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INCORPORATION OF A C_2 FRAGMENT IN THE COURSE OF PHOTOLYSIS OF SOME AROMATIC SCHIFF'S BASES IN ETHANOL

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PRODUCTS of an unexpected type were encountered in the course of some photochemical investigations of ring-closure reactions in Schiff's bases analogous to the photochemical conversion of stilbene to phenanthrene (1).

Ultraviolet irradiation of the Schiff's base from β-naphthylamine and benzaldehyde (2) (I, R = H) in ethanol in the presence of air gave as the main product (30 - 40% yield) a crystalline material, m.p. 188°, which analysed well for $C_{19}H_{13}N$ (found: C, 89.3%; H, 5.1%; N, 5.4%; calculated: C, 89.4%; H, 5.1%; N, 5.5%). The ultraviolet spectrum (in ethanol) showed λ_{max} 279 mμ (ϵ 26700), λ_{max} 326 mμ (ϵ 5800), λ_{max} 340 mμ (ϵ 9000), and λ_{max} 357 mμ (ϵ 9800).

The mass spectrum* showed the parent peak at m/e 255, confirming the molecular weight. The only peaks of significant intensity apart from the strong parent peak were at M-1 and M-2, due to the presence of a diaryl-type structure (3). The NMR spectrum† showed a doublet (half of an AB quartet) at 527 and 535.5 c/s of relative intensity 1 proton and an extended multiplet between 520 and 440 c/s of relative intensity 12 protons.

The above evidence shows that the product is the known (4) 2-phenyl-5,6-benzoquinoline (II, R = H), i.e. that a <u>C_2 fragment has been incorporated</u>

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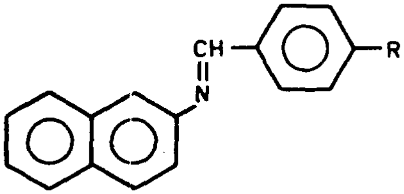
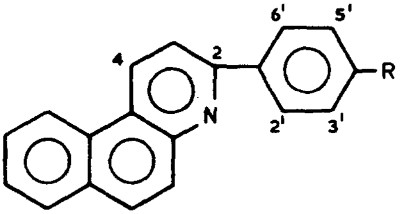
*Taken on an Atlas CH4 mass spectrometer.

†Taken in 7% deuteriochloroform solution on a Varian A60 spectrometer. Chemical shifts are quoted in c/s at 60 Mc/s downfield from tetramethylsilane as internal reference.

in the course of the reaction. The downfield doublet in the NMR spectrum is assigned to H_4.



I



II

In confirmation, an analogous irradiation of the Schiff's base from β-naphthylamine and anisaldehyde (5) (I, R = OMe) gave 2-(4'-methoxyphenyl)-5,6-benzoquinoline (II, R = OMe), m.p. 197°, whose structure was assigned on the following evidence:

The ultraviolet spectrum (in ethanol) showed λ_{max} 262 mμ(ϵ 27500), λ_{max} 283 mμ (ϵ 35400), λ_{max} 305 mμ (shoulder) (ϵ 23700), λ_{max} 363 mμ (ϵ 125000), λ_{max} 345 mμ (ϵ12200). The mass spectrum established the molecular weight as 285. There were also relatively strong peaks at m/e 270, 242, and 241, and metastable peaks which indicated the occurrence of the following ion transitions:

$285^+ \longrightarrow 270^+ + 15$, $270^+ \longrightarrow 242^+ + 28$, and $242^+ \longrightarrow 241^+ + 1$.

These data suggest that the molecular ion eliminates a methyl radical from its methoxyl group and forms a resonance-stabilized keto carbonium ion which consecutively loses CO and a hydrogen atom. This results in the formation of a stable cyclic radical ion; the reactions are predictable on the basis of the structure II, R = OMe. The NMR spectrum* showed a doublet of relative intensity 1 proton at 529 and 538 c/s (half of an AB quartet, H_4), an A_2B_2 multiplet of relative intensity 4 protons with principal peaks at 497, 488, 429,

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* See second footnote on page 659

and 420 c/s ($H_{2'}$,$H_{6'}$ and $H_{3'}$,$H_{5'}$), an extended multiplet of relative intensity 7 protons between 525 and 450 c/s (remaining aromatic protons on the benzoquinoline ring), and a singlet of relative intensity 3 protons at 232 c/s (methoxyl group).

The mechanism and scope of this novel reaction and the nature of the other products are under investigation. It seems probable that the C_2 fragment is derived from acetaldehyde formed by photo-oxidation of ethanol.

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