

RING CLEAVING SELENYLATION AND SULFENYLATION OF CYCLOPROPANE DERIVATIVES PROMOTED BY  $TiCl_4$

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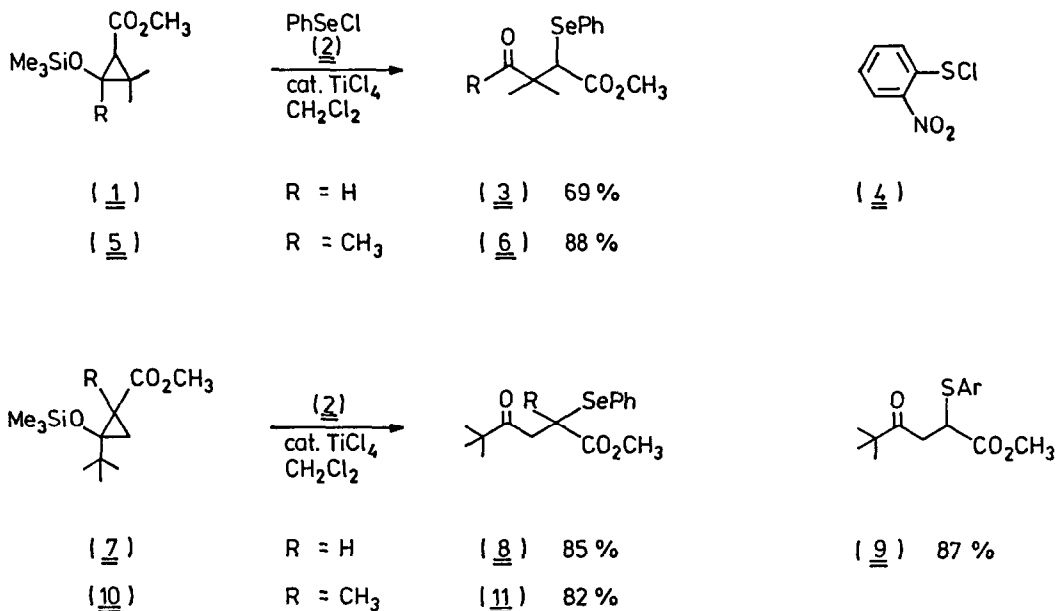
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Summary: A synthesis of 2-selenenyl and sulfenyl 4-oxoesters based on Lewis acid promoted activation of methyl 2-trimethylsiloxy cyclopropanecarboxylates is reported. A mechanistic scheme for this new C-Se and C-S forming reaction is disclosed.

Ring cleavage of cyclopropanes by electrophilic reagents has received remarkable interest<sup>1</sup>. However, no attention has been given to the reactions of simple cyclopropane derivatives<sup>2</sup> with selenenyl or sulfenyl halides<sup>3</sup> although the ring opened products might be of considerable synthetic value<sup>4</sup>.

We recently found that the vicinal acceptor-donor substituted cyclopropane (1)<sup>5</sup> reacts rather slowly with phenylselenenyl chloride (2) affording (3)<sup>6</sup> in good yield. According to <sup>1</sup>H NMR control conversion of (1) into (3) is complete after 24 h at 25°C and  $Me_3SiCl$  is deliberated as second product. However, adding a catalytic amount of  $TiCl_4$  (0.04 eq.) to a mixture of (1) and (2) in  $CH_2Cl_2$  at -78°C causes an instantaneous exothermic reaction (colour change) and allows isolation of (3) in 69 % after warm up to room temperature.

Scheme I:

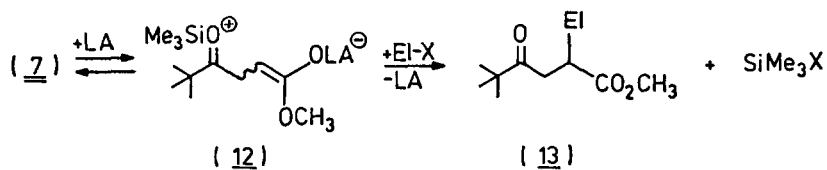


Similarly cyclopropanes (5), (7) and (10)<sup>5</sup> are transformed into selenenyl esters (6), (8) and (11) in high yields (scheme I). Compounds like (11) might serve as precursors for  $\alpha$ -methylene  $\gamma$ -butyrolactones <sup>4a</sup>.

Whereas (1) is not transformed by sulfenyl chloride (4)<sup>7</sup> to the analogous sulfenyl ester with or without  $\text{TiCl}_4$  promotion, a clean conversion of (7) into (9)<sup>8</sup> can be observed after addition of a catalytic amount of  $\text{TiCl}_4$ .

A mechanistic rationalization of this new method for C-Se and C-S bond formation is suggested in scheme II: ring opening of (7) by the Lewis acid LA to a ketene acetal (12), followed by the attack of an electrophile  $\text{El-X}$  to this moiety and extrusion of LA delivers 2-substituted 4-oxoesters (13). Without electrophile this type of cyclopropanes undergoes Lewis acid induced cis-trans equilibration<sup>9</sup>.

Scheme II:



We propose that according to scheme II other electrophiles  $\text{El-X}$  will provide a variety of synthetically useful functionalized 4-oxoesters of type (13)<sup>10</sup>. This aspect as well as chemoselectivity and stereoselectivity of these reactions will be reported in due time<sup>11</sup>.

#### References and Notes

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3. Review concerning addition reactions to alkenes: G. H. Schmid, D. G. Garratt, "The Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley: London, 1977, p. 828 and 855.
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5. E. Kunkel, I. Reichelt, H.-U. Reissig, *Liebigs Ann. Chem.* **1984**, 512; I. Reichelt, H.-U. Reissig, *Liebigs Ann. Chem.* **1984**, 536.
6. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$ =9.63 (s,1H), 7.8-7.1 (m,5H), 3.70 (s,1H), 3.59 (s,3H), 1.27 (s,9H).
7. Usually sulfenyl halides are less reactive than selenenyl halides; compare ref. 3.
8. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$ =8.5-7.2 (m,4H), 3.39, 3.04 and 4.41 (ABX-system,  $J_{AB}$ =18 Hz,  $J_{AX}$ =9.2 Hz,  $J_{BX}$ =5.8 Hz,3H), 3.73 (s,3H), 1.23 (s,9H).
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11. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully appreciated.

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