SYNTHESES AND REACTIONS OF 2-INDOL-3-YL-1,3-OXATHIOLIUM SALTS[1)]

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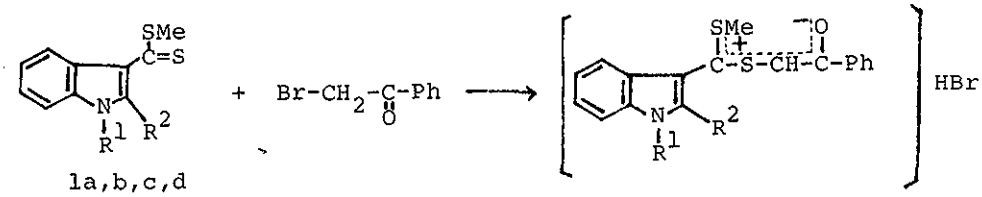
The reaction of methyl indole-3-dithiocarboxylates (1a,b,c,d) with phenacyl bromide in acetone gave 2-indol-3-yl-1,3-oxathiolium bromides (2a,b,c,d) which reacted with active methylene compounds to form 2-indol-3-ylthiophene derivatives (3a,b,c,d)

We had previously reported that 3-(α,α-bismethylthiomethylene)-indolenium methyl sulfates, which were prepared from methyl indole-3-dithiocarboxylates, reacted with active methylene compounds to form 3-(methylthio)vinylindole derivatives in good yields[2)]. In our present communication, we report the syntheses and reactions of 2-indol-3-yl-1,3-oxathiolium salts.

These 2-indol-3-yl-1,3-oxathiolium salts were prepared by the following manner: A solution of methyl indole-3-dithiocarboxylates (1a,b,c) and phenacyl bromide in absolute acetone was refluxed for 8 hr on a boiling water bath and then the solvent was evaporated to one-third volume. The concentrated

solution was allowed to stand at room temperature for 4 hr and the precipitated yellow needles were collected on a filter and recrystallized from a mixture of methanol and acetone to give 2-indol-3-yl-1,3-oxathiolium bromide (2a,b,c,d) in 40 - 60% yields. The compounds 2a and 2b were also obtained by reaction of thioamides(1e,f,g) with phenacyl bromide using Hartman's method[3-5].

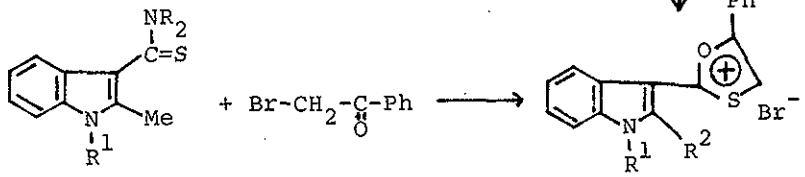
Although some syntheses of 1,3-oxathiolium salts from thioamides or thiolesters and a few syntheses of 1,3-dithiolium salts from dithiocarboxylates have been reported[7,8], there has been to date no reported synthesis of 1,3-oxathiolium salts *from dithiocarboxylates*.



1a,b,c,d

a; R^1=H, R^2=Me, b; R^1=R^2=Me

c; R^1=H, R^2=Ph, d; R^1=Me, R^2=Ph



1e,f,g

e; R^1=H, NR_2= 

f; R^1=Me, NR_2= 

g; R^1=H, NR_2= 

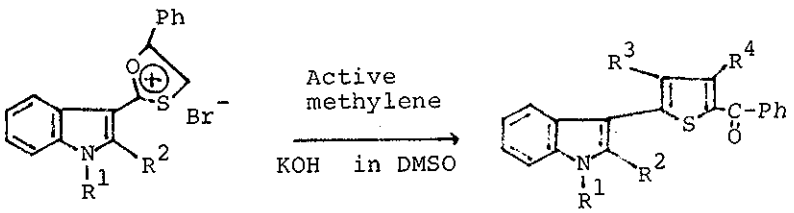
2a,b,c,d

2	R^1	R^2	mp(°C)	UV λ_{max}^{EtOH} nm (logε)
a	H	Me	284	280(4.48)
b	Me	Me	284	285(4.45)
c	H	Ph	253	247(4.51), 287(4.32)
d	Me	Ph	274	246(4.53), 300(4.17)

Reaction of 2b with malononitrile in the presence of powdered potassium hydroxide in dimethyl sulfoxide gave in 72% yield yellow needles of a compound mp 220°, which was shown to be 4-amino-5-benzoyl-3-cyano-2-(1,2-dimethylindol-3-yl)-thiophene from spectral data and elemental analysis.

Similarly, reaction of 2d with active methylene compounds-malononitrile, ethyl acetoacetate, and acetylacetone afforded 5-benzoyl-2-indol-3-ylthiophene derivatives (3b,c,d) in 50 -80% yield.

Recently, Hirai and Ishiba reported the reaction of 1-aryl-1,3-oxathiolium salts with active methylene to form thiophene derivatives[6]. Our results fall into the same category.



3a,b,c,d

3	R^1	R^2	R^3	R^4	mp(°C)	IR(KBr) cm^{-1}	UV λ_{max}^{EtOH} nm(log ε)
a	Me	Me	CN	NH_2	220	3400(NH) 3290(NH) 2210(CN) 1610(C=O)	270(4.14) 352(4.03) 400(4.32)
b	Me	Ph	CN	NH_2	218	3280(NH) 3300(NH) 2200(CN) 1590(C=O)	294(4.23) 400(4.24)
c	Me	Ph	COOEt	Me	154	1700(C=O) 1620(C=O)	290(4.32) 380(3.96)
d	Me	Ph	Ac	Me	167	1675(C=O) 1628(C=O)	290(4.35) 380(3.97)

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