxide) was boiled for 30 min., then treated with a further quantity of dimethyl sulphate (0·50 g.), heated for 15 min., and poured into ice-water kept alkaline with dilute aqueous sodium hydroxide. Extraction with benzene and evaporation of the dried (Na_2SO_4) extract yielded N-*methyl*-5 : 6-*benzophenanthridone* (0·14 g.) as a buff solid, m. p. 132—135°, which formed white needles, m. p. 140—141° (Found: C, 83·9; H, 5·0; N, 5·6. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·05; N, 5·5%), from methanol.

The infrared spectrum of this compound was identical with that of the compound, m. p. 137°, described by Abramovitch, Hey, and Long.[6]

9-*Methoxy*-5 : 6-*benzophenanthridine.*—5 : 6-Benzophenanthridone (0·20 g.), phosphorus oxychloride (6 ml.), and dimethylaniline (0·50 ml.) were heated under reflux for 4 hr. Liquids were then removed at reduced pressure, the last traces being eliminated by the addition and evaporation of three successive quantities of benzene. The residue was treated with ice and water, and the mixture extracted with chloroform. Evaporation of the dried (Na_2SO_4) extract left a brown gum which on trituration with light petroleum (b. p. 40—60°) yielded 9-chloro-5 : 6-benzophenanthridine as a pink, gritty solid, m. p. 105—108° (0·17 g.).

The chloro-compound (0·17 g.) was heated under reflux with methanolic sodium methoxide [from sodium (0·23 g.) and methanol (10 ml.)] for 6 hr. After the methanol had been removed at reduced pressure, the residue was treated with ice and water and extracted with benzene. Evaporation of the dried (Na_2SO_4) extract left a brown oil which on trituration with methanol gave 9-*methoxy*-5 : 6-*benzophenanthridine* (0·08 g.; m. p. 73—75°) as a pink solid which formed clusters of ivory-coloured needles, m. p. 75—76° (Found: C, 83·7; H, 5·2; OMe, 12·2. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·05; OMe, 12·0%), from methanol.

N-*Methyl*-3 : 4-*benzophenanthridone.*—(i) Methylated under the conditions described above, impure 3 : 4-benzophenanthridone (0·40 g.) yielded a brown gum (0·35 g.). After traces of tar had been removed by passage in benzene over alumina the residue was triturated with methanol and a quantity of *N*-methyl-5 : 6-benzophenanthridone filtered off. Concentration of the mother-liquors at room temperature under reduced pressure yielded the crude product (0·15 g.), m. p. 92—99°. Two crystallisations from light petroleum (b. p. 60—80°) gave N-*methyl*-3 : 4-*benzophenanthridone* as white needles, m. p. 120—121° (Found: C, 83·75; H, 5·1; N, 5·4%).

(ii) 3 : 4-Benzophenanthridine [2] (0·4 g.) was heated under reflux with methyl iodide (1·24 g.) and absolute methanol (20 ml.) for 3 hr.; 3 : 4-benzophenanthridine methiodide separated as yellow crystals (0·40 g.). This (0·30 g.) in dioxan (7·5 ml.) and water (7·5 ml.) was treated with potassium hydroxide (0·40 g.) in water (1·2 ml.). Potassium ferricyanide (0·60 g.) in water (5 ml.) was added and the mixture was heated, with frequent shaking, for 30 min. on

the water-bath. After dilution with water the precipitated material was extracted with ether. Evaporation of the dried (Na_2SO_4) extract left a yellow-green oil which on trituration with light petroleum yielded a white solid (0·11 g.), m. p. 114—118°. Crystallisation from light petroleum (b. p. 60—80°) gave *N*-methyl-3 : 4-benzophenanthridone as white needles, m. p. 120—121° alone or mixed with a specimen obtained as above. Both specimens exhibited the same slight blue fluorescence in ethanol.

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