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NEW SIX-MEMBERED AROMATIC BETAINES FROM 8-ACYLAMINOQUINOLINES

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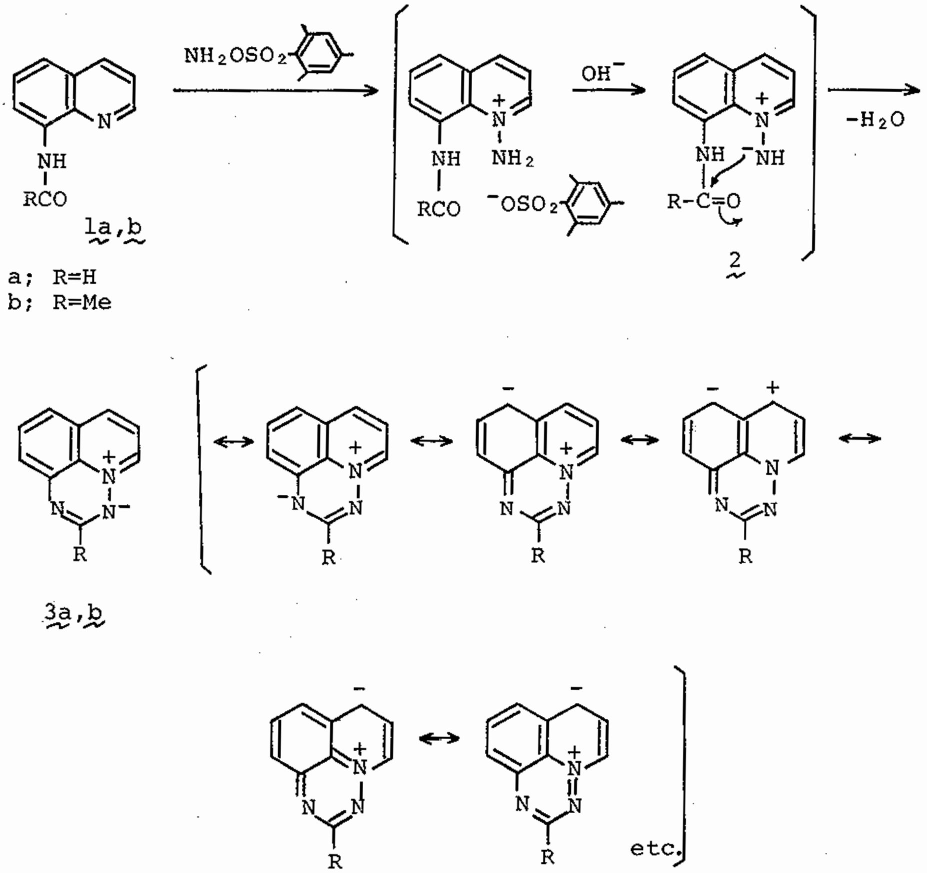
Some spectral and chemical properties of new six-membered aromatic betaines (3a and 3b) which are synthesized from the corresponding 8-acylamino-quinolines via N-amination followed by cyclization with alkaline treatment, are described.

Interest in syntheses and cycloaddition reactions of six-membered aromatic betaines has been increasing.[1] Here we describe the synthesis and some properties of a new class of tricyclic six-membered aromatic betaines, (3a) and (3b).

Reaction of 8-formylaminoquinoline (1a) with an equimolar quantity of O-mesitylenesulfonylhydroxylamine[2] in CH_2Cl_2 at room temperature for 1 day followed by treatment with 10% potassium hydroxide gave 44% yield of (3a) [characterized as its picrate,[3] mp 238-240° (decomp.)] as red and hygroscopic crystals. Similarly 8-acetylaminoquinoline (1b) gave (3b), mp 173-174°, in 12% yield.

The betaine structures of (3) were confirmed on the basis

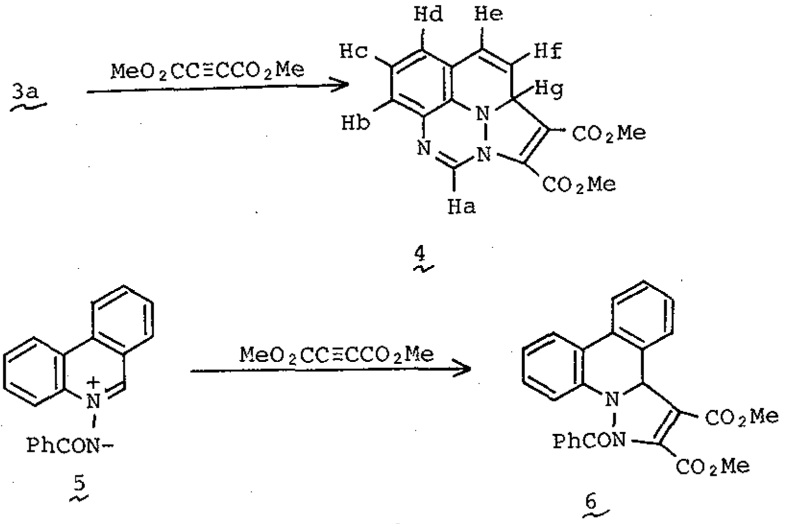


Scheme 1

of spectral and chemical evidence. Compound (3a) showed the correct molecular ion peak at m/e 169 in its mass spectrum. The uv spectrum of (3a) exhibited the most intense band at 344 nm and several weaker absorption bands at 422, 480, 512, and 550 nm. These absorptions disappeared by addition of one drop of 1N HCl solution. In the nmr spectrum the signal of aromatic protons (δ 6.6-7.6) is at higher magnetic fields relative to those of quinoline [δ 7.0-8.3, 8.84 (H-2)].[4] The red color and the high-field shift of the aromatic proton signal of (3a) suggest considerable delocalization of the negative charge over the quinoline ring (see resonance structures). This transformation can be formulated as proceeding via N-imine (2) which underwent intramolecular cyclization to (3) (Scheme 1).

Compound (3b) showed essentially similar spectral properties to those of (3a) [nmr δ ($CDCl_3$) 6.55-7.6 (6H, m, aromatic protons), 2.01 (3H, s, CH_3)].

When compound (3a) was refluxed with excess dimethyl acetylenedicarboxylate in methanol for 1 hr under nitrogen, 1:1 cycloadduct (4), mp above 290°, was obtained in 47% yield. The structure of (4) was demonstrated by its nmr spectrum, which reveals a singlet (1H, Ha) at δ 6.85, an ABX multiplet consisting of a quartet (1H, Hb) at δ 7.65 and a multiplet (2H, Hc, Hd) between δ 7.05-7.25, a doublet (1H, J 10 Hz, He) at δ 6.93, a doublet (1H, J 4 Hz, Hg) at δ 6.38, a double doublet (1H, J 10 and 4 Hz, Hf) at δ 6.05, and two methoxyl singlets at δ 3.55 and 4.05. Thus, the behavior of (3a) toward dimethyl acetylenedicarboxylate parallels that of phenanthridinium N-benzoyliminobetaine (5)[5] which gives adduct (6).



Scheme 2

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