Novel reactivity of tetracoordinate 1,2λ^4-oxaselenetanes: oxirane formation reaction with retention of configuration

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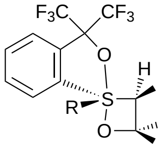
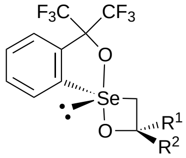
Stable tetracoordinate 3-phenyl-1,2λ^4-oxaselenetanes give the corresponding oxiranes upon thermolysis; in sharp contrast to Corey–Chaykovsky type reactions, oxirane formation proceeds with retention of configuration, and the reaction can be recognised as a new type of carbon–oxygen ligand coupling reaction of λ^4-selenanes.

The reactions of carbonyl compounds with phosphorus ylides (Wittig reaction) afford alkenes *via* 1,2λ^5-oxaphosphetanes,[1] while those with group 16 element (S, Se, Te) ylides (Corey–Chaykovsky type reaction) give oxiranes.[2] The latter type of oxirane formation reaction has been proposed to involve the formation of an *anti*-betaine followed by a back side attack of an oxido anion on the β-carbon.[2,3] In the course of our study on oxetanes bearing a highly coordinate main group element at the position adjacent to the oxygen atom,[4] we have reported the syntheses and isolations of tetra- and penta-coordinate 1,2-oxathietanes **1** and **2**, and the oxirane formation reaction with retention of configuration in the thermolysis of **2**.[5] This stereochemistry suggests another possible mechanism for the Corey–Chaykovsky reaction, *i.e.* the formation and carbon–oxygen ligand coupling reaction[6] of intermediary highly coordinate 1,2-oxathietanes, which prompted us to examine the reactivity of such a species on changing the central atom from sulfur to a heavier chalcogen. Although no oxirane formation was observed in the thermolysis of the first tetracoordinate 1,2λ^4-oxaselenetanes **3** having no substituent at the 3-position,[7] 3-phenyl derivatives were expected to give the corresponding oxiranes in view of the reactivity of the sulfur analogues. We now report on the first example of oxirane formation from tetracoordinate 1,2λ^4-oxaselenetanes and the stereochemistry of the reaction.



1 R = lone pair
2 R = O



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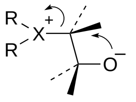
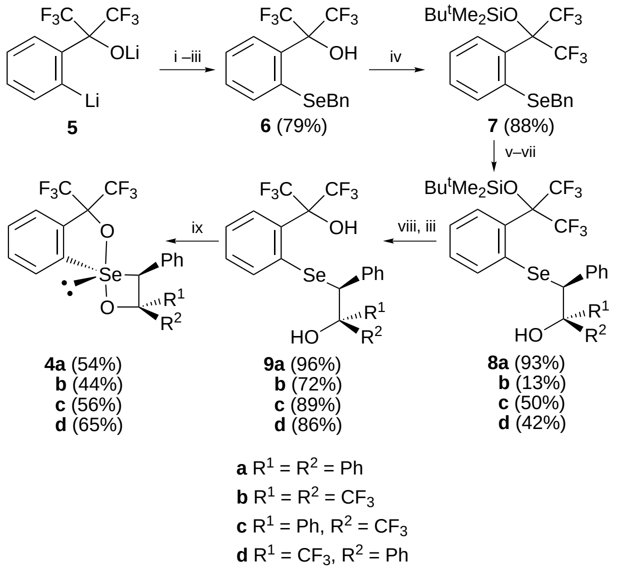


anti-betaine

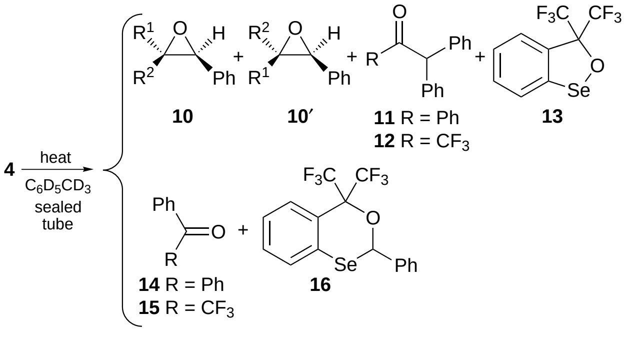
Tetracoordinate 3-phenyl-1,2-oxaselenetanes **4**‡ were synthesised from **5**[8] by the same method as that for the synthesis of sulfur analogues **1** (Scheme 1).[5]§ The ^{19}F and ^1H NMR spectra of the crude reaction mixtures showed the signals due to the diastereoisomers of **4** in which the phenyl group was *cis* to the lone pair. However, the *cis* isomers were less stable toward hydrolysis than **4** and gradually decomposed in the course of purification. All compounds **4** were stable colourless plates at room temperature in the air. The relative stereochemistry between the 3- and 4-positions of **4c** and **4d** was determined by differential NOE experiments; an NOE between the methine proton of the 3-carbon and the *ortho*-protons of the phenyl group of the 4-carbon was observed for **4c** but not for **4d**.



Scheme 1 *Reagents and conditions*: i, Se, THF, 0 °C, then 25 °C, 12 h; ii, BnBr, 0 °C, then 25 °C, 2 h; iii, aq. NH_4Cl; iv, $Bu^tMe_2SiOSO_2CF_3$, Et_3N, CH_2Cl_2, 0 °C, then 40 °C, 1 d; v, LDA (2 equiv.), THF, −78 °C, 20 min; vi, $R^1R^2C{=}O$, THF, −78 °C, 30 min; vii, flash column chromatography (for **8c** and **8d**); viii, $Bu^n{}_4NF$ (2 equiv.), THF, 0 °C, 30 min; ix, Et_3N (2 equiv.), Br_2 (1 equiv.), CCl_4, 0 °C, then 25 °C, 4 h.

The results of thermolysis ($C_6D_5CD_3$, in a degassed sealed tube) of **4** are summarised in Scheme 2 and Table 1. Although the yield of oxirane **10a** from the 3,4,4-triphenyl derivative **4a** was low because of concomitant phenyl-migrated ketone formation, **4b** gave oxirane **10b** almost quantitatively. Furthermore, thermolysis of **4c** and **4d** afforded the corresponding oxirane stereospecifically in high yield with retention of the relative stereochemistry of the starting oxaselenetanes, although a small amount (2%) of an inverted product was obtained from **4c**.

These results indicate that the stereochemistry of the oxirane formation from 1,2-oxaselenetanes **4** is the reverse of that

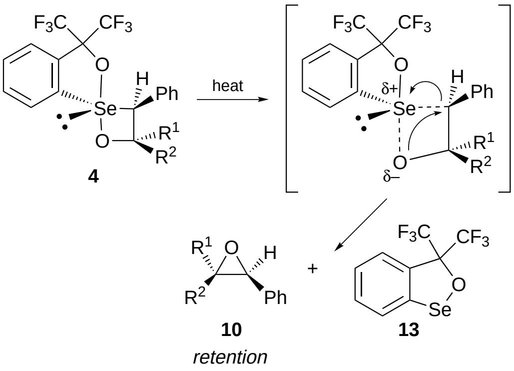


Scheme 2

Table 1 Yields of products in the thermolysis of 1,2λ^4-oxaselenetanes **4**

					Yield (%)[a]							
	R^1	R^2	T/°C	t	**10**	**10′**	**11**	**12**	**13**	**14**	**15**	**16**
4a	Ph	Ph	130	3 d	43	—[b]	52	—	95	—[c]	—	5
4b	CF$_3$	CF$_3$	200	6 d	quant.	—[b]	—	—	quant.	—	—	—
4c	Ph	CF$_3$	200	30 h	88	2	—	8	97	—	2	2
4d	CF$_3$	Ph	200	5 h	quant.	—	—	—	quant.	—	—	—

[a] Estimated by ^{19}F and ^{1}H NMR spectroscopy. [b] **10′** is equal to **10**. [c] Observed by GC–MS.



Scheme 3

expected from the back side attack of the oxido anion, and hence the reaction can be recognised as a carbon–oxygen ligand coupling reaction of λ^4-selenanes (Scheme 3). In the thermolysis of **4**, migration of the phenyl group on the 4-carbon¶ and deprotonation from the 3-position by the oxido anion can be considered to be sterically inhibited by the phenyl group on the 3-position, which is absent in **3**. Moreover, it can be assumed that the phenyl group on the 3-carbon assists the Se–C bond cleavage by stabilising the anionic character of the 3-carbon induced in the transition state.

In the case of the sulfur analogues **1**,[5a,b] oxirane formation was observed to a minor extent, with fragmentation back to the starting ketone or isomerisation *via* a 1,3-proton shift being the major decomposition pathways; this made it difficult to elucidate the reaction mechanism although oxirane formation from **1** with retention of configuration was observed.[9] In sharp contrast, in the reaction of **4c** and **4d**, yields of oxirane were almost quantitative and the stereochemistry exhibited 96 and 100% retention of configuration, respectively. The present results and the stereochemistry of the thermolysis of **2**[5c] strongly suggest that such a concerted oxirane formation from highly coordinate oxachalcogenetanes generally proceeds regardless of the central atom or its coordination number.‖

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Footnotes and References

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‡ *Selected data* for **4c**: colourless plates (hexane–Et$_2$O); mp 192.4–194.0 °C (decomp.); ^{1}H NMR (CDCl$_3$, 500 MHz): δ 6.21 (s, 1 H, SeC*H*Ph), 7.32–7.41 (m, 3 H), 7.44–7.51 (m, 3 H), 7.54 (d, ^3J 7.6, 4 H), 7.64–7.68 (m, 2 H), 7.75–7.81 (m, 1 H), 8.57 (d, ^3J 7.9, 1 H); ^{77}Se NMR (CDCl$_3$, 95 MHz): δ 792.9 (q, $^4J_{\mathrm{SeF}}$ 27). Calc. for $C_{24}H_{15}F_9O_2Se$: C, 49.25; H, 2.58. Found: C, 49.25; H, 2.64%.

For **4d**: colourless plates (hexane–Et$_2$O); mp 149.0–150.5 °C (decomp.); ^{1}H NMR (CDCl$_3$, 500 MHz): δ 6.46 (s, 1 H, SeC*H*Ph), 6.85 (d, ^3J 7.4, 2 H), 7.16–7.32 (m, 8 H), 7.74–7.79 (m, 2 H), 7.85–7.90 (m, 1 H), 8.57 (d, ^3J 8.0, 1 H); ^{77}Se NMR (CDCl$_3$, 51.5 MHz): δ 781.0 (s). Calc. for $C_{24}H_{15}F_9O_2Se$: C, 49.25; H, 2.58. Found: C, 49.39; H, 2.70%. Satisfactory ^{13}C and ^{19}F NMR spectra were obtained for both **4c** and **4d**.

§ In the synthesis of **8b**, other products formed by an electrophilic reaction of hexafluoroacetone at the *para*-position of the benzyl group were obtained.

¶ The phenyl migration in **4c** and **4d** was additionally retarded by the electronic effect of the adjacent trifluoromethyl group.

‖ Although the stereochemistry of the oxirane formation from 4,4-diaryl-3-phenyl derivatives has not been elucidated, it is unlikely that the trifluoromethyl group at the 4-position changed its stereochemistry completely, because the electron-withdrawing group of the position can electronically stabilise both the ground state and the transition state.

1 For reviews, see I. Gosney and A. G. Rowley, in *Organophosphorus Reagents in Organic Synthesis*, ed. J. I. G. Cadogan, Academic Press, New York, 1979, pp. 17–153; B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863.

2 For the Corey–Chaykovsky reaction, see J. Aubé, in *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 1, pp. 822–825. For aminosulfoxonium ylides, see C. R. Johnson, *Acc. Chem. Res.*, 1973, **6**, 341. For selenonium ylides, see A. Krief, W. Dumont, D. Van Ende, S. Halazy, D. Labar, J.-L. Laboureur and T. Q. Lê, *Heterocycles*, 1989, **28**, 1203. For telluronium ylides, see A. Osuka and H. Suzuki, *Tetrahedron Lett.*, 1983, **24**, 5109; L.-L. Shi, Z.-L. Zhou and Y.-Z. Huang, *Tetrahedron Lett.*, 1990, **29**, 4173; Z.-L. Zhou, Y.-Z. Huang, L.-L. Shi and J. Hu, *J. Org. Chem.*, 1992, **57**, 6598.

3 C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.*, 1971, **93**, 5303; T. Durst, R. Viau, R. Van Den Elzen and C. H. Nguyen, *J. Chem. Soc., Chem. Commun.*, 1971, 1334; J. M. Townsend and K. B. Sharpless, *Tetrahedron Lett.*, 1972, 3313; T. Durst, C. R. Johnson, C. W. Schroeck and J. R. Shanklin, *J. Am. Chem. Soc.*, 1973, **95**, 5298.

4 T. Kawashima and R. Okazaki, *Synlett*, 1996, 600 and references cited therein.

5 (*a*) T. Kawashima, F. Ohno and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2094; (*b*) F. Ohno, T. Kawashima and R. Okazaki, *J. Am. Chem. Soc.*, 1996, **118**, 697; (*c*) T. Kawashima, F. Ohno, R. Okazaki, H. Ikeda and S. Inagaki, *J. Am. Chem. Soc.*, 1996, **118**, 12 455.

6 For a recent review, see S. Oae and Y. Uchida, *Acc. Chem. Res.*, 1991, **24**, 202. For a recent example, see S. Ogawa, S. Sato and N. Furukawa, *Tetrahedron Lett.*, 1992, **33**, 7925.

7 T. Kawashima, F. Ohno and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 10 434.

8 E. F. Perozzi, R. S. Michalak, G. D. Figuly, W. H. Stevenson III, D. B. Dess, M. R. Ross and J. C. Martin, *J. Org. Chem.*, 1981, **46**, 1049.

9 F. Ohno, T. Kawashima and R. Okazaki, unpublished results.

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