

FORMATION OF 1,3-OXATHIOLES AND 1,3-OXASELENOLS BY REACTIONS OF
CARBONYL-STABILIZED SULFONIUM YLIDES WITH ELEMENTAL SULFUR AND SELENIUM

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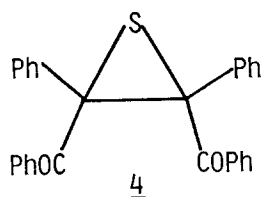
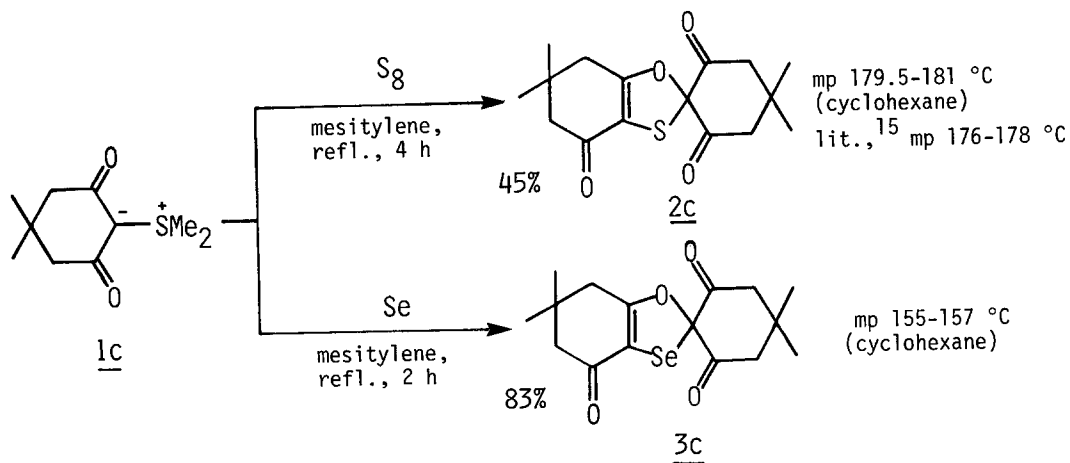
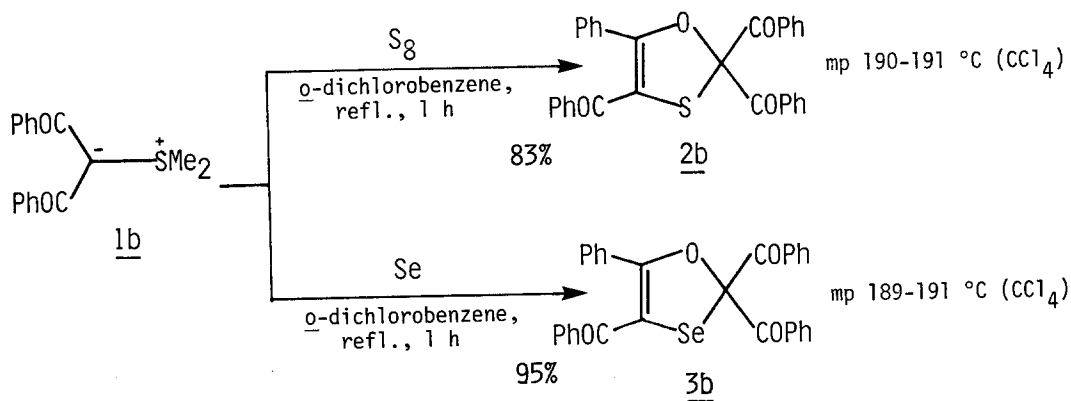
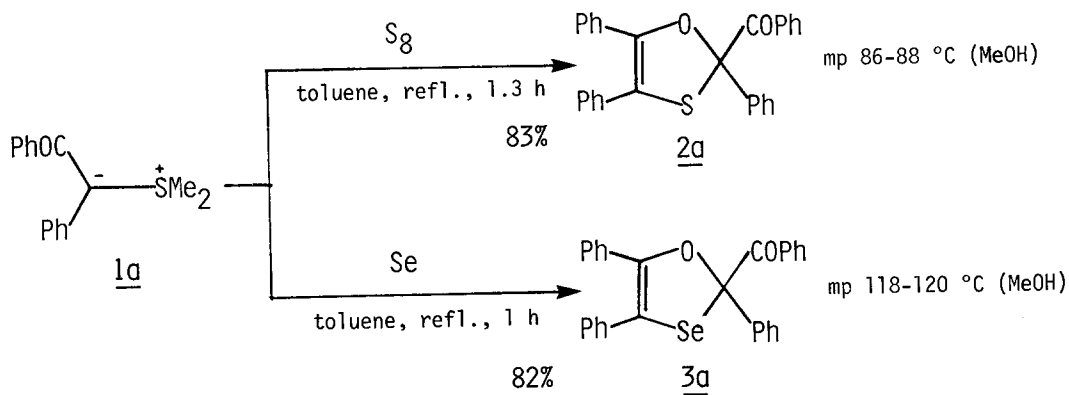
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Abstract: Carbonyl-stabilized sulfonium ylides readily react with elemental sulfur and selenium to afford 1,3-oxathiole and 1,3-oxaselenole derivatives, respectively, in good yields, thus providing a simple method for constructing these ring systems which uses easily accessible compounds as starting materials.

In our continuing interest in reactions of elemental sulfur and selenium with organic reactive intermediates,² we investigated the reactions of sulfonium ylides with these elements. Herein we report the formation of 1,3-oxathioles and 1,3-oxaselenoles in good yields by reactions of sulfur and selenium with carbonyl-stabilized sulfonium ylides.

Heating the sulfonium ylide 1a (5 mmol) and sulfur (5 mg-stoms) in refluxing toluene (25 mL) for 1.3 h affords a yellow crystalline compound, C₂₈H₂₀O₂S, in 83% yields after purification with silica gel column chromatography. Although all of the available experimental data suggest the 1,3-oxathiole 2a as the structure of this compound, the melting point of our compound, 86-88 °C, is lower than any other reported melting points on 2a. The followings are the reported melting points: 106-112 °C,⁴ 107-110 °C,⁴ 110-111 °C,⁵ 109-111 °C,⁶ 104-105 °C,⁷ 93-94 °C,⁸ 104-106 °C,^{9,10} 106 °C,¹¹ and 107 °C.¹² The initial structure given to 2a in 1965 is the thiiran 4,⁴⁻⁸ and the revised structure 2a was proposed in 1974.⁹ Intricacies about the structure of this compound are such that our compound was subjected to X-ray analysis in order to determine its structure unambiguously. The analysis revealed that it has the 1,3-oxathiole structure 2a. A perspective view of 2a is shown in Figure 1.

After we had completed the X-ray analysis work, we found that a part of crystals of 2a obtainable from the mother liquor of recrystallization melt



at 106-111 °C. Recrystallization of the compound, mp 86-88 °C, from methanol using a piece of the above crystals as seed raised the melting point to 110-112 °C,¹⁴ which corresponds to one of the reported melting points.^{5,6} We therefore conclude that 2a exists in at least two distinct crystalline forms (polymorphism).

In a similar manner, ylides 1b and 1c were allowed to react with sulfur to provide oxathioles 2b and 2c, respectively. The oxathiole 2c is a known compound and the properties of 2c obtained by the present method agreed with those reported in every respect.¹⁵

Since the above reaction provided a simple method for preparing highly substituted 1,3-oxathioles, the reaction of the foregoing ylides with selenium was next examined. All of the ylides reacted with selenium more readily than with sulfur and afforded the corresponding 1,3-oxaselenoles 3a-c in excellent yields, thus providing a facile method for constructing this scarcely studied ring system.¹⁶ For example, heating the ylide 1a (5 mmol) and selenium powder (5 mg-atoms) in refluxing toluene (25 mL) for 1 h afforded the oxaselenole 3a in 82% yield. The IR and ¹HNMR spectra of 3a-c are very similar to those of the corresponding 2a-c.¹⁷ The oxaselenoles 3a-c are orange crystals,¹⁸ while the oxathioles 2a-c are yellow.

The reaction probably proceeds as below. Ylides 1 react with sulfur and selenium to give thio- and selenoketones 5 as the initial products. Subsequent reaction of 5 with 1 leads to the final products 2 and 3.

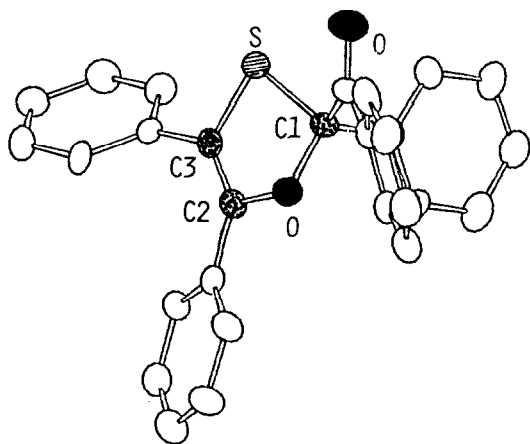
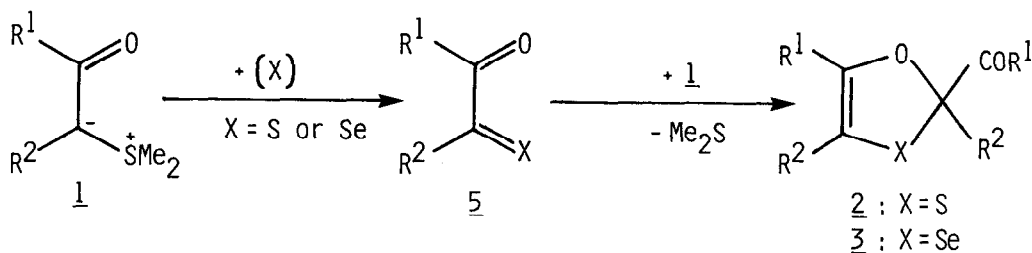


Figure 1 Perspective View of 2a
 Relevant bond distances and angles:
 C1-O, 1.419 (11) Å; C1-S, 1.843 (14) Å;
 C2-O, 1.409 (16) Å; C3-S, 1.756 (11) Å;
 C2-C3, 1.336 (13) Å; O-C1-S, 104.9 (6)°;
 C1-O-C2, 111.5 (7)°; O-C2-C3, 113.7 (8)°;
 C2-C3-S, 112.6 (8)°; C3-S-C1, 88.7 (6)°.



References and Notes

1. X-Ray analysis work was performed by this author.
2. The previous paper is concerned with the formation of 2-thio- and 2-seleno-1,3-benzodithioles by reactions of sulfur and selenium with 1,3-benzodithiol-2-ylidene carbenes; J. Nakayama, H. Sugiura, and M. Hoshino, *Tetrahedron Lett.*, 24, 2585, (1983).
3. The melting point does not change upon repeated recrystallization from methanol or hexane.
4. D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, 30, 636 (1965).
5. D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Am. Chem. Soc.*, 91, 2097 (1969).
6. A. Padwa, D. Crumrine, and A. Shubber, *J. Am. Chem. Soc.*, 88, 3094 (1966).
7. G. Kresze and W. Wucherpfennig, *Angew. Chem.*, 79, 109 (1967).
8. C. J. Ireland and J. S. Pizey, *J. Chem. Soc., Chem. Commun.*, 4 (1972).
9. U. Jacobsson, T. Kempe, and T. Norin, *J. Org. Chem.*, 39, 2722 (1974).
10. C. Bak and K. Praefcke, *Chem.-Ztg.*, 102, 456 (1978).
11. C. Bak, G. Höhne, and K. Praefcke, *Chem.-Ztg.*, 102, 66 (1978).
12. H. Fauduet and R. Burgada, *Nouv. J. Chim.*, 3, 555 (1979).
13. A single crystal of 2a, mp 86-88 °C, was prepared by slow crystallization from methanol. The crystal data are monoclinic, space group C 2/c, a = 23.136 (8), b = 12.911 (4), c = 13.020 (4) Å, $d_{\text{calcd}} = 1.28 \text{ g cm}^{-3}$ for Z = 8 (asymmetric unit $\text{C}_{28}\text{H}_{20}\text{O}_2\text{S}$). The intensity data were measured on a Rigaku automated diffractometer with Mo K α radiation. A single crystal with the maximum dimension of 0.3 mm was used. The number of the significant reflections [$|F_o| > 3\sigma(|F_o|)$] is 1800 ($2\theta < 60^\circ$). The structure was solved by the direct method and refined by block-diagonal least-squares methods. The final refinement, with anisotropic temperature factors for C, O, and S, gave an R factor of 0.096 (the hydrogen atoms were not included).
14. The both crystals are yellow (the compound of high melting point is slightly deeper in color than that of low melting point). However, the IR spectra (KBr disk) of the both crystals differ appreciably each other. Some discrepancy is found in the reported IR spectra on 2a.^{9,10,12}
15. G. F. Koser and S.-M. Yu, *J. Org. Chem.*, 41, 125 (1976).
16. As far as we know, only two reports describe the formation of this heterocycle: C. Bak, K. Praefcke, and L. Hendriksen, *Chem.-Ztg.*, 102, 361 (1978); A. Robert and A. Le Marechal, *J. Chem. Soc., Chem. Commun.*, 447 (1978).
17. The IR spectrum of 3a is very similar to that of 2a of high melting point (see note 14).
18. UV $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ): 3a, 228 (27000), 308sh (6400), 396sh (840); 3b, 254 (34000), 366 (4350), 420 (2280); 3c, 243 (1690), 298sh (3380), 308 (3480), 388 (120).

(Received in Japan 24 January 1985)