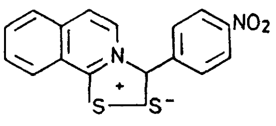
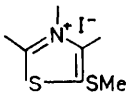
Synthesis of Mesoionic 3-*p*-Nitrophenylimidazol[2,3-a]isoquinolinium 2-Thione

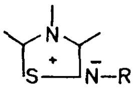
By P. B. TALUKAR,* S. K. SENGUPTA, and A. K. DATTA
(*East India Pharmaceutical Works Ltd., Calcutta*-61, *India*)

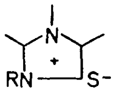
Summary The methiodide of mesoionic 3-*p*-nitrophenylthiazoloisoquinolinium-2-thione reacts smoothly with primary aliphatic amines to give mesoionic imidazoloisoquinolinium thiones (IV).

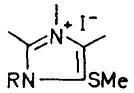
SEVERAL types of molecular transformations in the field of mesoionic chemistry have been reported.[1,2] The conversion[2] of mesoionic 1,3,4-thiadiazole to mesoionic *s*-triazoles is an elegant route from one mesoionic system to another. In this context, we report the transformation of 3-*p*-nitrophenylthiazolo[2,3-a]isoquinolinium 2-thione[3] (I) to imidazoloisoquinolinium thiones (IV).


(I)


(II)


(III)


(IV)


(V)

R = Me, Pr^n, Bu^n, CH_2Ph, CH_2CH_2Ph

Treatment of a suspension of the methiodide[3] (II) in $H{\cdot}CO{\cdot}NMe_2$ with a primary aliphatic amine, followed by stirring at room temperature for 3 h and separation of the product with EtOH, gave (IV) as dark-red plates. The reaction is slower in methanol.

On the basis of elemental analyses and spectral data, the products were formulated as (IV). *E.g.* the presence of moderately intense bands around 1335 cm^{-1} (ν_{C-S}-)[2,4] and the absence of any band around 1570 cm^{-1} (ν_{C-N} conj.) in their i.r. spectra are in agreement only with structure (IV). Further, absorption spectra (λ_{max} MeOH at 223, 255, and *ca.* 333 nm) of the methiodides (V; R = Me, Pr^n, and Bu^n, respectively) were found to be superimposable with those of protonated (IV) indicating a formal negative charge on *exo*-sulphur.

The isomeric compound (III) may be an intermediate in the transformation (II) → (IV), but this is difficult to establish and the reaction may proceed *via* a mechanism analogous to that proposed[5] for the conversion of a thiazolium salt or a disulphide to imidazolinethione. But it is interesting to note that the reaction gave identical products under nitrogen, and a high recovery of the substrate (II)

(>50% after 24 h) is possible even after treatment with diethylamine, piperidine, or aniline.

While the absorption spectrum of (I) shows a characteristic λ_{max} at 435 nm, this occurs as a prominent shoulder in (IV) around 420 nm. Distinct bands appear in aprotic solvents (IV, R = Bu^n): λ_{max} 398 and 480 nm (ϵ = 12,320 and 13,480, acetone); 390 and 467 nm (ϵ = 12,120 and 12,510, acetonitrile). The u.v. absorption pattern is practically identical for all the compounds and shows a band near 260 nm attributed[5] to imidazolinethiones.

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