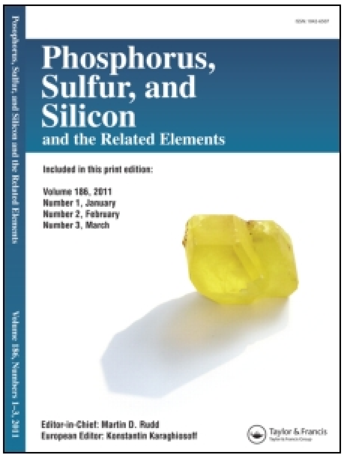

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Kentaro Okuma[a]; Shinobu Maekawa[a]
[a] Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka, Japan

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Synthesis of Thione-Propiolic Acid Adducts

Kentaro Okuma
Shinobu Maekawa
Department of Chemistry, Faculty of Science, Fukuoka University,
Fukuoka, Japan

Reaction of adamantane-2-thione with propiolic acid gave a novel type of cycloadducts, spiro[adamantane-2,2′-(1,3)-oxathiin]6-one, quantitatively. Thiocamphor and thiofenchone also reacted with propiolic acid to give the corresponding adducts stereoselectively. The observation of second-order reaction kinetics and highly stereoselective addition strongly support a cycloaddition mechanism for the thermal addition. The reaction of selenoketones with propiolic acid afforded a similar cylcoadduct. This is the first example of the reaction of monomeric thiones or selones with acetylenic acids.

Keywords Cycloaddition; propiolic acid; selone; thiodioxenone; thione

INTRODUCTION

Thioketones (**1**) are well known to react with dienes to give the corresponding Diels–Alder adducts.[1] α,β-Unsaturated thioketones readily dimerize, and these dimers have been employed as sources of the monomers by the retro Diels–Alder reaction. The monomers reacted with dienophiles to give the corresponding adducts. Dihydrobenzothiopyrans were synthesized by the reaction of thiobenzophenones with dimethyl acetylenedicarboxylate. Recently, we have reported the reaction of monomeric thiones **1** with benzyne to give the corresponding four-membered benzothietes in good yields.[2] However, to our knowledge, there is no report on the reaction of monomeric thiones **1** with acetylenic acids, which would produce a new type of heterocycles, thiodioxenones. Herein, we report the first cycloaddition of thiones with propiolic acid.

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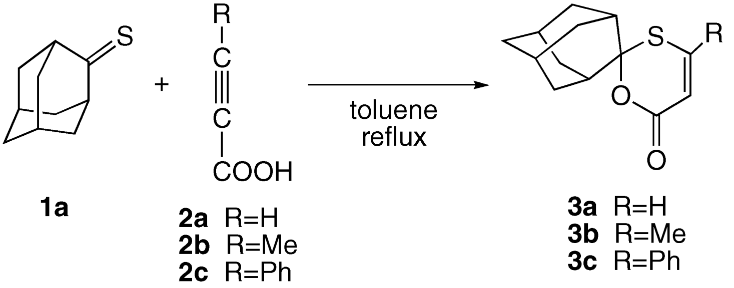
Address correspondence to Kentaro Okuma, Department of Chemistry, Faculty of Science, Fukuoka University, Junan-ku, Fukuoka 814-0180, Japan. E-mail: kokuma@fukuoka-u.ac.jp

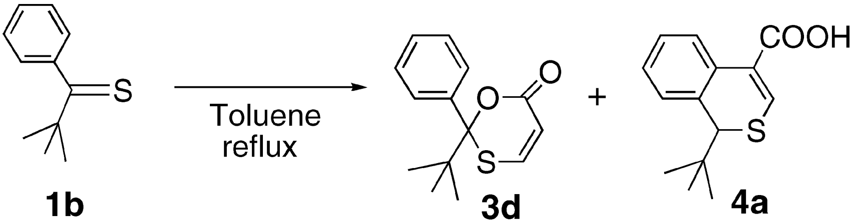
RESULTS

Treatment of adamantane-2-thione (**1a**) with propiolic acid (**2a**) in refluxing toluene resulted in the formation of a new type of cycloadduct, spiro[adamantane-2,2′-(1,3)-oxathiin]6-one (**3a**), in quantitative yield. Similarly, 2-butynoic acid (**2b**) and phenylpropiolic acid (**2c**) reacted with **1a** to give the corresponding 1,3-oxathiin-6-ones (**3b**, **3c**), which are thio analogues of dioxenones (Scheme 1). Dioxenones, which are produced by cycloaddition of ketones with Meldrum's acid,[3] are well known for the precursors of many natural products.



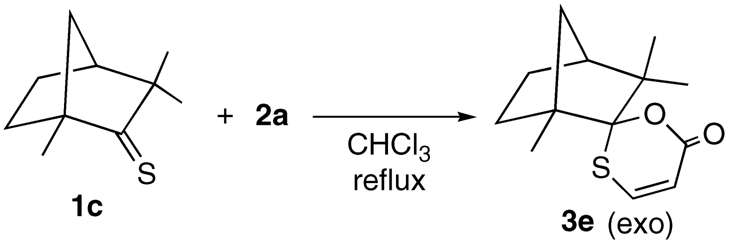
SCHEME 1

When thiopivalophenone (**1b**), one of the aromatic thiones, was chosen as a substrate, 2-*tert*-butyl-2-phenyl-[1,3]oxathiin-6-one (**3d**) was obtained in 65% yield (Scheme 2). Less than 15% of normal cycloadduct (**4a**) was also obtained as a side product, suggesting that the formation rate of **3d** was faster than that of **4a**.



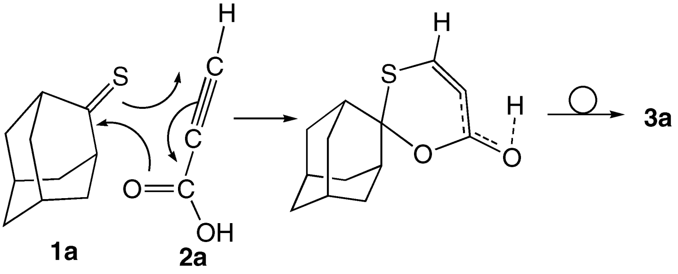
SCHEME 2

Other monomeric thiones such as thiofenchone (**1c**) afforded the corresponding cycloadduct (**3e**) (83%). Interestingly, only one isomer (*exo*-form) was obtained, suggesting that the reaction proceeded diastereospecifically (Scheme 3). The structure of *exo*-**3e** was confirmed by its X-ray crystallographic analysis.



SCHEME 3

The observation of second-order reaction kinetics and highly stereoselective addition strongly supports a cycloaddition mechanism for the thermal addition (Scheme 4). The large, negative entropy of activation is consistent with a rigid, cyclic transition state, which indicates the relative independence of reaction rate on solvent.

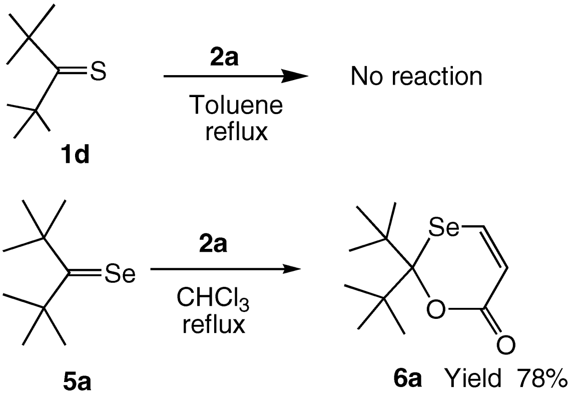


SCHEME 4

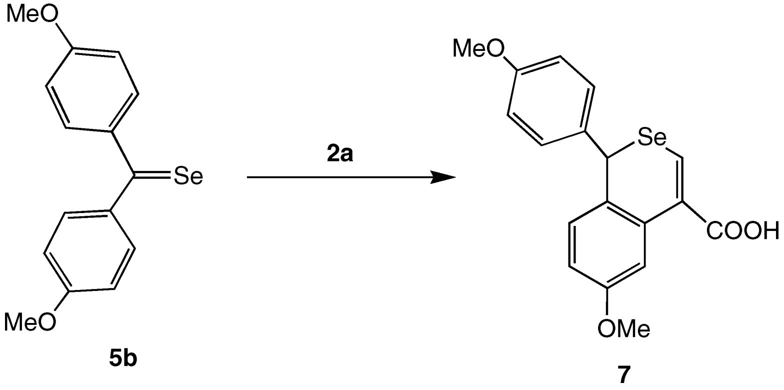
Reaction of di-*tert*-butyl selenoketone (**5a**) with **2a** gave the corresponding cycloadduct (**6a**), whereas di-*tert*-butyl thioketone (**1d**) recovered thione in almost quantitatively (Scheme 5).

On the other hand, the reaction of 4,4′-dimethoxyselenobenzophenone (**5b**) with **2a** gave the corresponding [4 + 2] cycloadduct (**7**) exclusively (Scheme 6).

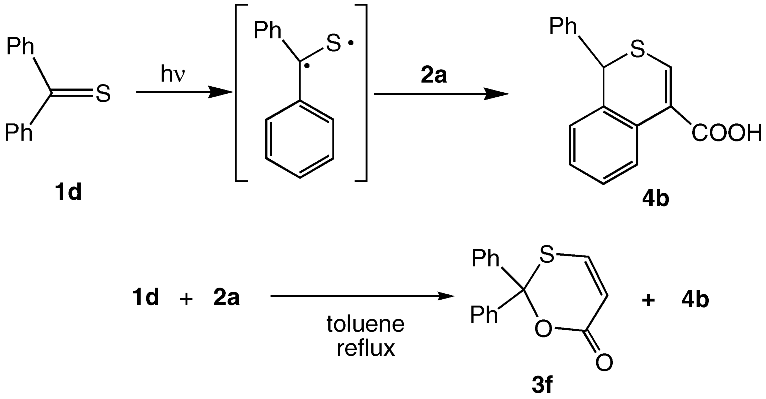
In 1970, Ohno *et al.* described the photocycloaddition of thiobenzophenone (**1e**) with **2a**, which furnished 1-phenyl-1*H*-isothiochromene-4-carboxylic acid (**4b**). The authors assumed that addition of π, π^* triplet state of **1e** to the acetylenic bond preceded and was followed by intramolecular hydrogen migration.[4] To investigate the thermal behavior of thiobenzophenone, we then tried the reaction of **1e** with **2a**. Treatment of thione **1e** with **2a** in refluxing toluene resulted in the formation of 2,2-diphenyl-2*H*,6*H*-1,3-oxathiin-6-one (**3f**) and **4b** in 35 and 32% yields, respectively (Scheme 7).



SCHEME 5



SCHEME 6



SCHEME 7

Selenobenzophenone is more reactive toward **2a** than thiobenzophenone, which results in the exclusive formation of isoselenochromene derivative *via* less-hindered transition state. The present reaction is the first example on the formation of thiodioxenone (**3**) from thiobenzophenone.

The difference in the reactivity between **1** and **5** might be due to their carbon-heteroatom bond lengths. Bond lengths of thiones are in the range of 1.630–1.661 Å, whereas those of selones are in the range of 1.774–1.790 Å. Thus, selones are more reactive than the corresponding thiones toward alkenes or other dienophiles.

In summary, we have developed a new type of cycloadducts from monomeric thiones with propiolic acid derivatives. The reaction might proceed through concerted mechanism.

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