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INCORPORATION OF ONE OR TWO R-C-C- FRAGMENTS IN THE COURSE OF PHOTOLYSIS OF SOME SCHIFF'S BASES IN PRIMARY ALCOHOLS $R-CH_2-CH_2-OH$

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AS previously reported[1], irradiation of a Schiff's base from β-naphthylamine in ethanol results in the incorporation of a C_2 fragment, derived from the solvent, with the formation of a substituted benzo[f]quinoline (I).

Since then Cava and Schlessinger[2], by irradiation of 1-naphthal-1-naphthylamine in ethanol, obtained as the main product dibenzo[c,i]phenanthridine without the inclusion of the solvent used in the reaction.

We now report the formation of another type of substituted benzo[f]-quinoline (II). This reaction involves a novel participation of the solvent. Such compounds are derived by replacing the aldehyde part of the original Schiff's base by the aldehyde formed from the alcohol used as the solvent. Furthermore, we have established that by using higher primary alcohols, side chains of appropriate length are introduced into benzo[f]quinoline, with formation of the compounds (I) and (II). These were identified by their n.m.r. spectra[*], mass spectra[†], and elementary composition.

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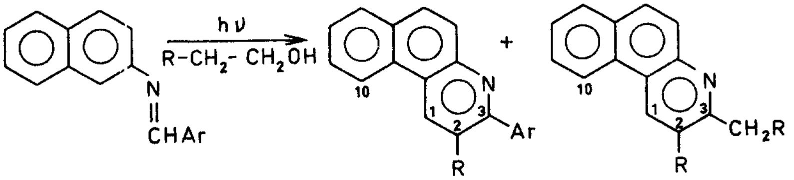
[*] Taken in approximately 5% deuteriochloroform solution on a Varian A60 spectrometer. Chemical shifts are quoted in p.p.m. downfield from tetramethylsilane used as internal reference.

[†] Taken on an Atlas CH_4 mass spectrometer.



I II

Irradiation of benzal-β-naphthylamine in isoamyl alcohol gave a 25% yield of (I) R = $CH(CH_3)_2$, m.p. 139°[*]. The n.m.r. spectrum showed a broadened singlet of 1 proton intensity at δ 8.96 (H_1), a multiplet of 1 proton intensity at δ 8.7 (H_{10}), an extended multiplet of 10 proton intensity between δ 7.4 and 8.2 (remaining aromatic protons), a septet of 1 proton intensity at δ 3.40, and a doublet of 6 proton intensity at δ 1.35 with J = 7 c/s (isopropyl group at C_2). The same reaction mixture also gave a 20% yield of (II) (R = $CH(CH_3)_2$), m.p. 58-59°. The n.m.r. spectrum showed a broadened singlet (1 proton) at δ 8.75 (H_1), a multiplet of 1 proton intensity at δ 8.6 (H_{10}), an extended multiplet of 5 proton intensity between δ 7.4 and 8.2 (remaining aromatic protons), a septet of 1 proton intensity at δ 3.42 and a doublet of 6 proton intensity at δ 1.39 (isopropyl group at C_2), a doublet of 2 proton intensity at δ 2.98, a symmetrical multiplet of 1 proton intensity at δ 2.37, and a doublet of 6 proton intensity at δ 1.04 (sec-butyl sidechain at C_3).

Irradiation of benzal-β-naphthylamine in n-hexanol gave a 25% yield of (I) (R = n-C_4H_9), m.p. 102-3°. The n.m.r. spectrum showed a broadened singlet of 1 proton intensity at δ 8.85 (H_1), a multiplet of 1 proton intensity at δ 8.7 (H_{10}), an approximate triplet of 2 proton intensity at δ 2.92 (benzylic methylene at C_2), an extended multiplet of 10 proton intensity between δ 7.3 and 8.1 (remaining aromatic protons), a broad absorption of 4 proton intensity

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[*] All the compounds described in this paper gave satisfactory analytical results.

between δ 1.1 and 1.9 (methylene groups in side chain), and a multiplet of a shape characteristic of terminal methyl groups in straight-chain paraffins[3] of 3 proton intensity at δ 0.9.

The same reaction mixture also gave a 37% yield of (II) (R = n-C_4H_9), m.p. 60-61°. The n.m.r. spectrum showed a broadened singlet of 1 proton intensity at δ 8.64 (H_1), a multiplet of 1 proton intensity at δ 8.6 (H_{10}), an extended multiplet of 5 proton intensity between δ 7.5 and 8.0 (remaining aromatic protons), a multiplet (possibly two approximate overlapping triplets) of 4 proton intensity at δ 2.9 (benzylic methylene groups at C_2 and C_3), a broad absorption of 10 proton intensity between δ 1.2 and 2.0 (methylene groups in the sidechains), and two overlapping, characteristic terminal methyl absorptions[3] of 6 proton intensity at δ 1.0.

By changing the Ar group in I from Ph to 4-MeO-C_6H_4-, 4-O_2N-C_6H_4-, and 2-Cl-C_6H_4- the corresponding derivatives were prepared in yields similar to those reported above. The rate of the reaction (as judged by the changes in the ultraviolet spectra of samples from the reaction mixtures) differed, however, characteristically for various substituents.

This extension of our previous findings is of interest when compared with the recent results of Cava and Schlessinger[2] and Badger et al.[4]. It indicates a considerable selectivity of the photochemical transformations of Schiff's bases, and calls for further investigations.

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