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

Harjit Singh*, Subhash C. Malhotra

* Department of Chemistry, Guru Nanak Dev University, Amritsar, India

To cite this Article

To link to this Article: DOI: 10.1080/00397918108063636
URL: http://dx.doi.org/10.1080/00397918108063636

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
HETEROCYCLES IN ORGANIC SYNTHESIS-III: A FACILE SYNTHESIS OF ISOQUINOLINYL VINYL SULPHIDES.

Harjit Singh* and Subhash C. Kalhotra,
Department of Chemistry,
Guru Nanak Dev University,
Amritsar-143005, India

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

The hydroxide ion attacked mainly C₁₀b of dihydrothiazolo [2,3-α] isoquinolinium cations(I, II) resulting in the C₁₀b-S bond cleavage reactions. 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-α] 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 $\delta$ 138.065, 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 $\geq C = S$ ($\delta$ 175-90) was absent. From these data, and its $^1$H n.m.r. spectrum at $\delta$ 3.0 and $\delta$ 2.95 (overlapping 2H triplets, $-CH_2-CH_2-$), $\delta$ 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, $^1$H n.m.r. spectrum at $\delta$ 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=CH$_3$) gave 1-(propenylthio)isoquinoline (IVc), a brown liquid (65%),
HETEROCYCLES IN ORGANIC SYNTHESIS. III

M⁺, m/e 201. Its ¹H n.m.r. spectrum exhibited a methyl H doublet at δ 1.85 (J 7 Hz) indicating its attachment to an olefinic carbon (CH₃-C=H) 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 1.5 Hz) indicating cis orientation for CH₃ and H on the double bond and E configuration for the product.

Thus under anhydrous conditions, dihydrothiazolo[2,3-2] isoquinolinium cations undergo proton abstraction at C₂ 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.
References:
1b. References 3, 4 in 1a.