New Route to Bicyclic Lactones: Use of Benzeneselenenyl Chloride

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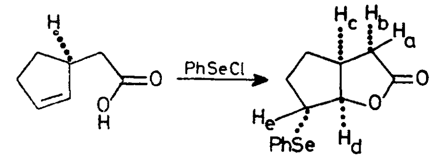
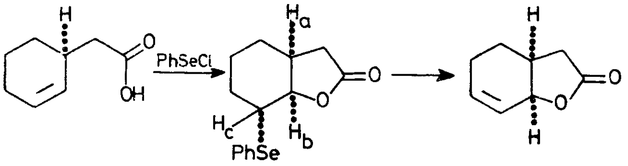
Summary γδ-Unsaturated acids react with PhSeCl in a process that is a new general route to bicyclic lactones.

Attachment of a benzeneseleno-group (PhSe–) to organic molecules is an important process because the resulting selenides have many applications in synthesis.[1]

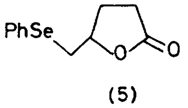
We have discovered that fused-ring lactones can be prepared by a new and efficient route that gives products containing the benzeneseleno-group, *e.g.*, (**1**) → (**2**) and (**3**) → (4). This type of transformation is an intramolecular process related to the stereospecific *trans* addition of $PhSeOCOCF_3$,[2] and similar species,[3] to double bonds.



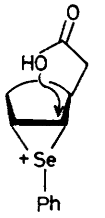
(1) (2)



(3) (4) (6)



(5)



(7)

The reaction of $\gamma\delta$-unsaturated acids with electrophiles is very sensitive to the status of the carbon α to the carboxy group,[4] lactonization being strongly favoured[5] by the presence of α substituents. However, when we examined the response of pent-4-enoic acid to PhSeCl (1 equiv.) we found that it is converted (refluxing EtOAc, 3·5 h) in 95% yield into the γ-lactone (**5**); ν_{max} (film) 1770 cm^{-1}; δ($CDCl_3$) 4·6 (m, 1H), 3·1 (m, 2H), and 1·65—2·7 (m, 4H). Substituents α to the carboxy group are evidently not required in this system for ring closure.† The acid (**1**) gave, similarly (room temp., 12 h), the lactone (**2**) (73%); ν_{max} (film) 1773 cm^{-1}; δ($CDCl_3$) 4·88 (H_d, d, J_{cd} 6·3, $J_{de} < 0·5$ Hz), 3·87 (H_e, br m), 3·10 (H_c, br m), 2·81 (H_b, d of d, J_{ab} 18·2, J_{bc} 9·8 Hz), and 2·32 (H_a, d of d, J_{ab} 18·2, J_{ac} 2·9 Hz). The acid (**3**) afforded (refluxing EtOAc, 7 h) the lactone (**4**) (82%); ν_{max} (film) 1780 cm^{-1}; δ($CDCl_3$) 4·40 (H_b, t, $J_{ab} = J_{bc}$ = 4 Hz), and 3·68 (H_c, q, J 4 Hz). The stereochemistry of the ring junction was confirmed by selenoxide fragmentation to the known[6] compound (**6**), elimination having occurred away from the lactone C–O group.

Mechanistically, the efficient production of *cis*-fused lactones may be the result of steric factors so that intermediates of type (**7**) are formed directly.‡ However, if the reagent reacts with the double bond in a reversible fashion, then lactonization *via* (**7**) could occur irrespective of the extent to which there is initial discrimination between the two faces of the substrate. We observed that PhSeCl reacts rapidly at −70 °C with the unsaturated acids but that several hours at a higher temperature are required for the carboxy group to be converted into a γ-lactone. Cyclisation also occurs in CH_2Cl_2 and the sodium salts of (**1**) and (**3**) can be converted into the corresponding lactones in AcOH.

New compounds had both correct combustion analytical values and mass measurements.

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† 2,2-Diphenylpent-4-enoic acid, specifically chosen for its substitution pattern, reacts with 2,4-dinitrobenzeneselenenyl bromide to give a γ-lactone (M. de M. Campos and N. Petragnani, *Chem. Ber.*, 1960, **93**, 317).

‡ Intermediate (**7**) could be the initial species (formed by interaction between the double bond and the reagent), or it could arise from a β-chloroselenide (*cf.* G. H. Schmid and D. G. Garratt, *Tetrahedron Letters*, 1975, 3991).

[1] For a recent example, see G. Stork and S. Raucher, *J. Amer. Chem. Soc.*, 1976, **98**, 1583.
[2] D. L. J. Clive, *J.C.S. Chem. Comm.*, 1974, 100; H. J. Reich, *J. Org. Chem.*, 1974, **39**, 428.
[3] K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1974, **39**, 429.
[4] M. de M. Campos, *Chem. Ber.*, 1960, **93**, 1075.
[5] L. do Amaral and S. C. Melo, *J. Org. Chem.*, 1973, **38**, 800.
[6] J. Klein, *J. Amer. Chem. Soc.*, 1959, **81**, 3611.