Formation of a Bridged Aza-compound in the Chemiluminescent Reaction between 9,10-Diphenylanthracene Cations and n-Butylamine

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Summary Analyses of the products of the chemiluminescent reaction between n-butylamine and electrogenerated mono-cations of 9,10-diphenylanthracene showed the formation of 9,10-dihydro-9,10-diphenyl-*endo*-9,10-(n-butylimino)anthracene (I).

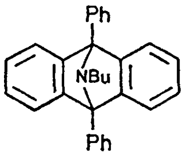
IN our study of the electrochemistry and chemiluminescence of aromatic cations in reaction with nucleophilic agents,[1] we analysed the product composition from the reaction, at room temperature, between electrogenerated mono-cations of 9,10-diphenylanthracene (A) and n-butylamine ($BuNH_2$). The results prove interesting in view of the electrochemical synthesis of bridged compounds and the mechanistic behaviour.

Ca. 85% of A was oxidized to the monocation $A^{+\cdot}$ at a large platinum-gauze electrode in a three-electrode oxygen-free cell, with purified[2] acetonitrile as solvent and 0·1M KPF_6 as supporting electrolyte. Reference and counter electrodes, in separate compartments, contained the same solution plus $Hg \mid Hg_2Cl_2 \mid$ saturated KCl electrodes. The stability of $A^{+\cdot}$ was proved by cyclic voltammetry and by coulometry. The generated $A^{+\cdot}$ was titrated with $BuNH_2$ using the deep-blue colour of the cation as indicator. Equimolar amounts of $BuNH_2$ and $A^{+\cdot}$ were consumed in the reaction.

After evaporation and separation of the supporting electrolyte, the product was chromatographed on silica gel with chloroform as eluent, and the two fractions obtained were further chromatographed on silica gel with ethanol (96%). Each of the original two fractions gave one major and two minor fractions.

All six fractions were analysed by mass spectrometry. The first major product (50% yield based on $A^{+\cdot}$; *cf.* ref. 3), was identified as A, which was confirmed by its characteristic fluorescence spectrum. The second major product (*ca.* 35% yield) had a molecular weight of 401·2113, corresponding to $C_{30}H_{27}N$ (calc. 401·2143).

Upon exposure to air in daylight, some decomposition of this latter major product occurred to the 9,10-diperoxide of A, which was identified by its mass spectrum. This indicates that the 9- and 10-positions are involved in the production of compound $C_{30}H_{27}N$, the n.m.r. spectrum of which in $CDCl_3$ or CCl_4 shows twice as many aromatic protons as aliphatic protons, as required by formula (I). Further, addition of excess of D_2O to the solution in CCl_4 caused no change in the position of any proton peak, showing that the nitrogen atom does not carry a proton. From these results we conclude that compound $C_{30}H_{27}N$ is a tertiary amine with structure (I).



(I)

We suggest that the mechanism is as in reactions (1)—(3).

$$A^{+\cdot} + BuNH_2 \rightarrow ANH_2Bu^{+\cdot} \text{ (attack at 9-position)} \qquad (1)$$

$$ANH_2Bu^{+\cdot} + A^{+\cdot} \rightarrow ANH_2Bu^{2+} + A \qquad (2)$$

$$ANH_2Bu^{2+} + BuNH_2 \rightarrow ANHBu^{+} + BuNH_3^{+} \qquad (3)$$

In reaction (3) bridge formation of N to the 10-position yields the conjugate acid of (I). The formation of A in step (2) occurs in part through an excited state, the measured chemiluminescence being identical with the fluorescence spectrum of A.

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