Tetrahedron Letters,Vol.25,No.11,pp 1197-1200,1984
Printed in Great Britain

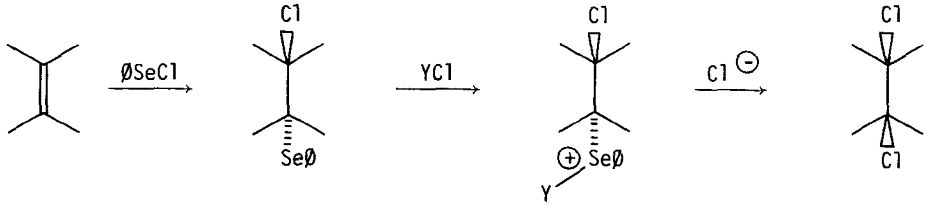
0040-4039/84 $3.00 + .00

THE *CIS* CHLORINATION OF ALKENES USING SELENIUM REAGENTS

Angelo M. Morella and A. David Ward*
Department of Organic Chemistry, University of Adelaide,
P.O. Box 498, Adelaide, South Australia, 5001.

Abstract: The phenylselenenyl chloride adduct from alkenes can be oxidised and the seleno moiety can be displaced by chloride to give high yields of dichlorides with *cis* geometry.

Phenylselenenyl chloride is known[1] to add to alkenes in a *trans* manner to yield adducts of structure (2). This communication reports that many of these adducts can be oxidized, either by chlorine or by further phenylselenenyl chloride, to yield adducts of structure (3). The phenylseleno group of (3) can be displaced readily by a suitable soluble source of chloride (tetra-n-butylammonium chloride) to yield the dichlorides (4). The total procedure can be conveniently carried out as a one-pot operation and hence constitutes a convenient method for the *cis* chlorination of an alkene that occurs readily under mild conditions.



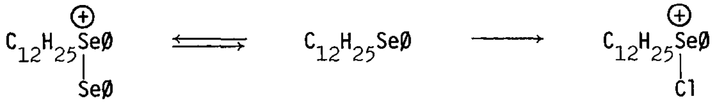
(1) (2) (3) (4)

Y = ØSe, Cl

The reaction appears to be general for a wide range of alkenes as shown in the Table. The geometry of the dichloride products were determined by ^{13}C n.m.r. spectroscopy[2] and for all the cases shown in the Table only one dichloride stereoisomer was observed. The displacement of the phenylseleno group in secondary selenides by bromide[3] is known to proceed with inversion of configuration;[4] hence it is reasonable to expect that an analogous displacement with chloride would yield the same geometry.

The reactions of alkenes which can generate a tertiary carbonium ion occur more rapidly and are often complex compared to those of mono and disubstituted alkenes. Thus α-methylstyrene reacts at room temperature, in a variety of solvents, without an added chloride source to yield the corresponding dichloride. 1-Phenylcyclohexene reacts, even at -78° in dichloromethane, to yield two dichlorides in overall quantitative yield. The major isomer (77%) appears from n.m.r. data[5,6] to be the *trans* product while the minor isomer (23%) is the *cis* dichloride. This alkene reacts with chlorine to form a complex mixture of products containing only 32% of the *trans* dichloride indicating that the formation of the two dichlorides by the selenium based method is not due to reversion of the initial adduct followed by chlorination of the alkene. Similarly 2,3-dimethyl-2-butene reacts, at low temperature, to yield mainly 2,3-dichloro-2,3-dimethylbutane whereas chlorination of this alkene yields almost exclusively 3-chloro-2,3-dimethyl-1-butene.[7] 1-Methylcyclohexene formed a complex mixture using our procedure. The n.m.r. spectra of the product indicated that the methyl group had almost completely disappeared. Norbornene also gave complex mixtures both with our procedure and with normal chlorination.[7]

In general, chlorine was a more satisfactory oxidising agent than phenylselenenyl chloride for the conversion of (2) to (3). This may be because of the greater stability of (3, Y = Cl) compared to (3, Y = ØSe). When dodecylphenylselenide (5) was treated with phenylselenenyl chloride the adduct (6) rapidly reverts to (5), either on attempted distillation or in the presence of excess alkene. The adduct (7), obtained using chlorine, does not revert to (5) under either of these conditions.

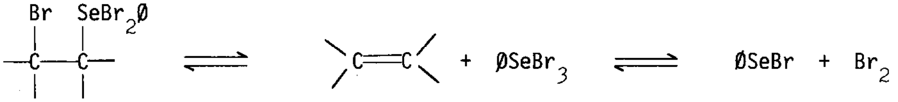


$$\underset{\text{SeØ}}{C_{12}H_{25}\overset{\oplus}{\text{Se}}\text{Ø}} \rightleftharpoons C_{12}H_{25}\text{SeØ} \longrightarrow \underset{\text{Cl}}{C_{12}H_{25}\overset{\oplus}{\text{Se}}\text{Ø}}$$

(6) (5) (7)

We have been unable to effect an analogous *cis* bromination of alkenes using similar conditions and have obtained only *trans* dibromides. We suggest that this is because the selenodibromide (8) is in equilibrium with the alkene and phenylseleninyl tribromide (9). The tribromide is known[8] to be in equilibrium with bromine and phenylselenenyl bromide. The active brominating agent under these circumstances is molecular bromine. An alternative explanation involving displacement of the phenylseleno group with retention of configuration is not likely since it has been shown[4] in other systems that this occurs with inversion.

The method we have outlined above is experimentally a more convenient procedure than others described in the literature[9] for the preparation of *cis* dichlorides and has the substantial advantage that, in the majority of cases, it produces an isomerically pure product in good yield. One example of the pyrolytic decomposition of a selenide dichloride (3) has been reported[10] to yield a mixture of products, including the dichloride (4).



(8) (9)

Table *Preparation of* <u>*cis*</u>*-Dichlorides*[a]

Substrate	Reflux Time	Yield (%)
1-octene	10 min	80
3-phenylpropene	40 min	94
styrene	20 min	100
cyclohexene	20 min	78 *cis*[b,c]
cis-2-octene	10 min	87 *erythro*[b,d]
cis-2-octene	23 h[e]	79 *erythro*[b,d]
cis-2-hexene	20 min	55 *erythro*[b]
trans-2-hexene	20 min	62 *threo*[b]
α-methylstyrene	2 h[e]	99[f]

[a] The following example indicates the general procedure. Cyclohexene (150 μl, 1.48 mmol) was added to a solution of phenylselenenyl chloride (0.351 g, 1.83 mmol, 1.23 eq) in dry acetonitrile (10 ml), followed by a solution of chlorine in carbon tetrachloride (2.3 M, 860 μl, 1.34 eq) and tetra-N-butylammonium chloride (0.419 g, 1.02 eq). The mixture was refluxed under nitrogen for twenty minutes, then cooled and oxidised with hydrogen peroxide (28%, 540 μl, 3 eq) for ten minutes and then poured into sodium bicarbonate solution (10%, 30 ml). The mixture was extracted with carbon tetrachloride (3 x 10 ml), the combined organic extracts were washed with water (20 ml), dried ($MgSO_4$), filtered through silica, evaporated and distilled to yield *cis* 1,2-dichlorocyclohexane (0.176 g, 78%) b.p. 115-125°/ 60 mm.

[b] None of the other stereoisomer was observed.

[c] The *cis* isomer had ^1H n.m.r. (CCl_4) δ 4.14, m, 2H, $W_{\frac{1}{2}H}$ 12.4Hz; 2.67-0.93, m, 8H. ^{13}C n.m.r. ($CDCl_3$) 62.7, 32.4, 22.0. The *trans* isomer had ^1H n.m.r. (CCl_4) δ 4.05, m, 2H, $W_{\frac{1}{2}H}$ 10Hz; 2.85-1.20, m, 8H. ^{13}C n.m.r. ($CDCl_3$) δ 62.9, 33.1, 22.8. Literature values[11] are δ 4.22, $W_{\frac{1}{2}H}$ 11-12Hz for the *cis* isomer and δ 4.02, $W_{\frac{1}{2}H}$ 9-10Hz for the *trans* compound.

[d] *Cis*-2-octene gives a mixture of *threo* and *erythro* (3:1) 2,3-dichloroctane with chlorine in carbon tetrachloride.

[e] Room temperature reaction.

[f] Chloroform used as solvent. Yield was 76% using acetonitrile.

References

1. D. Liotta and G. Zima, *Tetrahedron Lett.*, 4977, 1978.
2. H.J. Schneider and M. Lonsdorfer, *Org.Mag.Res.*, *16*, 133, 1981.
3. M. Sevrin, W. Dumont, L. Hevesi and A. Krief, *Tetrahedron Lett.*, 2647, 1976.
4. M. Sevrin and A. Krief, *J.Chem.Soc.,Chem.Commun.*, 656, 1980.
5. Both *cis* and *trans* 1,2-dichloro-1-phenylcyclohexane were prepared analytically pure. The *cis* isomer had ^{1}H n.m.r. (CCl_4) δ 7.76-7.36, m, 2H; 7.37-7.03, m, 3H; 4.57-4.07, m, 1H; 2.87-1.13, m, 8H. ^{13}C n.m.r. ($CDCl_3$) δ 129.7, 128.6, 128.2, 126.5, 68.3, 66.1, 43.7, 33.5, 26.0, 21.9. The *trans* isomer had ^{1}H n.m.r. (CCl_4) δ 7.48-6.93, m, 5H; 4.61, bs, 1H; 2.97-1.19, m, 8H. ^{13}C n.m.r. ($CDCl_3$) δ 144.4, 128.5, 126.3, 74.0, 65.1, 31.2, 30.1, 21.5, 18.7.
   These δ values and peak patterns are very similar to those given for the corresponding dibromides.[6]
6. P.L. Barili, G. Bellucci, F. Marioni, I. Morelli and V. Scartoni, *J.Org.Chem.*, *38*, 3472, 1973.
7. M.L. Poutsma, *J.Amer.Chem.Soc.*, *87*, 4295, 1965.
8. K.J. Wynne and P.S. Pearson, *Inorg.Chem.*, *11*, 1196, 1972.
9. S. Uemura, O. Onoe and M. Okano, *Bull.Chem.Soc.Jap.*, *47*, 3121, 1974 and references cited therein.
10. H.J. Reich and J.E. Trend, *Can.J.Chem.*, *53*, 1922, 1975.
11. H.M. van Dort and T.J. Sekuur, *Tetrahedron Lett.*, 1301, 1963.

(Received in UK 3 January 1984)