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ANNELATION OF THE BENZINDOLIZINE RING TO THE QUINOXALINE NUCLEUS

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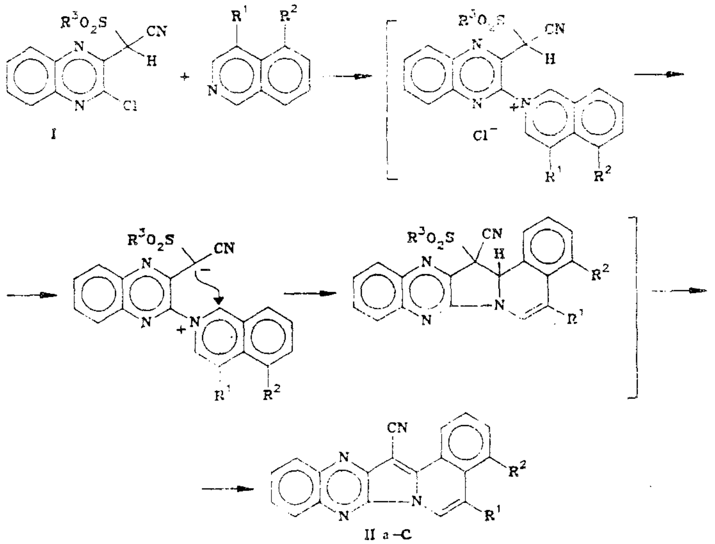
We have found that α-sulfonyl-3-chloro-2-quinoxalylacetonitriles (I) [1] react with isoquinolines (fusion at 160°C, or boiling for 2-4 h in DMF), to give benz[5,6]indolizino[2,3-b]quinoxalines (II) [mp >300°C (from DMF)], in near-quantitative yields.



II a $R^1=R^2=H$, b $R^1=H$, $R^2=NO_2$, c $R^1=Br$, $R^2=NO_2$; $R^3=CH_3$, C_6H_5, $4\text{-}CH_3C_6H_4$

Clearly, nucleophilic replacement of the chlorine atom occurs initially. It is characteristic that of the two possible routes for subsequent intramolecular nucleophilic attack (at $C_{(1)}$ or ($C_{(3)}$ of the isoquinoline nucleus), in all instances only the first is followed, to give the above isomer. Finally, aromatization occurs by elimination of sulfinic acid. The structures of the products were established by their PMR spectra (solvent CD_3COOD), (IIa) and (IIb) showing two doublets (J = 9 Hz) at 7.9-8.6 ppm (5-H) and 9.20-9.36 ppm (6-H), and (IIc) a singlet at 9.44 ppm (6-H). The 1-H proton in the spectra of (IIa-c) resonates at low field (9.33-9.66 ppm, doublet, J = 9 Hz) owing to descreening by the adjacent nitrile group. The IR spectra of (IIa-c) show strong absorption for the conjugated nitrile group at 2210-2200 cm^{-1}.

Quinoline does not react with (I), obviously as a result of the considerable steric hindrance arising when the quaternary quinolinium salt is formed in the initial stage of the reaction.

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NEW SYNTHESIS OF CAFFEINE METHIODIDE AND ITS HOMOLOG

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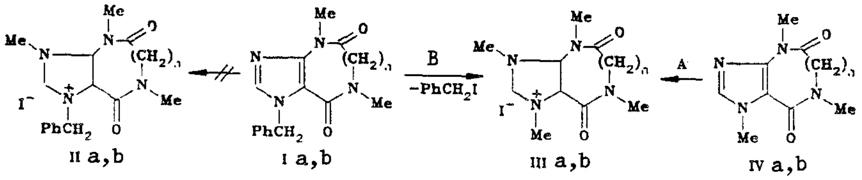
It has been found that on heating 7-benzyltheophyllin (Ia) with an excess of methyl iodide in DMF, instead of the expected salt (IIa), there is obtained caffeine methiodide (IIIa).



I–IV a n=0; b n=1

The homolog of Ia (Ib) is converted under similar conditions into 1,4,7-trimethylimidazo[4,5-e][1,4]diazepin-(6H)-5,8-dione methiodide (IIIb). In each case, benzyl iodide was detected in the reaction mixture.

The structures of (IIIa) and (IIIb) were confirmed by direct synthesis from caffeine IVa) and its homolog (IVb).

Caffeine Methiodide (IIIa). A. A mixture of 1.8 g (0.01 mole) of caffeine, 25 ml of DMF, and 2.5 ml of methyl iodide was boiled for 6 h. The solid which separated was filtered off, washed with ether, and the filtrate diluted with ether to give a further small amount of product. Overall yield 2.5 g (79%), mp 360°C (subl.).

B. A mixture of 2.7 g (0.01 mole) of 7-benzyltheophyllin, 20 ml of DMF, and 2.5 ml of methyl iodide was boiled for 6 h. The solvent was removed under reduced pressure, and the crystalline solid filtered off to give 2.7 g (83%) of product, mp 360°C (subl.).

A mixed melting point with the material obtained by method A gave no depression.

1,4,7-Trimethyl-5,6,7,8-tetrahydro-4-imidazo[4,5-e][1,4]diazepine-5,8-dione (IIIb) Methiodide. A. Compound (IIIb) was obtained as described in [1].

B. A mixture of 2.8 g (0.01 mole) of (Ib), 20 ml of DMF, and 3 ml of methyl iodide was boiled for 4 h. The solvent was removed under reduced pressure, and the dry residue treated with a mixture of acetone and ether (1:1) and kept overnight. The solid was filtered off, and washed with ether to give 3.2 g (92%) of product, mp 200-202°C.

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