

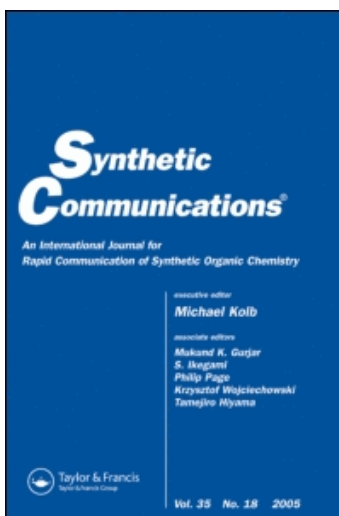
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Heterocycles in Organic Synthesis. III A Facile Synthesis of Isoquinolinyl Vinyl Sulphides

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HETEROCYCLES IN ORGANIC SYNTHESIS-III^{1a} A FACILE
SYNTHESIS OF ISOQUINOLINYL VINYL SULPHIDES.

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Vinyl sulphides find a substantial application in organic synthesis.² The synthetic utility of heterocyclic vinyl sulphides due to the ease in extrusion of heterocyclic ring³ should be more versatile. Here, we report the synthesis of isoquinolinyl vinyl sulphides from dihydrothiazolo [2,3-a] isoquinolinium cations, depicting another use of heterocycles in organic synthesis.⁴

The hydroxide ion attacked mainly C_{10b} of dihydrothiazolo [2,3-a] isoquinolinium cations (I, II) resulting in the C_{10b}-S bond cleavage reactions.^{1b} Under anhydrous conditions the bases should abstract a proton attached at C-2 or C-3 forming an S or N ylide which on subsequent bond cleavage would provide an S and/or N vinyl derivative. Now it has been found that dihydrothiazolo [2,3-a] isoquinolinium cations,

on fusion with anhydrous potassium carbonate under vacuum, furnish 1-vinylthioisoquinoline derivatives (IVa-c) in synthetically useful yields.

Thus 2,3,5,6-tetrahydrothiazolo [2,3-a] isoquinolinium perchlorate (I), gave a brown liquid product (65%), M^+ , m/e 189. In its ^{13}C n.m.r. spectrum, the nine sp^2 hybridised carbon signals appeared at δ 138.069, 137.787, 132.137, 131.487, 129.213, 127.914, 126.861, 126.374 and 112.158 indicating that two of the sp^3 hybridised carbon atoms of the precursor have been transformed into sp^2 hybridised carbon atoms and $>C=S$ (δ 175-90)⁵ was absent. From these data, and its 1H n.m.r. spectrum- δ 3.0 and δ 2.95 (overlapping 2H triplets, $-CH_2-CH_2-$), δ 3.60-3.77 (m, 2H, vinylic H), 4.32 (t, 1H, vinylic H), and 6.75 - 7.60 (m, 4H, aromatic H), the product was assigned the structure, 1-(vinylthio) 3,4-dihydroisoquinoline (IVa).

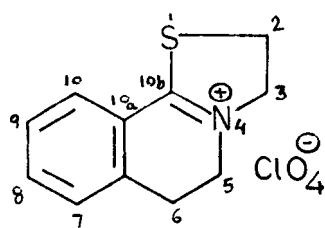
Likewise 2,3-dihydrothiazolo [2,3-a] isoquinolinium perchlorate (IIa; R=H) gave 1-(vinylthio)isoquinoline (IVb), yellow crystalline solid (70%), m.p. 122°C, M^+ , m/e 187.04554, 1H n.m.r. spectrum- δ 5.17 - 5.46 (m, 2H, vinylic H), 6.83 (d, 1H, vinylic H), 7.45 - 9.00 (m, 6H, aromatic H).

Similarly, 3-methyl-2,3-dihydrothiazolo [2,3-a] isoquinolinium perchlorate (IIb; R=CH₃) gave 1-(propenylthio)isoquinoline (IVc), a brown liquid (65%),

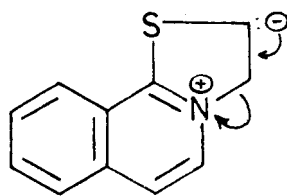
M^+ , m/e 201. Its 1H n.m.r. spectrum exhibited a methyl H doublet at δ 1.85 (J 7Hz) indicating its attachment to an olefinic carbon ($CH_3-CH=$) and signals at δ 5.72 - 7.21 (m, 2H, vinylic H) and δ 7.33 - 8.27 (m, 6H, aromatic H). The doublet at δ 1.85 further split into doublets (J 1.5Hz) indicating cis orientation for CH_3 and H on the double bond and E configuration for the product. Thus under anhydrous conditions, dihydrothiazolo[2,3-a]isoquinolinium cations undergo proton abstraction at C_2 even with a weak base to form S ylide(III) which by subsequent ring opening gives S-vinyl derivatives.

Experimental

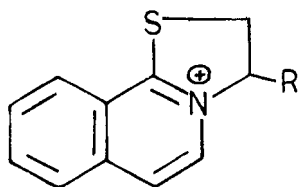
The cations I, IIa and IIb, 1g each, was thoroughly mixed with anhydrous potassium carbonate(3g) by grinding and the mixture was heated in a sublimation apparatus at a temperature of 150-180°C, under reduced pressure(15mm) for 3 hrs. The solid IVb and oily products(IVa,c) deposited on the cold thimble were scratched/washed with dichloromethane. The process of heating and collecting the products was repeated three times. The fused mass was treated with water and was extracted with dichloromethane(3x60ml). The extract was washed with water and dried with sodium sulphate. The solvent was removed and the residue was mixed with the product collected from the thimble. The products were purified over a short column filled with alumina using pet.ether or benzene as eluent.



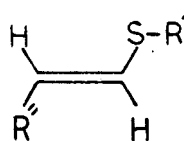
I



III



II a, R=H

b, R=CH₃

R'

R''

IV a, 3,4-dihydro-
isoquinolinyl-1

b, Isoquinolinyl-1

c, Isoquinolinyl-1 CH₃**References:**

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