HETEROCYCLES, Vol 20, No 10, 1983

DOUBLE SULFUR TRANSFER AND 1,2,3-TRITHIOLANE FORMATION IN THE PHOTOLYSIS OF A MESOIONIC 5-ACETYL-4-THIAZOLONE

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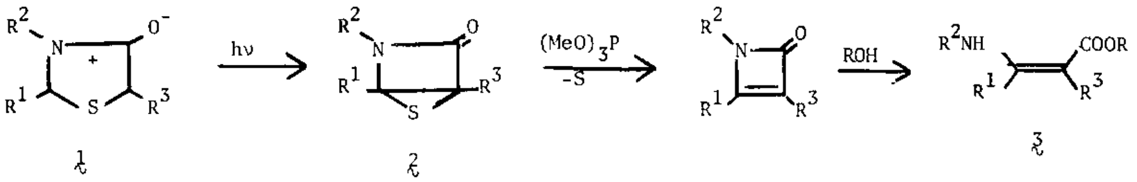
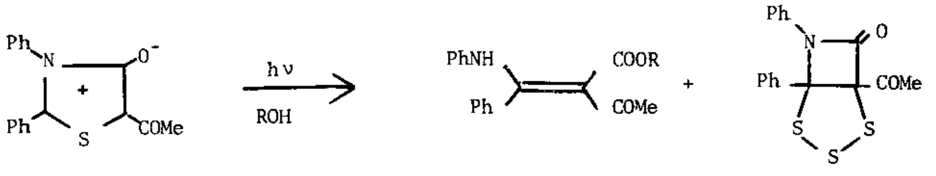
Abstract - The photolysis of anhydro-5-acetyl-2,3-diphenylthiazolium hydroxide (**1a**) in alcohols yielded alkyl 2-acetyl-3-anilinocinnamates (**3**) and 1-acetyl-5,6-diphenyl-6-aza-2,3,4-trithiabicyclo[3.2.0]heptan-7-one (**4**), in a ratio of 2.6:1. A mechanism which involves two consecutive transfers of sulfur atoms between radical intermediates is suggested.

The photolysis of mesoionic 4-thiazolones has been reported[1,2] to yield complex mixtures, probably through rearrangements, decomposition and redox processes which involve the initial bicyclic product **2**. If, however, the photolysis is carried out in alcohols in the presence of sulfur acceptors (e.g. trimethyl phosphite), enamino esters (**3**) are formed in high yields[2,3], via the pathway outlined:



In light of these results, the photolysis of anhydro 5-acetyl-2,3-diphenylthiazolium hydroxide[4] (**1a**, $R^1=R^2=Ph, R^3=COMe$) was peculiar. In methanol (without phosphite) it gave two products which were identified as **3a** (68%) and **4** (26%). Similarly in tert-butyl alcohol it yielded **3b** (65%) and **4** (27%). Thus one molecule of the substrate **1a** served as a sulfur acceptor from two others.



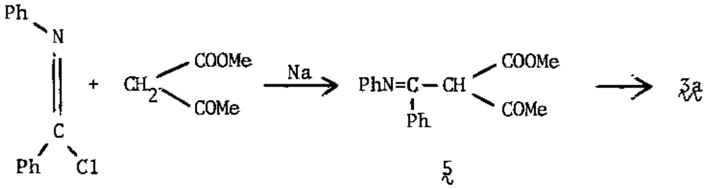
1a

3a, R = Me

3b, R=t-Bu

4

Compounds 3a (mp 81°C) and 3b (mp 118°C) were identified through spectral properties (ir, ^1H and ^{13}C NMR and ms) which were in accord with the assigned structures and stereochemistry (hydrogen bond between the ester carbonyl and the NH group). Furthermore, 3a was identical with a product obtained in the reaction of diphenylimidoyl chloride with methyl acetoacetate, which was previously[5] assigned erroneously as 5.



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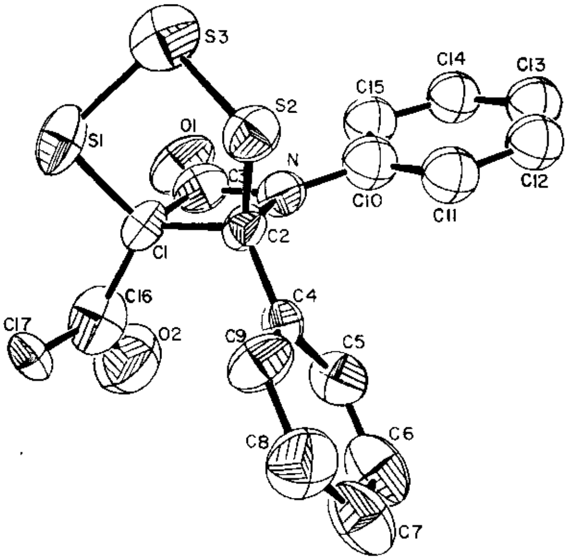
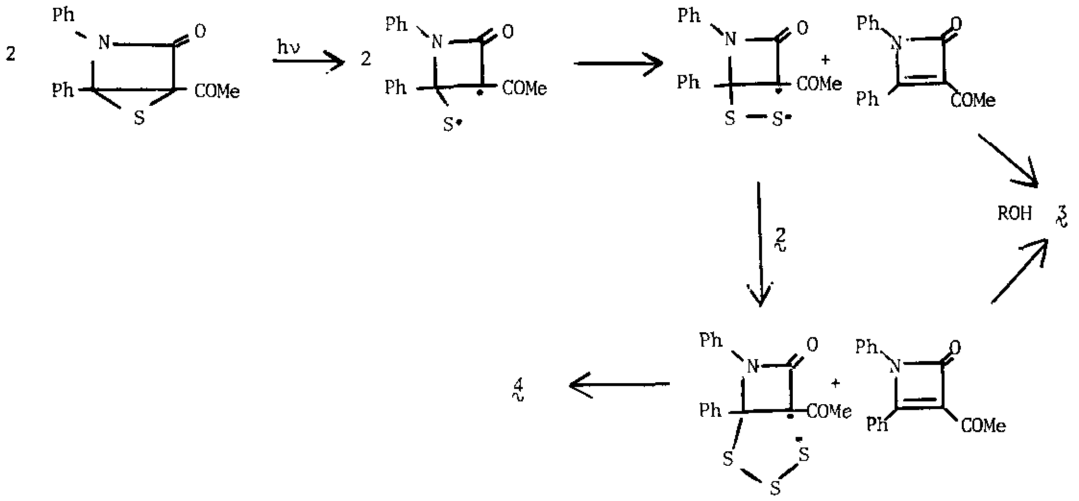
Compound 4 (mp 109°C, $C_{17}H_{13}NO_2S_3$ by analysis and ms) showed ir carbonyl absorptions at 1750 (β-lactam) and 1710 cm^{-1} (ketone). The complete structure was determined by X-ray crystallography[6] (see Figure).

Perspective drawing of 4



Significant bond lengths (Å) and angles (°)	
C_1-C_2	1.6226
C_1-S_1	1.8136
C_2-S_2	1.8316
S_1-S_3	2.0614
S_2-S_3	2.0437
C_3-C_1-S_1	113.96
N-C_2-S_2	113.77
C_1-S_1-S_3	94.18
C_2-S_2-S_3	94.74
S_1-S_2-S_3	93.26

The few reported[7,8] preparations of the 1,2,3-trithiolane system all utilize addition of elementary sulfur to double bonds. We have excluded the possibility of sulfur extrusion and subsequent cycloaddition in the present case by conducting the photolysis in the presence of a large excess of sulfur, which caused no change in products ratio. We therefore suggest that the formation of **4** involves two consecutive transfers of sulfur atoms between the radical intermediates, followed by cyclization of the tri-S biradical. The fact[9] that generally $RS_3\cdot$ and $RS_2\cdot$ radicals are more stable than $RS\cdot$ (because of the unpaired electron participation in the S-S bonds) make the process thermodynamically reasonable.



A similar mechanism can be drawn starting with cleavage of the other C-S bond. The question why this type of sulfur transfer has been observed only in the case of **1** and not in the photolysis of other mesoionic 4-thiazolones is still open.

REFERENCES AND NOTES

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6. Crystallography data: monoclinic crystals, space group C_2/C. a = 12.329 Å, b = 10.223 Å, c = 15.925 Å, $\beta = 91.16^0$, Z = 4. Data were collected on a Philips PW 1100/20 diffractometer (graphite monochromatized Mo K_α radiation). Structure was determined by direct method (MULTAN 78) and refined (SHELX 76) on the basis of 1231 reflections ($I > 2\sigma(1)$) to R = 0.0865. We wish to thank Dr. S. Cohen for his help with the X-ray work.

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Received, 3rd June, 1983