Journal of Organometallic Chemistry, 96 (1975) 251—256

THE USE OF SELENIUM(IV) CHLORIDE FOR THE PREPARATION OF DIARYLSELENIUM DICHLORIDES

E. ROY CLARK and MOHAMMED A. AL-TURAIHI

Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET (Great Britain)

(Received March 10th, 1975)

Summary

Two new synthetic routes for the preparation of diarylselenium dichlorides are reported both of which use selenium(IV) chloride as a starting meterial. In the first method, bis(*p*-methoxyphenyl) and bis(*p*-ethoxyphenyl)-selenium dichlorides are prepared by the reaction of $SeCl_4$ with anisole and phenetole respectively. In the second, diphenylselenium dichloride is prepared by the reaction of $SeCl_4$ with tetraphenyllead, a reaction in which the lead—carbon bond is cleaved.

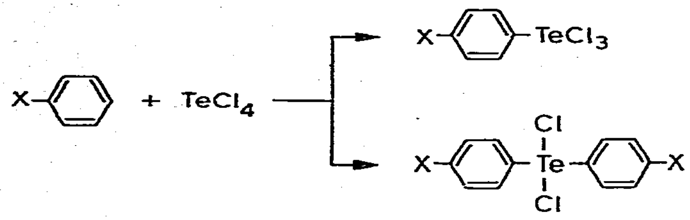
The far infrared and Raman spectra of the diarylselenium dichlorides are reported.

The synthetic routes to diarylselenium dihalides [1-3] and diaryltellurium dihalides [1,4,5] have been reviewed. There are certain similarities in the available routes for the selenium and tellurium compounds. Whilst benzene reacts with $SeCl_4$ in the presence of anhydrous aluminium(III) chloride to give a moderate yield of diphenyl selenide [6], a higher molecular ratio of benzene again using the Lewis acid $AlCl_3$, results in triphenylselenonium chloride $(C_6H_5)_3Se^+Cl^-$ [7,8]:

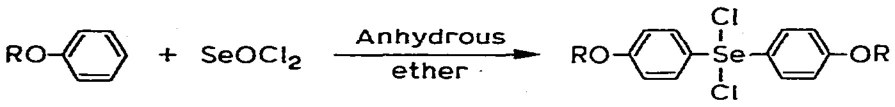
$$SeCl_4 + 3C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3Se^+Cl^- + 3HCl$$

An analogous method [9] using a molecular ratio of $AlCl_3/TeCl_4$ of 3/1 gave a 60% yield of $(C_6H_5)_3TeCl$. Products isolated at lower $AlCl_3/TeCl_4$ ratios, by quenching the reaction products when lower equivalents of hydrochloric acid were evolved, were diphenyltellurium dichloride and phenyltellurium trichloride.

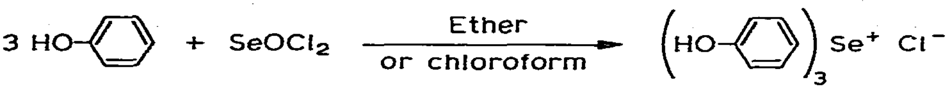
Whilst the presence of $AlCl_3$ is essential for the reaction of C_6H_6 and $TeCl_4$, no Lewis acid need be used when certain activating sustituents X (where $X = RO, HO, R_2N, RS$) are present [9—12]. Thus $TeCl_4$ with C_6H_5X gives a mixture of products:



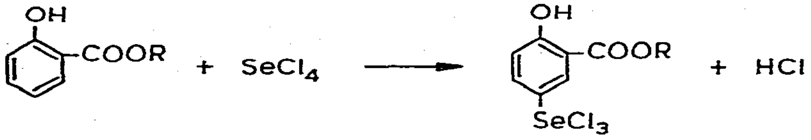
These activating substituents also have to be present for the reaction between selenium oxychloride and an aromatic compound to take place [13,14]:



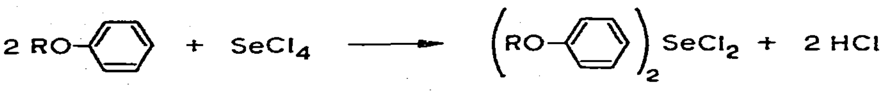
Under certain conditions this reaction can be modified to give triarylselenonium chloride as the main product [15].



Selenium(IV) chloride has been found to react with esters of salicylic acid, in the absence of any solvent, to form the arylselenium trichloride, a reaction in which the hydrogen *para* to the hydroxyl group is involved [16]:



The reaction of $SeCl_4$ with aromatic ethers does not appear to have been reported however. We find that anisole and phenetole will also react with $SeCl_4$ in the absence of any solvent and under controlled conditions to give good yields of bis(*p*-methoxyphenyl)selenium dichloride and bis(*p*-ethoxyphenyl)selenium dichloride respectively.



The synthesis of aryltellurium chlorides by treatment of various aryllead compounds with tellurium(IV) chloride or aryltellurium trichlorides has been described [17].

$$(C_6H_5)_4Pb + TeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2PbCl_2$$

The analogous reaction with $SeCl_4$ has been investigated:

$$(C_6H_5)_4Pb + SeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2SeCl_2 + (C_6H_5)_2PbCl_2$$

The reaction of triphenyllead chloride with tellurium(IV) chloride in dioxane gives a 90% yield of phenyltellurium trichloride but the analogous reaction with selenium(IV) chloride gives a low yield of diphenylselenium dichloride:

$$2(C_6H_5)_3PbCl + SeCl_4 \rightarrow (C_6H_5)_2SeCl_2 + 2(C_6H_5)_2PbCl_2$$

The products from the reactions of $SeCl_4$ with anisole, phenetole, $(C_6H_5)_4Pb$, and $(C_6H_5)_3PbCl$ were characterised by their melting points, chemical analyses, infrared and Raman spectra.

The crystal structure of diphenylselenium dichloride has been investigated [18], and has been shown to be orthorhombic D_{2h}^{15}-*Pbca* space group with 8 molecules per unit cell. The crystal structures of the di(*p*-tolyl)selenium dichloride and di(*p*-tolyl)selenium dibromide belong to space group $P2_12_12$-D_2^3 with two molecules per unit cell [19], but the molecular structure of all these diarylselenium dihalides is basically that of a slightly distorted trigonal bipyramid with the selenium atom at the centre, halogens at the apices and two phenyl or *p*-tolyl groups plus the unshared pair of electrons in the equatorial positions. The bond distances Se—Br and Se—Cl in all these diarylselenium dihalides are larger than the sum of the covalent radii and the molecular symmetry is C_{2v}.

The infrared spectra of selenium compounds of the type $(C_6H_5)_2SeX_2$ where $X = NO_3$, CH_3CO_2, CH_3SO_3 and NCO have been discussed [20]. These compounds also possess a distorted trigonal bipyramid structure (molecular symmetry C_{2v}), and some of the bands associated with the vibrations of the phenyl groups have been assigned [20]. The far infrared and Raman spectra of diarylselenium dichlorides have not previously been reported in detail and are given in Table 1. The assignments given here are based on the published data for the analogous tin and tellurium compounds $(C_6H_5)_2SnCl_2$ [21] and $(C_6H_5)_2TeCl_2$ [22] which have similar structures.

The infrared and Raman spectra of dimethylselenium dihalides and dimethyltellurium have been reported [23,24] and bands at 293 and 270 cm^{-1} assigned to ν(Se—Cl). For the diarylselenium dichlorides the values are ν_s(Se—Cl) 250-275 cm^{-1} and ν_{as}(Se—Cl) 245-255 cm^{-1}. This is consistent with

TABLE 1

THE IR AND RAMAN OF SOME DIARYLSELENIUM DICHLORIDE 360-100 cm^{-1}

$(C_6H_5)_2SeCl_2$		Bis(*p*-methoxyphenyl)-selenium dichloride		Bis(*p*-ethoxyphenyl)-selenium dichloride		Assignment
IR	Raman	IR	Raman	IR	Raman	
329s	335vw	344s	345vw	356m	355vw	t or ν(Se—Ph)
307s	310vw	310w	310vw	336vs	338vw	t'
275vs	267vs	255s	250vs	272s	263vs	ν_s(Se—Cl)
	248s	245s		253m		ν_{as}(Se—Cl)
225vs	225w	245s		253m		Phenyl u
203vs		235s	235m(sh)	225s	225w	Phenyl u'
173w		190m		186w	180vw	Phenyl x
151m						Phenyl x'
140m	132m	135s		134s	135m	$\delta(SeCl_2)$
	120w		127mw			
105vw	107ms		112ms	110w	110m	Unassigned

the long bond length Se—Cl reported for diphenylselenium dichloride [18]. The weak Raman bands at $\Delta\nu$ 120-135 cm^{-1} may be assigned to the Cl—Se—Cl deformation mode [25]. The assignments of bands associated with vibrations of the phenyl groups were made in comparison with the published data for diphenyltin dichloride [21], diphenyltellurium dichloride [22], diphenyl selenide, bromobenzene, and *p*-bromoanisole. As expected the phenyl *t*, and *u* modes all occur at slightly higher wave numbers than those for the corresponding diaryltellurium dichlorides [22]. The phenyl *u* modes appear as shoulders or are hidden under the main Raman bands but for $(C_6H_5)_2SeBr_2$ the main Raman bands but for $(C_6H_5)_2SeBr_2$ the main Raman band at $\Delta\nu$ 157 cm^{-1}, ν(Se—Br) is well clear of the phenyl *u* band at $\Delta\nu$ 249 cm^{-1} [26].

Experimental

Tetraphenyllead and triphenyllead chloride were prepared by conventional methods [27-29]. Selenium(IV) chloride was obtained from B.D.H. Limited. Toluene, benzene, diethyl ether and chloroform were dried as recommended by Vogel [30].

Reaction between selenium(IV) chloride and tetraphenyllead

$SeCl_4$ (4.4 g; 0.02 mol) and 10.3 g (0.02 mol) of tetraphenyllead in a total volume of 80 ml toluene or benzene were heated under reflux for 6 h. The precipitated diphenyllead dichloride was filtered off from the hot reaction mixture and the filtrate evaporated under vacuum to about 15 ml. This red coloured solution was allowed to cool in a refrigerator for two days when yellow crystals were obtained which were recrystallised twice from benzene. Yield 35%. Improved yields (50%) were obtained by reaction in the cold over 14 h, followed by evaporation after removal of the diphenyllead dichloride. M.p. 177°C (lit. [31] m.p. 178°). (Found: C, 47.95; H, 3.42; Se, 26.06. $C_{12}H_{10}SeCl_2$ calcd.: C, 47.72; H, 3.28; Se, 25.98%.)

Reaction between selenium(IV) chloride and triphenyllead chloride

$SeCl_4$ (4.4 g; 0.02 mol) and 9.4 g (0.02 mol) of triphenyllead chloride in a total volume of 100 ml toluene were heated under reflux for 6 h. The precipitated diphenyllead dichloride was filtered off from the hot reaction mixture and the filtrate evaporated under vacuum to about 15 ml. After two days in a refrigerator yellow crystals formed which were recrystallised from benzene. Yield 20%; m.p. 178°C (lit. [31] m.p. 178°). (Found: C, 48.33; H, 3.50; Se, 26.17. $C_{12}H_{10}SeCl_2$ calcd.: C, 47.72; H, 3.28; Se, 25.98%.)

Reaction of selenium(IV) chloride with anisole and phenetole

Selenium(IV) chloride (11.25 g; 0.1 mol) was added to 0.2 mol of anisole or phenetole contained in a 100 ml flask fitted with a drying tube. Owing to the exothermic nature of the reaction and strong evolution of hydrochloric acid gas the contents of the flask were cooled in an ice bath for 45 min and finally left at room temperature overnight for 26 h. The yellow-orange crystals which formed in the dark-red coloured liquid were filtered off and washed with a little dry diethyl ether. The dried crystals were dissolved in the smallest possible volume of dry chloroform; reprecipitated by addition of dry diethyl ether, filtered off and dried in a vacuum dessicator. Bis(*p*-methoxyphenyl)selenium dichloride, yield 45% m.p. 163°C (lit. [14] m.p. 163°). (Found: C, 46.19; H, 4.03; Se, 21.86. $C_{14}H_{14}O_2SeCl_2$ calcd.: C, 46.30; H, 3.87; Se, 21.70%.) Bis(*p*-ethoxyphenyl)selenium dichloride, yield 67%, m.p. 139°C (lit. [14] m.p. 139°). (Found: C, 48.84; H, 4.64; Se, 20.18. $C_{16}H_{18}O_2SeCl_2$ calcd.: C, 49.00; H, 4.60; Se, 20.16%.)

Diphenylselenium dichloride, bis(*p*-methoxyphenyl)- and bis(*p*-ethoxyphenyl)-selenium dichlorides were prepared by conventional methods [14,32] and gave satisfactory elemental analyses. The IR and Raman spectra and meltings points of these compounds were identical with those prepared by the new methods described above.

Raman spectra

These were recorded on a Cary 81 Laser Raman spectrometer (exciting line 6328 Å) and a Coderg Raman spectrometer (exciting line 4880 Å).

IR spectra

All compounds were examined as KBr disc on *a*) a Perkin—Elmer 457 infrared spectrophotometer (4000-250 cm^{-1}), *b*) a Perkin—Elmer 225 grating infrared spectrophotometer or *c*) on a Fourier spectrophotometer FS. 620 (Research and Industrial Instruments Co) over the range 250-20 cm^{-1}.

Chemical analyses

Carbon and hydrogen were determined by the usual combustion method. The selenium content was determined by addition of KI and titration with standard thiosulphate solution [33].

Acknowledgements

We thank Dr. G. Davidson of Nottingham University for the use of laser Raman spectrometer; Dr. D.M. Adams of Leicester University for carrying out some Raman spectra; Mrs. B. Taylor for carrying out carbon and hydrogen analyses and Mr. A. Collett for computer facilities.

References

1 H. Rheinbold, Methoden der Organischen Chemie (Houben-Weyl), Vol. IX, Stuttgart, 1955.
2 T.W. Campbell, H.G. Walker, G.M. Coppinger, Chem. Rev., 50 (1952) 279.
3 D.L. Klayman and W.H.H. Günther (Eds.), Organic Selenium Compounds; their Chemistry and Biology, Wiley, New York, 1973.
4 N. Petragnani and M. de Moura Campos, Organometal. Chem. Rev., 2 (1967) 61.
5 W.C. Cooper (Ed.), Tellurium, Van Nostrand Reinhold, New York, 1971.
6 F. Krafft and A. Kaschau, Chem. Ber., 29 (1896) 428.
7 W.E. Bradt and J.F. Green, J.F. Green, J. Org. Chem., 1 (1937) 540.
8 H.M. Leicester and F.W. Bergstron, J. Amer. Chem. Soc., 51 (1929) 3587.
9 W.H.H. Günther, J. Nepywoda and J.Y.C. Chu, J. Organometal. Chem., 74 (1974) 79.
10 K.J. Irgolic and R.A. Zingaro, in E.I. Becker and M. Tsutsui (Eds.), Organometallic Reactions, Vol. 2, Ch. 2, Wiley-Interscience, New York, 1970, and references therein.
11 H. Rheinbold, Methoden der Organischen Chemie (Houben-Weyl), Vol. IX, Stuttgart, 1955, p. 1153.
12 J. Bergman, Tetrahedron, 28 (1972) 3323.

13 F. Kunkell, Chem. Ber., 28 (1895) 609.
14 F.N. Alquist and R.E. Nelson, J. Amer. Chem. Soc., 53 (1931) 4033.
15 G.T. Morgan and F.H. Burstall, J. Chem. Soc., 133 (1928) 3260.
16 R.E. Nelson, E.F. Degering and J.A. Bilderbeck., J. Amer. Chem. Soc., 60 (1938) 1239.
17 B.C. Pant, J. Organometal. Chem., 54 (1973) 191.
18 J.D. McCullough and G. Hamburger, J. Amer. Chem. Soc., 64 (1942) 508.
19 J.D. McCullough and R.E. Marsh, Acta Crystallogr., 3 (1950) 41.
20 V. Horn and R. Paetzold, Spectrochim. Acta, 30A (1974) 1489.
21 A.L. Smith, Spectrochim. Acta, 24A (1968) 695.
22 W.R. McWhinnie and M.G. Patel, J. Chem. Soc., Dalton Trans., (1972) 199.
23 G.C. Hayward and P.J. Hendra, J. Chem. Soc. A, (1969) 1760.
24 K.J. Wynne and J.W. George, J. Amer. Chem. Soc., 87 (1965) 4750.
25 K.J. Wynne, P.S. Pearson, M.G. Newton and J. Golen, Inorg. Chem., 11 (1972) 1192.
26 C.A. Tucker, B.Sc. Project Thesis, University of Aston in Birmingham, 1975.
27 M.D. and R.W. Weiss, Organometallic Compounds, Methods of Synthesis, physical constants and chemical reactions, Vol. 11, Springer, Berlin/New York, 1967, p. 526, 554.
28 L.S. Foster, W.M. Dix and I.J. Gruntfest., J. Amer. Chem. Soc., 61 (1939) 1685.
29 W.C. Setzer, R.W. Leeper and H. Gilman, J. Amer. Chem. Soc., 61 (1939) 1609.
30 A.I. Vogel, A Text Book of Practical Organic Chemistry, Qualitative Organic Analysis, 3rd. ed., Longmans, 1958, p. 169, 173.
31 F. Krafft and W. Vorster, Chem. Ber., 26 (1893) 2818.
32 H.M. Leicester, Organic Syntheses, Coll. Vol. 2, Wiley, New York, 1943, pp. 238-239.
33 J.D. McCullough, J. Amer. Chem. Soc., 64 (1942) 2675.