

FORMATION OF 1,4-THIAZINE 1,1-DIOXIDES BY THE CYCLOADDITION--EXTRUSION--RING EXPANSION

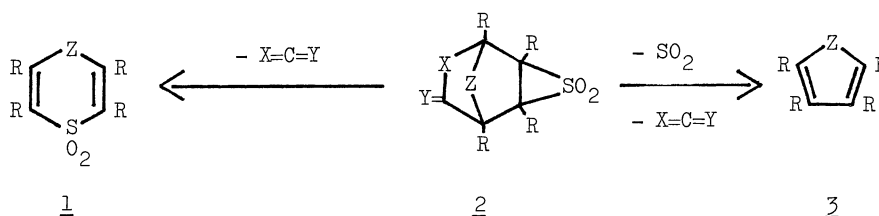
REACTIONS OF MESOIONIC OXAZOLONES WITH DIPHENYLTHIIRENE DIOXIDE

Hiroshi MATSUKUBO, Masanobu KOJIMA, and Hiroshi KATO*

Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

The reactions of diphenylthiirene dioxide 5 with a mesoionic oxazol-5-one 4a and an oxazolin-5-one 9 gave the corresponding 4H-1,4-thiazine 1,1-dioxides 7.

It was recently reported^{1, 2} that the cycloaddition--extrusion reactions of five-membered meso-ionic compounds with diphenylcyclopropenone and related compounds give a variety of six-membered fully conjugated heterocycles. As an extension of this work, we thought it would be of interest to investigate the reactions of mesoionic compounds with a thiirene dioxide. In this case, the initial adduct 2 has two potentially extrudable groups, and it may decompose either to a six-membered heterocycle 1 by extrusion of the X=C=Y group, or to a five-membered ring 3 by extrusion of both the SO₂ and the X=C=Y groups. The reactions of diphenylthiirene dioxide with a six-membered mesoionic compound,³ a diazoalkane,⁴ and pyridinium ylides⁵ are known to give adducts resulting from extrusion of sulfur dioxide, although the reactions with sulfonium ylides⁵ and enamines⁶ give compounds incorporating a sulfonyl group as one of the reaction products.

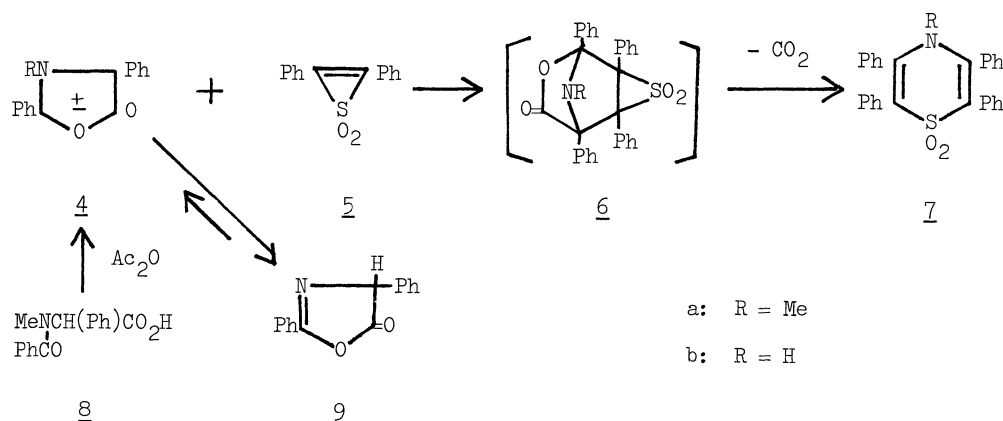


When mesoionic 3-methyl-2,4-diphenyloxazol-5-one 4a (1.2 mmol) and 2,3-diphenylthiirene dioxide 5 (1.2 mmol) in benzene (10 ml) was allowed to stand at room temperature, a precipitate of 4-methyl-2,3,5,6-tetraphenyl-4H-1,4-thiazine 1,1-dioxide 7a separated out within 2.5 hr [83%; m.p. 299--300°C (dec.); Found: C, 77.54; H, 4.96; N, 3.03%. Calcd. for C₂₉H₂₃NO₂S: C, 77.48; H, 5.16; N, 3.12%.

IR (KBr): 1295 and 1130 cm^{-1} (SO_2); NMR (CDCl_3): δ 7.22 and 7.30--6.90 (br s and m, 2OH, Ph) and 2.75 (s, 3H, NMe); MS: m/e 385 (100%, $\text{M}^+ - \text{SO}_2$). The thiazine dioxide 7a was also formed in 63% yield when 2-(N-methylbenzamido)-2-phenylacetic acid 8 and the thiirene dioxide 5 (0.74 mmol each) were warmed at around 60°C for 1.5 hr in acetic anhydride (5 ml).

The reaction of the thiirene dioxide 5 and 2,4-diphenyl-2-oxazolin-5-one 9 in benzene resulted only in the decomposition of 5 to diphenylacetylene. However, when the two components (1 mmol each) were warmed in anhydrous dimethylformamide (2 ml), which shifts the equilibrium of the oxazolinone 9 to the mesoionic tautomer 4b,⁷ 2,3,5,6-tetraphenyl-4H-1,4-thiazine 1,1-dioxide 7b was formed in 58% yield [m.p. 243°C (dec.), Lit.⁸ 264°C].⁹

These results show that the mesoionic oxazolone 4 underwent cycloaddition across the 2,3-double bond of the thiirene dioxide 5 to give the intermediate cycloadduct 6, from which carbon dioxide was preferentially extruded, and an ensuing or a simultaneous cleavage of the three-membered ring occurred to give the thiazine dioxide 7.



REFERENCES AND NOTES

* To whom inquiries should be addressed.

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- 9) Although the m.p. of our sample did not agree with the literature value,⁸ it gave a correct analysis, and the spectral data were virtually identical with the reported values.

(Received August 29, 1975)