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Synthesis and Stability Trends of Selenothioic Acid S-Esters

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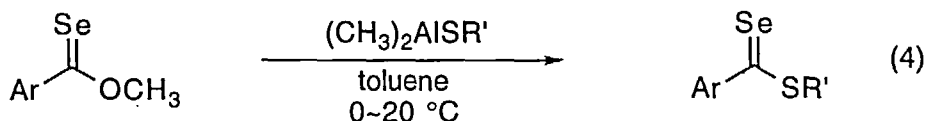
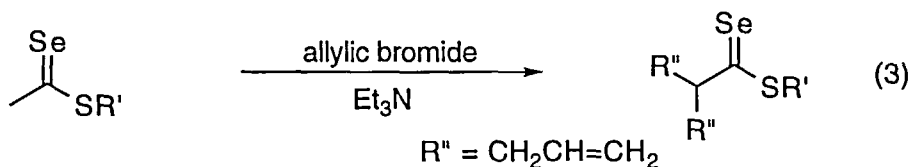
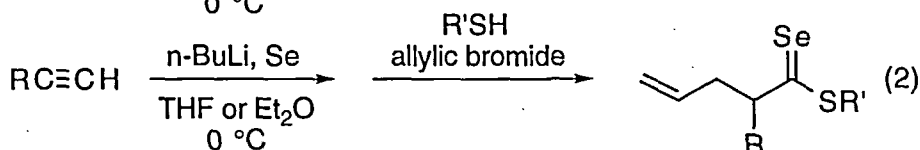
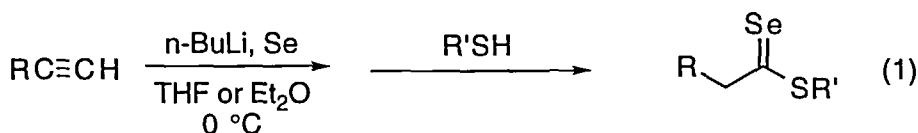
SYNTHESIS AND STABILITY TRENDS OF SELENOTHIOIC ACID S-ESTERS

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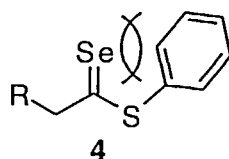
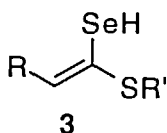
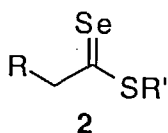
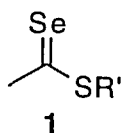
The synthesis and stability of selenothioic acid *S*-esters are discussed.

The chemistry of thioesters having selenocarbonyl group is of current interest.¹ Very recently, we have synthesized selenothioic acid *S*-esters (RC(Se)SR') for the first time.² They are relatively stable purple to violet blue compounds although their stability is highly dependent on the substituents next to selenocarbonyl group and sulfur atom. Further studies have established several types of their synthetic methods.



The first reaction was applicable to the preparation of monosubstituted aliphatic esters (eq. 1).³ The similar reaction using allylic bromides as a trapping agent leading to γ,δ -unsaturated esters (eq. 2).⁴ Two allylic groups were introduced to unsubstituted esters *via* seleno-Claisen rearrangement at one time (eq. 3).⁵ The aromatic acid esters were prepared by the reaction utilizing the high oxophilicity of aluminum atom toward oxygen atom (eq. 4).⁶

These methods allowed us to prepare a variety of selenothioic acid *S*-esters and to study their stability systematically. In a series of aliphatic selenothioic acid *S*-esters, trisubstituted esters are more stable than disubstituted esters. Noteworthy is that unsubstituted esters **1** are more stable than monosubstituted esters **2** probably because the latter appears to be easily isomerized to eneselenols **3** which undergo further decomposition process. Introduction of aromatic substituents does not necessarily enhance the stability of the esters. For example, attempts to isolate selenothioacetic acid *S*-phenyl ester failed and resulted in the formation of the dimers of the esters. In order to enhance the stability of *S*-aryl esters, the reaction using various kind of aromatic thiols have been carried out. *S*-2,6-Dimethylphenyl and *S*-naphthyl esters could be isolated through silica gel column chromatography although in low yields. Even so, they decomposed more easily than *S*-alkyl esters. Furthermore, attempts to synthesize aromatic acid *S*-aryl esters are not successful. There may exist the electronic repulsion between selenium atom of selenocarbonyl group and phenyl group attached to sulfur atom as in **4**.



REFERENCES

1. T. Murai, S. Kato, in *Comprehensive Organic Functional Group Transformations*, ed by A. R. Katritzky, O. Meth-Cohn, C. W. Rees, Pergamon, Oxford, 1995, Vol. 5, p 545.
2. S. Kato, T. Komuro, T. Kanda, H. Ishihara, T. Murai, *J. Am. Chem. Soc.*, **115**, 3000 (1993).
3. T. Murai, A. Hayashi, T. Kanda, S. Kato, *Chem. Lett.*, **1993**, 1469.
4. T. Murai, K. Kakami, N. Itoh, T. Kanda, S. Kato, *Tetrahedron*, **52**, 2817 (1996).
5. T. Murai, H. Takada, T. Kanda, S. Kato, *Chem. Lett.*, **1995**, 1057.
6. T. Murai, Y. Ogino, T. Mizutani, T. Kanda, S. Kato, *J. Org. Chem.*, **60**, 2942 (1995).