A New Use of Cyclofunctionalisation With Selenenyl Reagents: An Example of Carbon–Carbon Bond Formation

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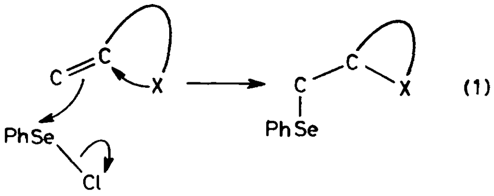
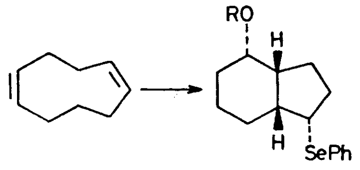
Summary (*Z*,*Z*)-Cyclonona-1,5-diene reacts stereoselectively with PhSeCl in AcOH to give (**2**; R = Ac).

Cyclofunctionalisation[1] is an efficient route to heterocycles[1,2] containing the synthetically useful benzeneselenogroup[3] [equation (1)]. We have found a transannular example of this process that demonstrates how it can be used to make a C–C bond [equation (1), X = C].†

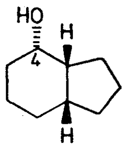


(1)

Under appropriate conditions the readily available[4] diene (**1**) reacts with PhSeCl to give the substituted hydrindan (**2**; R = Ac).[5] Thus, when an AcOH solution (0·04 M) of PhSeCl (1·02 equiv.) is added (0·3 equiv. min^{-1}) to the diene in AcOH (0·04 M) containing anhydrous NaOAc (1 equiv.) the liquid hydrindanyl acetate (**2**; R = Ac) is produced.‡ This compound, isolated 10 min after the end of the addition is treated with MeOH–H_2O–K_2CO_3 (5 ml, 0·85 ml, 84 mg, respectively, per mmol of acetate) at room temperature for 16 h and the crystalline alcohol (**2**; R = H) can be isolated as an analytically pure solid (m.p. 85—86 °C) in 68% yield [based on (**1**)]. Acetylation (Ac_2O, pyridine, 3·5 h, room temp.) of (**2**; R = H) regenerates (70%) the origina reaction product (**2**; R = Ac). Treatment of the alcohol (**2**; R = H) with Ph_3SnH[6] in refluxing PhMe gives the alcohol (**3**) (90%) shown, by comparison with an authentic sample[7] and by comparison of the derived sharp-melting acid phthalates,[7] to have the structure and stereochemistry defined by (**3**).§



(1) (2)



(3)

On the basis of the firmly established[8] *trans* mode of addition of selenenyl reagents to double bonds the transannular reactions[9] of (**1**) are expected to proceed as in (**4**) or (**5**)¶ to place the PhSe– and AcO– groups in a *cis*-1,4-relationship and *trans* to the bridgehead hydrogens. The validity of these predictions, and the preferential formation of (**6**) [= (**2**)] rather than (**7**), is established by the reduction to (**3**) together with the following observations.

The n.m.r. signal ($CDCl_3$; 100 MHz) centred at δ 5·0 due to H_a [see (**6**)] is a 1:2:2:2:1 quintet corresponding to a pair of overlapping triplets ($J_{ab} = J_{ac}$ = 5·2; J_{ad} = 12·1 Hz). The signal centred at δ 3·58 due to H_e is a sextet (J_{ef} = *ca*. J_{eh} = 9·9; J_{eg} = 5·8 Hz[10]). Dreiding models

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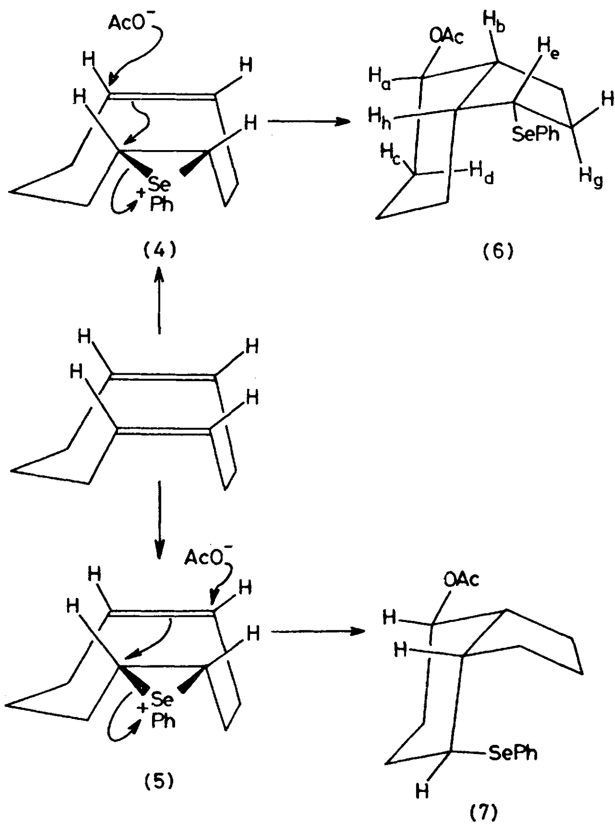
† For a previous attempt to make a C–C bond using PhSeCl, see ref. **1**.

‡ With EtOAc as solvent (and no NaOAc), a mixture of (**2**; R = Ac) and (**2**; R = H) is obtained.

§ Compound (**3**), and not the C-4 epimer, is the main product obtained by oxymercuration–reduction of (**1**) (*cf*. G. Nagendrappa and D. Devaprabhakara, *Tetrahedron Letters*, 1970, 4687; S. N. Moorthy and D. Devaprabhakara, *ibid*., 1975, 257).

¶ For simplicity, other conformations of (**7**) are not shown. The pathway *via* (**5**) involves a boat transition state and has not been observed in other (ref. 9 and the ref. in footnote §) transannular reactions of (**1**).



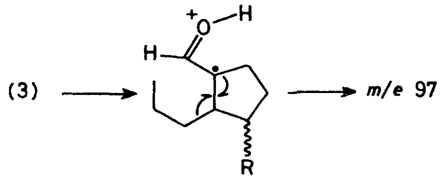
(4)

(6)

(5)

(7)

reveal that the observed pair of splitting patterns due to H_a and H_e would not arise from (**7**). Therefore, as anticipated on mechanistic grounds,[9] the PhSe– group is attached to the C_5-ring in the orientation shown. This assignment is corroborated by mass spectral measurements. A diagnostically significant peak (21% of base peak) occurs at *m/e* 97·0652 in the spectrum of (**3**) and corresponds to $[C_6H_9O]^+$. Such a species is expected in terms of one of the standard fragmentation pathways of cyclohexanols[11] [see (**8**); R = H]. When (**2**) is reduced with Ph_3SnD[6] the alcohol produced should, and does, give a corresponding peak for $[C_6H_8DO]^+$ (**8**; R = D) (13·5% of base peak, *m/e* found 98·0714, calc. 98·0716).



(8)

Correct mass measurements and satisfactory (±0·3) combustion analytical data were obtained for all new compounds.

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[10] *Cf.* Footnote 13 of ref. 5b.

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