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Tuvia Sheradsky^a; Norbert Itzhak^a

^a Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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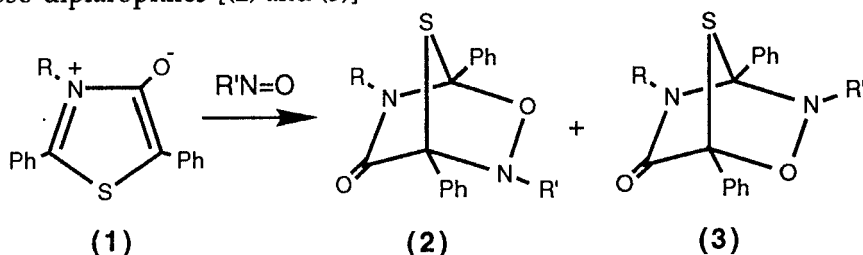
REACTIONS OF MESOIONIC THIAZOLONES WITH NITROSO-DIPOLAROPHILES

TUVIA SHERADSKY and NORBERT ITZHAK
 Department of Organic Chemistry, The Hebrew University,
 Jerusalem 91904, Israel

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.

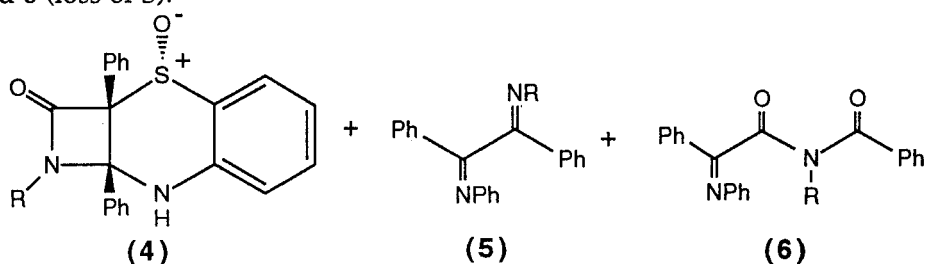
INTRODUCTION

We have previously studied¹ reactions of thiazolium-4-olates(**1**) with azo-dipolarophiles, and in view of the new interesting chemistry exhibited by the cycloadducts, this study was now extended to include adducts with nitroso-dipolarophiles [(**2**) and (**3**)]

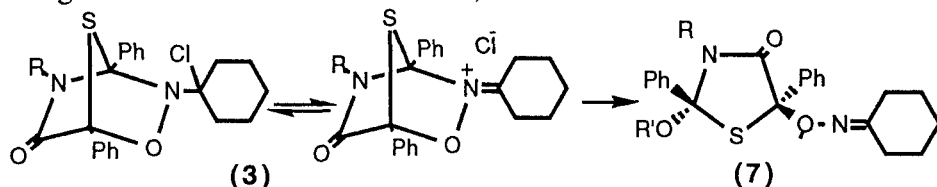


RESULTS

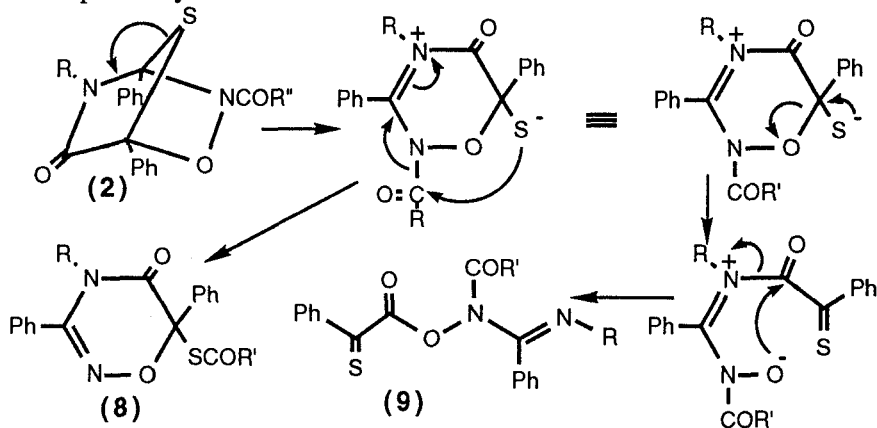
Reactions of compounds **1** with nitrosobenzene (in benzene, room temperature) yielded adducts **2** ($R' = \text{Ph}$) exclusively. Upon standing, **2** was transformed to a mixture of **4** (an isomer of **2**), **5** (loss of a carbonyl, O and S) and **6** (loss of S).



The reactions with 1-chloro-1-nitrosocyclohexane were carried out in ethanol-ether, as the cyclohexane moiety is usually cleaved off under these conditions² to give N-unsubstituted adducts. The only products obtained were 7, formed by attack of the ethanol at a bridhead carbon in the adduct 3,



Acynitroso derivatives were generated either by direct oxidation of the corresponding hydroxamic acids or by transfer³ from cyclopentadiene adducts. Reactions with 1 led to both 2 and 3 ($R = \text{COR}''$) 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 products. Compounds 4 and 5 were also formed in a similar pathway.



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