A New Route to 9-Phenanthrylamine

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The preparation of 9-phenanthrylamine in high yield, by way of phenanthryne, from 9-bromophenanthrene and sodamide in liquid ammonia is described. The properties of di-9-phenanthrylamine, obtained as a by-product, are compared with those described in conflicting literature reports.

VARIOUS routes are cited in the literature for the preparation of 9-phenanthrylamine,[1-7] all with low overall yields; the highest (54%) involves the seven-stage synthesis by Goldberg *et al.*[8]

9-Phenanthrylamine has now been obtained as its hydrochloride in 90% yield from the reaction of 9-bromophenanthrene, prepared as described by Dornfeld *et al.*,[9] with sodamide (from 2·2 equiv. of sodium) in liquid ammonia. The reaction involves nucleophilic attack of amide ions on 9-bromophenanthrene and on the subsequently formed 9-phenanthryne intermediate, which has been described for reactions of this type.[10]

Traces of di-9-phenanthrylamine, m. p. 235°, insoluble in hot dilute hydrochloric acid and giving a green solution in sulphuric acid, were also isolated. It shows an NH stretching absorption near 3380 cm.$^{-1}$. Japp and Findlay[1] described the formation of di-9-phenanthrylamine, m. p. 237°, as an ether-insoluble by-product from the reaction between molten 9-phenanthrol and gaseous ammonia; the main product was 9-phenanthrylamine. Later, however, Schmidt and Lumpp,[11] without referring to the work of Japp and Findlay, claimed to have obtained di-9-phenanthrylamine, m. p. 370°, which gave a blue solution in sulphuric acid, from the reaction between phenanthrol and aqueous ammonia. In both of these references the analyses are in accordance with those calculated for di-9-phenanthrylamine, and no further structural evidence is given.

Since the completion of this work, Ali *et al.*[12] have described the formation of 9-phenanthrylamine in 22% yield by the action of potassamide (from 5 equiv. of potassium) in liquid ammonia on 9-bromophenanthrene; the main product was tetrabenzophenazine. These authors suggest that addition of amide ions to 9-phenanthryne would give an anion derived from 9-phenanthrylamine, and that this is converted into *NN'*-dihydrotetrabenzophenazine, which is readily oxidised to the parent phenazine. With 1 equivalent or less of potassamide, 9-phenanthrylamine was obtained only in traces.

EXPERIMENTAL

9-Phenanthrylamine.—To a stirred solution of sodamide in liquid ammonia, prepared as described by Vogel[13] from sodium (13·6 g.) and liquid ammonia (*ca.* 2700 ml.) with hydrated ferric nitrate (0·85 g.), 9-bromophenanthrene (68 g.) was added during 30 min. The reaction flask was lagged, and stirring was continued for 24 hr., after which ammonium chloride (17 g.) was added to quench the reaction.[14] The ammonia evaporated off, and the residue was extracted with ether. Insoluble material was filtered off and the solution was treated with ether saturated with hydrogen chloride. The precipitated 9-phenanthrylamine hydrochloride was washed with ether and dried (54 g., 89·2%), m. p. 272—275° (sublimes) (lit.,[15] *ca.* 275°). A sample was dissolved in hot water (sparingly soluble), and the solution was basified with ammonia; the resulting 9-phenanthrylamine had m. p. 133—135° (from ethanol) (lit.,[6] 137—138°).

The ethereal filtrate from the hydrochloride was concentrated and cooled; yellow needles of di-9-phenanthrylamine (0·1 g.) separated, m. p. 232—235° (lit.,[1] 237°,[11] 370°) (Found: C, 90·9; H, 5·2; N, 3·8. Calc. for $C_{28}H_{19}N$: C, 91·0; H, 5·2; N, 3·8%), insoluble in warm dilute hydrochloric acid, and giving a green solution in sulphuric acid.

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