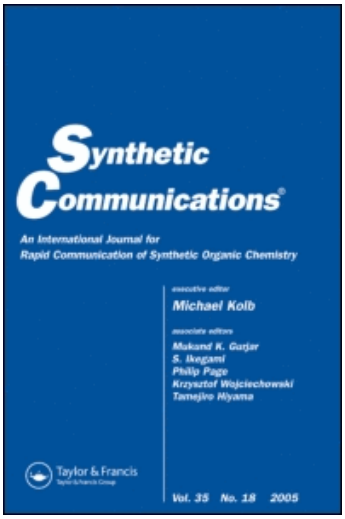


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# Heterocycles in Organic Synthesis-ii[1] Synthesis of Ethylenedisulphide Derivatives (-S- $CH_2$- $CH_2$- S-) from 2,3-Dihydrothiazolo [2, 3-a] Isoquinolinium and Pyridinium Cations

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# HETEROCYCLES IN ORGANIC SYNTHESIS-II[1] SYNTHESIS OF ETHYLENEDISULPHIDE DERIVATIVES ( $-S-CH_2-CH_2-S-$ ) FROM 2,3-DIHYDROTHIAZOLO [2,3-a] ISOQUINOLINIUM AND PYRIDINIUM CATIONS

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Heterocycles have recently been used advantageously for the synthesis of other categories of compounds.[2] Here, we report that with thiolate ions, 2,3-dihydrothiazolo [2,3-a] pyridinium[3](I); 2,3,5,6-tetrahydrothiazolo [2,3-a] isoquinolinium[4](II) and 2,3-dihydrothiazolo [2,3-a] isoquinolinium[5](III) cations, available from the condensations of ethylene dibromide with pyridine-2(1H)-thione[3]; 3,4-dihydroisoquinoline-1(2H)-thione[4] and isoquinoline-1(2H)-thione[5], form ethylene disulphide derivatives(IVa-f) possessing one pyridyl/isoquinolyl and second heterocyclic or nonheterocyclic moiety - a novel category of organic compounds, in synthetically useful yields.

2,3-Dihydrothiazolo [2,3-a] pyridinium perchlorate (I, X = $ClO_4$) and pyridyl-2-thiolate ion in anhydrous dimethylformamide solution gave a product (85%), m.p. 118°, $M^+$, m/e 248. Its $^1H$ n.m.r. spectrum showed a singlet at $\delta$ 3.92 ($H_{aliphatic}$) and a multiplet at $\delta$ 6.8-8.35 ($H_{aromatic}$) which integrated in the ratio 1:2. The $^{13}C$ n.m.r. spectrum[6] showed only six signals, one for $sp^3$ hybridised carbon at $\delta$ 30.26 (t, $-CH_2-$) and five signals at $\delta$ 119.45(d), 122.39(d), 135.91(d), 149.54(d) and 158.79(s) for the pyridyl $sp^2$ hybridised carbon atoms. These data which depicted a highly symmetrical structure could satisfactorily be explained by the structure-2,2'-(ethylenedithio) dipyridine(IVa). An authentic sample of IVa was obtained by condensing pyridine-2(1H)-thione with half an equivalent of ethylene dibromide.

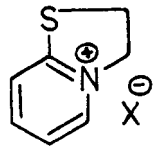
Likewise, 2-[[2-(ethylthio)ethyl] thio] pyridine (IVb)[7]; 2-[[2-(phenylthio) ethyl] thio] pyridine(IVc)[7]; 3,4-dihydro-1[[2-(phenylthio)ethyl] thio] isoquinoline (IVd), m.p. 79°; 3,4-dihydro-1-[[2-(ethylthio)ethyl] thio] isoquinoline(IVe)[7] and 1-[[2-(ethylthio)ethyl] thio] isoquinoline(IVf), m.p. 80° were obtained in 80,81,80,75% and 80% yields from ethylthiolate and I; phenylthiolate and I; phenylthiolate and II; ethylthiolate and II and ethylthiolate and III respectively.

All these compounds gave satisfactory mass and $^{1}H$ n.m.r. spectra. In the $^{1}H$ n.m.r. spectra of IVb-f, due to their unsymmetrical nature, the ethylene moiety constituted two separate triplets as against a singlet in IVa.

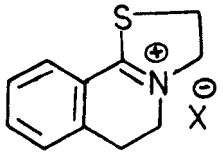
## Experimental

Sodium pyridyl-2 or phenyl or ethylthiolate(.01 mole) was added with stirring to a solution of 2,3-dihydrothiazolo [2,3-a] pyridinium(I) or 2,3,5,6-tetrahydrothiazolo [2,3-a] isoquinolinium(II) or 2,3-dihydrothiazolo [2,3-a] isoquinolinium(III) perchlorates (.01 mole) in anhydrous dimethyl formamide (50 ml). The reaction mixture attained a dark brown colour and was stirred for 4 hrs at room temperature to complete the reaction (T.L.C). The solvent was removed in vac. and the residue was treated with water and was neutralised with dilute acetic acid. It was extracted with dichloromethane (3 x 50 ml). The extract was washed with water (3 x 150 ml) and dried with sodium sulphate. The solvent was removed and the crude residue consisting of one major component (T.L.C) was purified over a short column filled with alumina using pet. ether or benzene as eluent.

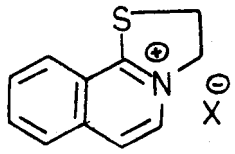
We thank Prof. P.J. Scheuer and Prof. R.L.Khetarpal for mass and $^{13}C$ n.m.r. spectra and Dr.K. Loening for help in nomenclature.



I



II



III

$R\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R'$

IV

| | R | R' |
|---|---|---|
| (a) | pyridyl-2 | pyridyl-2 |
| (b) | pyridyl-2 | ethyl |
| (c) | pyridyl-2 | phenyl |
| (d) | 3,4-dihydro-isoquinolyl-1 | phenyl |
| (e) | 3,4-dihydro-isoquinolyl-1 | ethyl |
| (f) | isoquinolyl-1 | ethyl |

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6. The multiplicity given in brackets pertains to the off-resonance proton decoupled spectrum.
7. Yellow coloured thick liquids.