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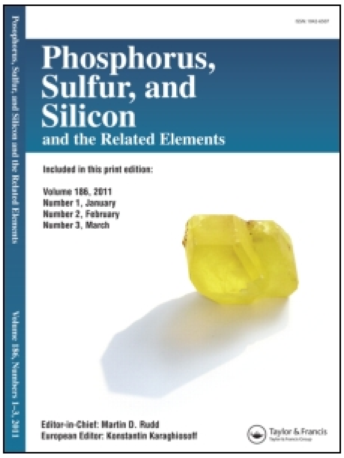

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SYNTHESIS OF THE FIRST BENZODISELENAGERMOLES AND ONE SPIROBISDISELENAGERMOLE

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SYNTHESIS OF THE FIRST BENZODISELENAGERMOLES AND ONE SPIROBISDISELENAGERMOLE

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The first examples of compounds $R^1R^2GeSe_2C_6H_4R^3$ (R^1,R^2 = CH_3, C_2H_5, C_3H_7, n-C_4H_9, i-C_5H_{11}, Ph, p-CH_3Ph, R^3 = H, CH_3, OCH_3) were easily obtained (40–80% yield) from electrophilic cleavage of diselenophenylene zirconocenes by dialkyl or diaryl dichlorogermanes. The synthesis of a spirodiselenagermole was achieved in the same way using germanium tetrachloride. Analytical data, ^1H and ^{77}Se NMR, mass spectra are perfectly consistent with the expected structures.

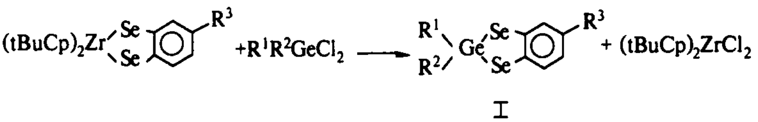
Key words: Diselenagermole; zirconium; ^1H NMR; ^{77}Se NMR; mass spectrometry.

INTRODUCTION

Although there are some papers dealing with dioxagermoles, benzodioxagermoles and benzodithiagermoles,[1–2] little is known about materials incorporating germanium-selenium bonds.[3,4] Two recent papers[5,6] concerning compounds having two selenium atoms directly bonded to one germanium atom prompt us to publish our contribution in this field. This paper reports the synthesis of the first benzodiselenagermoles as well as a spirodiselenagermole.

RESULTS AND DISCUSSION

Benzodiselenagermoles (I) were easily obtained (40–80% yield) by reacting dialkyl or diaryl dichlorogermanes with diselenophenylenetertiobutylzirconocenes for which the synthesis has been previously reported.[7–9]



I

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TABLE I

^{1}H and ^{77}Se-NMR and mass spectrometry data of compounds I and II

	NMR		
Compounds	$^{1}H(CDCl_3)$ ppm/TMS	$^{77}Se(C_6D_6)$ ppm/CH_3SeCH_3	Mass spectrometry Main fragments (M, %)
I_a	1.22(m/6,CH_3); 1.50(m/4,CH_2) 6.92(dd/2,H_4H_5); 7.48(dd/2,H_3H_6)	133.5	368(M^+,12); 339(M-C_2H_5,32); 310(M-2C_2H_5,22); 236($C_6H_4Se_2$,21); 156(C_6H_4Se,54)
I_b	1.01(m/6,CH_3); 1.57(m/8,CH_2) 6.92(dd/2,H_4H_5); 7.47(dd/2,H_3H_6)	151.9	396(M^+,12); 353(M-C_3H_7,28); 310(M-2C_3H_7,8)
I_c	0.90(d/6,CH_3); 1.10–1.57(m/10,CH + CH_2); 6.92(dd/2,H_4H_5); 7.47(dd/2,H_3H_6)	148.1	452(M^+,10); 381(M-C_5H_{11},29); 310(M-2C_5H_{11},5)
I_d	1.47(s/3,CH_3); 6.98(dd/2,H_4H_5); 7.43(m/3,Ph); 7.51(dd/2,H_3H_6); 7.75(m/2,Ph)	194.3	402(M^+,36); 387(M-CH_3,73); 325(M-Ph,6); 310(M-Ph-CH_3,16)
I_e	6.98(dd/2,H_4H_5); 7.43(m/6,Ph); 7.52(dd/2,H_3H_6); 7.77(m/4,Ph)	177.8	464(M^+,64); 387(M-Ph,73); 310(M-2Ph,8)
I_f	1.21(m/6,CH_3); 1.48(m/4,CH_2); 2.21(s/3,CH_3); 6.74(dd/1,H_4); 7.31(s broad/1,H_6); 7.34(d/1,H_3)	131.05 123.0	382(M^+,40); 353(M-C_2H_5,76); 324(M-2C_2H_5,24); 170($H_3CC_6H_3Se$,39)
I_g	1.01(m/6,CH_3); 1.56(m/8,CH_2); 2.20(s/3,CH_3); 6.74(dd/1,H_4); 7.30(s broad/1,H_6); 7.34(d/1,H_3)	147.0 141.9	410(M^+,32); 367(M-C_3H_7,74); 324(M-2C_3H_7,22); 170($H_3CC_6H_3Se$,33)
I_h	0.91(m/6,CH_3); 1.20–1.55(m/12,CH_2); 2.21(s/3,CH_3); 6.74(dd/1,H_4); 7.30(s broad/1,H_6); 7.34(d/1,H_3)	148.9 140.8	438(M^+,19); 381(M-C_4H_9,50); 324(M-2C_4H_9,13)
I_i	0.90(d/6,CH_3); 1.10–1.50(m/10,CH + CH_2); 6.75(dd/1,H_4); 7.30(s broad/1,H_6); 7.34(d/1,H_3)	146.1 138.0	466(M^+,21); 395(M-C_5H_{11},48); 324(M-2C_5H_{11},10); 170($H_3CC_6H_3Se$,14)

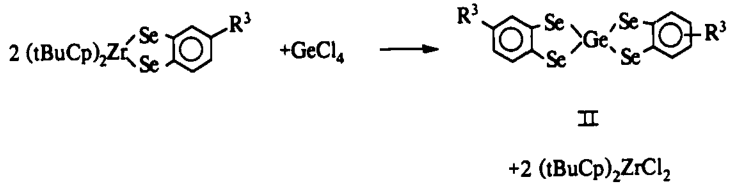
$\mathbf{I_j}$	1.45(s/3,CH_3); 2.24(s/3,CH_3); 6.80(dd/1,H_4); 7.39(m/5,Ph + H_3H_6); 7.74(m/2,Ph)	192.5 184.0	416(M^+,44); 401(M-CH_3,73); 339(M-Ph,7) 324(M-Ph-CH_3,22); 244(M-Ph-CH_3-Se,22) 170($H_3CC_6H_3Se$,52)
$\mathbf{I_k}$	2.23(s,3,CH_3); 6.80(dd/1,H4); 7.35(m,8,Ph + H3,H6); 7.73(m,4,Ph)	176.2 167.8	478(M^+,66); 401(M-Ph,75); 324(M-2Ph,9) 244(M-2Ph-Se,27)
$\mathbf{I_l}$	1.43(s,3,CH_3); 2.23(s/3,CH_3); 2.36(s,3,CH_3); 6.79(dd/1,H_4); 7.19–7.41(m/4,Ph + H_3H_6); 7.62(d/2,Ph)	193.3 184.8	430(M^+,36); 415(M-CH_3,75); 339(M-CH_3Ph,6); 324(M-CH_3Ph-CH_3,11) 244(M-CH_3Ph-CH_3-Se,26)
$\mathbf{I_m}$	1.46(s/3,CH_3); 3.75(s/3,OCH_3); 6.58(dd/1,H_4); 7.08(d/1,H_6); 7.35(d/1,H_3); 7.43(m/3,Ph); 7.74(m/2,Ph)	208.5 172.8	432(M^+,53); 417(M-CH_3,68); 340(M-CH_3-Ph,18)
$\mathbf{I_n}$	3.74(s/3,OCH_3); 6.58(dd/1,H_4); 7.09(d/1,H_6); 7.35(d/1,H_3); 7.43(m/6,Ph); 7.75(m/4,Ph)	191.9 156.2	494(M^+,17); 479(M-CH_3,8); 417(M-Ph,14); 402(M-Ph-CH_3,8)
$\mathbf{I_o}$	1.44(s,3,CH_3); 2.37(s,3,CH_3); 3.74(s/3,CH_3); 6.58(dd/1,H_4); 7.07(d/1,H_6); 7.22(d/2,Ph); 7.36(d/1,H_3); 7.63(d/2,Ph)	209.1 173.4	446(M^+,50); 431(M-CH_3,67); 340(M-CH_3-PhCH_3,14)
II	2.27(s/3,CH_3); 6.84(dd/1,H_4); 7.37(s broad/1,H_6); 7.40(d/1,H_3)	337.4 330.2	574(M^+,20); 324(M-CH_3PhSe_2,28); 250(CH_3PhSe_2,100); 170($H_3CC_6H_3$,Se58)

I_a:$R^1 = C_2H_5$, $R^2 = C_2H_5$, $R^3 = H$
I_b:$R^1 = nC_3H_7$, $R^2 = nC_3H_7$, $R^3 = H$
I_c:$R^1 = iC_5H_{11}$, $R^2 = iC_5H_{11}$, $R^3 = H$
I_d:$R^1 = CH_3$, $R^2 = Ph$, $R^3 = H$
I_e:$R^1 = Ph$, $R^2 = Ph$, $R^3 = H$
I_f:$R^1 = C_2H_5$, $R^2 = C_2H_5$, $R^3 = CH_3$
I_g:$R^1 = nC_3H_7$, $R^2 = nC_3H_7$, $R^3 = CH_3$
I_h:$R^1 = nC_4H_9$, $R^2 = nC_4H_9$, $R^3 = CH_3$
I_i:$R^1 = iC_5H_{11}$, $R^2 = iC_5H_{11}$, $R^3 = CH_3$
I_j:$R^1 = CH_3$, $R^2 = Ph$, $R^3 = CH_3$
I_k:$R^1 = Ph$, $R^2 = Ph$, $R^3 = CH_3$
I_l:$R^1 = CH_3$ $R^2 = pCH_3Ph$, $R^3 = CH_3$
I_m:$R^1 = CH_3$, $R^2 = Ph$, $R^3 = OCH_3$
I_n:$R^1 = Ph$, $R^2 = Ph$, $R^3 = OCH_3$
I_o:$R^1 = CH_3$, $R^2 = pCH_3Ph$, $R^3 = OCH_3$

This simple and particularly efficient organometallic route allows the direct introduction of the *o*-diselenophenylene moiety and leads to a large range of new compounds **I**.

A standard synthesis quite similar to that reported elsewhere[10,11] was as follows: under argon atmosphere, the dichlorogermane (1 mmol) in freshly distilled THF (10 mL) was slowly added at 25°C to a stirred solution of diselenophenylenetertiobutylzirconocene (1 mmol, THF 10 mL). When the colour had been discharged, the solvent was distilled off under reduced pressure and **I** were extracted with pentane or diethyl ether. The solid residue was practically pure $(t\text{-BuCp})_2ZrCl_2$. Compounds **I** were finally purified by chromatography (SiO_2, pentane-diethyl ether 8/2 or 9/1) and the solids thus obtained were recrystallized from hexane.

The spirodiselenagermole **II** was obtained by reacting germanium tetrachloride with a diselenophenylene zirconocene ($R^3 = CH_3$).



II: $R^3 = CH_3$

Among these new compounds, I_j, I_l, I_m, I_o and **II** have a chiral centre at the germanium atom. They were isolated as a racemic mixture.

All the products have been characterized by satisfactory elemental analyses, ^1H and ^{77}Se NMR and mass spectrometry. Spectroscopic data are reported in Table I.

The presence of the molecular peak in all the mass spectra confirms the proposed structure. The fragmentation pattern is characteristic for the progressive loss of alkyl or aryl substituents from the central germanium atom followed by the subsequent fragmentation of the selenium-containing ring.

The ^1H NMR spectra are also perfectly in accordance with the proposed structure. In particular, the double doublet of the AA'XX' system is observed in the range from δ 6.9–7.5 ppm for compounds $\mathbf{I_a}$ to $\mathbf{I_e}$. Three signals are observed for the germoles containing a methylated aromatic ring, but a partial coalescence remains for the protons close to the selenium atom. This accidental overlap is no longer present in the methoxy compounds for which the aromatic protons appear as three distinct signals in the range from δ 6–7.5 ppm. The unusual resonance observed for the ethyl groups bonded to germanium has been already observed and explained.[12]

As we have previously mentioned,[13] the ^{77}Se NMR is of great structural interest because chemical shifts are very sensitive to the nature of the substituent either on the germanium atom or on the benzene ring. The greater the electron-releasing ability of the substituent, the greater the effect observed. For example, Δδ reaches more than 40 ppm when a phenyl group replaces a methyl group on the germanium atom. Similar results can be observed by reference to the nature of the aromatic-ring substituent. Thus the signals corresponding to the two anisochronous selenium atoms for $\mathbf{I_k}$ ($R^3 = CH_3$) are about 8 ppm apart; whereas this separation increases to 36 ppm for $\mathbf{I_o}$ ($R^3 = OCH_3$) (Table 1).

We are presently working on the ditelluragermoles and on germoles containing two different analogous chalcogen atoms, sulphur-selenium, sulphur-tellurium, selenium-tellurium as well.

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REFERENCES

1. H. Lavayssière and G. Dousse, *J. Organomet. Chem.*, **297**, C17 (1985) and references therein.
2. H. Lavayssière, G. Dousse and J. Satgé, *Rec. Trav. Chim.* Pays-Bas, **107**, 440 (1988).
3. P. Rivière, M. Rivière-Baudet and J. Satgé, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone and E. W. Abel; Pergamon Press, N. Y., **2**, 443 (1982).
4. D. Seyferth and R. S. Henderson, *J. Organomet. Chem.*, **204**, 333 (1981).
5. M. Tomada, M. Shimoda, Y. Takenchi and Y. Itaka, *Chem. Lett.*, 535 (1988).
6. J. Gysling and H. R. Luss, *Organometallics*, **8**, 363 (1989), and references therein.
7. B. Gautheron, G. Tainturier, S. Pouly, F. Theobald, H. Vivier and A. Laarif, *Organometallics*, **3**, 1495 (1984).
8. G. Tainturier, B. Gautheron and S. Pouly, *N. J. Chem.*, **10**, 625 (1986).
9. P. Meunier, B. Gautheron and A. Mazouz, *J. Organomet. Chem.*, **320**, C39 (1987).
10. P. Meunier, B. Gautheron and A. Mazouz, *J. Chem. Soc. Chem. Commun.*, **5**, 424 (1986).
11. P. Meunier, B. Gautheron and A. Mazouz, *Phosphorus and Sulfur*, **33**, 33 (1987).
12. G. Dousse, Thèse, Toulouse (1977).
13. P. Granger, B. Gautheron, G. Tainturier and S. Pouly, *Org. Magn. Res.*, **22**, 701 (1984).