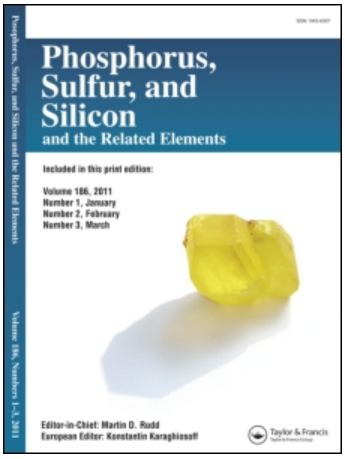

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Reactions of Mesoionic Thiazolones with Nitroso-Dipolarophiles

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REACTIONS OF MESOIONIC THIAZOLONES WITH NITROSO--DIPOLAROPHILES

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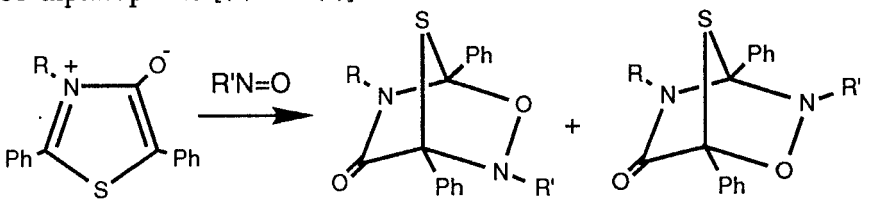
Abstract Reactions of a series of thiazolium-4-olates with nitrosobenzene, with 1-chloro-1-nitrosocyclohexane and with acylnitroso derivatives, gave initially strained bicyclic cycloadducts. These, upon heating, underwent some unusual rearrangements and fragmentations.

INTRODUCTION

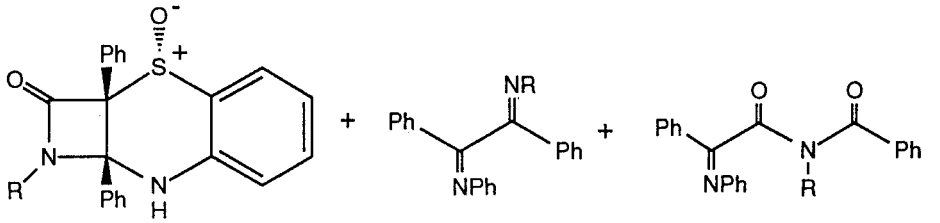
We have previously studied[1] reactions of thiazolium-4-olates(**1**) with azo-dipolarophiles, and in view of of the new interesting chemistry exhibited by the cycloadducts, this study was now extended to include adducts with nitroso-diplarophiles [(**2**) and (**3**)]



(1) **(2)** **(3)**

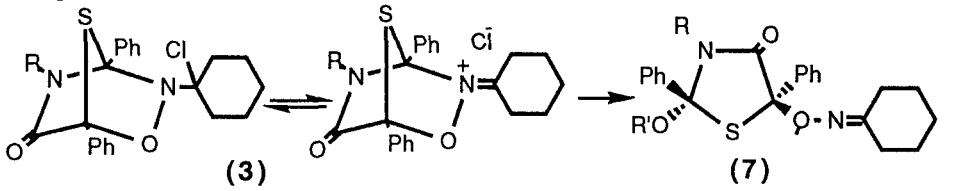
RESULTS

Reactions of compounds **1** with nitrosobenzene (in benzene, room temperature) yielded adducts **2**(R'=Ph) exlusively. Upon standing, **2** was transformed to a mixture of **4** (an isomer of **2**), **5** (loss of a carbonyl, O and S) and **6** (loss of S).



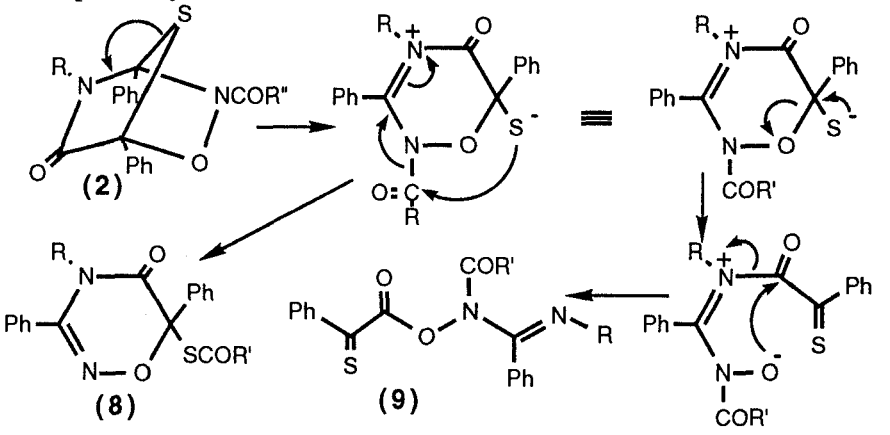
(4) **(5)** **(6)**

The reactions with 1-chloro-1-nitrosocyclohexane were carried out in ethanol-ether, as the cyclohexane moiety is usually cleaved off under these conditions[2] to give N-unsubstituted adducts. The only products obtained were **7**, formed by attack of the ethanol at a bridghead carbon in the adduct **3**,



(3) **(7)**

Acylnitroso derivatives were generated either by direct oxidation of the corresponding hydroxamic acids or by transfer[3] from cyclopentadiene adducts. Reactions with **1** led to both **2** and **3** (R = COR") which were not isolated as they reacted further to give a variety of products. Most interesting are the rearrangements of **2** to 8 and **9**. The mechanism is shown below and is typical of the reactivity of highly strained heterocyclic systems which contain several hetero atoms. It usually starts with a heterolytic cleavage of a bond to form a nonstabilized zwitterion. These zwitterions find sometimes very unusual ways to neutralize their charges, leading to unexpected producs. Compounds **4** and **5** were also formed in a similar pathway.



(2) **(8)** **(9)**

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