

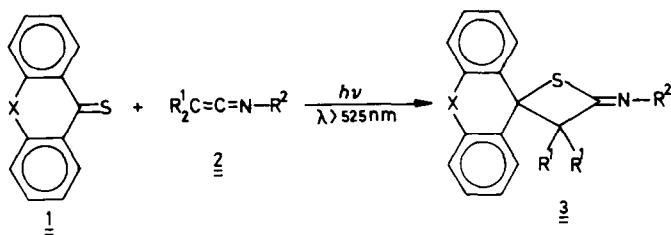
PHOTOCHEMICAL (2+2) CYCLOADDITION OF AROMATIC THIONES TO KETENIMINES.  
ACID CATALYZED REARRANGEMENT OF 2-IMINOTHIETANES.

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In the course of our studies on the photochemical (2+2)- and (4+2) cycloadditions of carbonyl- and thiocarbonyl compounds with acetylenes (1) and cumulated unsaturated systems like allenes (2), we extended our investigations with a study of the regiospecificity of the addition of excited thiones to ketenimines (it is known that monocarbonyl compounds give photochemical (2+2) cycloaddition to ketenimines with formation of 2- and 3-iminooxetanes (3,4)).

Irradiation of a 0.050 molar benzene solution of an aromatic thione 1 and 125 mol% of a ketenimine 2 through a  $K_2Cr_2O_7$  filter solution ( $T=1\%$  at 525 nm), gave almost quantitative formation of a 2-iminothietane 3. In the case of ketenimine 2c the irradiation was performed in the presence of pyridine (1%), or at  $-40^\circ C$  in dichloromethane.



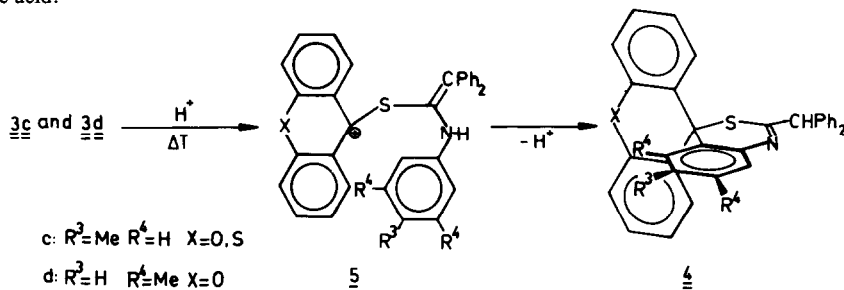
- |             |                      |              |
|-------------|----------------------|--------------|
| a: $R^1=Ph$ | $R^2=Me$             | $X=O, S, 2H$ |
| b: $R^1=Me$ | $R^2=Ph$             | $X=O, S, 2H$ |
| c: $R^1=Ph$ | $R^2=4-MeC_6H_4$     | $X=O, S$     |
| d: $R^1=Ph$ | $R^2=3,5-Me_2C_6H_3$ | $X=O$        |

Iminothietanes 3a and 3c were obtained directly crystalline in 80-90% yields from  $CH_2Cl_2$ /pentane. The reaction mixtures from thiones 1 and ketenimine 2b had to be purified by column chromatography (silica gel, benzene) in order to get crystalline products.

The structure of the 2-iminothietanes followed from spectral data. Their IR spectra (KBr) showed strong absorptions around  $1660\text{ cm}^{-1}$  ( $C=N$ ) (cf. 5). In the  $^{13}C$  NMR spectra ( $CDCl_3$ ) the carbon atoms of the thietane ring gave signals around 165 ppm for C(2), between 55-65 ppm for C(3) and between 70-85 ppm for C(4). In the mass spectra peaks could be found corresponding to the two possible ways of fragmentation of the thietane ring:  $[R^1C=C=N-R^2]^{\cdot+}$ ,  $[Ar_2C=S]^{\cdot+}$ ,  $[Ar_2C=CR^1]^{\cdot+}$  and  $[R^2-N=C=S]^{\cdot+}$ .

Similar spectral characteristics were reported by Dondoni *cs.* for the 2-iminothietane *thermally* formed from thio-benzophenone (1, X = 2H) and ketenimine (2, R<sup>1</sup> = Ph and R<sup>2</sup> = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (5).

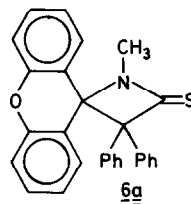
In solution iminothietanes 3a are thermally unstable and show cycloreversion to the starting materials when heated in CDCl<sub>3</sub> (or on chromatography over silica gel). Iminothietanes 3b appear to be stable under these conditions even with an excess of benzenesulfonic acid. As already mentioned iminothietane 3c could only be prepared in the presence of some pyridine or at low temperature. Warming in CDCl<sub>3</sub> caused smooth rearrangement to benzothiazine 4, while also some cycloreversion to the starting materials was observed; both reactions were strongly catalyzed by a trace amount of benzenesulfonic acid.



Recently, Dondoni *cs.* isolated benzothiazines from *thermal* addition of thiobenzophenone (1, X = 2H) to ketenimine 2b and 2c (5).

Conclusive evidence for the benzothiazine structure was obtained by irradiating xanthenethione (1, X = O) with ketenimine 2d at low temperature in CH<sub>2</sub>Cl<sub>2</sub>. The 2-iminothietane 3d was obtained by crystallization. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showed a singlet at 2.41 ppm for both the methyl groups. Acid catalyzed rearrangement of 3d gave a compound which exhibited in its <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) a singlet at 2.30 ppm and one at 1.47 ppm for the methyl groups. The same compound was isolated directly from a benzene solution of xanthenethione (1, X = O) and ketenimine 2d irradiated at about 18°C. The observed rearrangements of the fully aromatic substituted 2-iminothietanes 3c, probably occur via carbocation 5.

Preliminary investigation of the photolysis of some 2-iminothietanes 3, showed besides formation of isothiocyanate R<sup>2</sup>-N=C=S and alkene Ar<sub>2</sub>C=CR<sub>1</sub>, rearrangement to β-thiolactams like 6a (*cf.* 6).



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