Dimesitylgermylidene p-toluene sulfonamide: a new stable germanium–nitrogen doubly bonded species

F. El Baz [a], M. Rivière-Baudet [b,*], M. Ahra [a]

[a] Laboratoire de Chimie Organique et Organométallique, Université Ibnou Zohr, Faculté des Sciences, BP 28 / S, Agadir, Morocco
[b] Laboratoire d'Hétérochimie Fondamentale et Appliquée, UPRES-A 5069 du CNRS; Université Paul Sabatier, 31062 Toulouse cedex 4, France

Abstract

A new stable germanium doubly bonded species is obtained by dehydrohalogenation of the corresponding N-halogenogermyl p-toluene sulfonamide. The dimesitylgermylidene p-toluene sulfonamide is a stable and very reactive reagent leading to addition reactions with protic species such as water, t-butanol or chloroform. With 3,5-di-t-butyl ortho-diphenol, the reaction leads to the corresponding dimesitylgermadioxolane with elimination of p-toluene sulfonamide. With benzaldehyde, the dimesitylgermylidene sulfonamide leads to a pseudo-wittig reaction with formation of the corresponding benzylidene p-toluene sulfonamide. With 3,5-di-t-butyl ortho-quinone, the first step of the reaction involves a single electron transfer leading eventually to dimesitylgermadioxolane with evolution of p-toluene sulfonamidyl radicals characterized by duplication into N,N-bis(p-toluene sulfonyl)hydrazine. © 1997 Elsevier Science S.A.

1. Introduction

Our laboratory has been interested for several years in the finding of stable compounds of germanium doubly bonded species [1–3]. We observed recently that electron-withdrawing moieties on nitrogen could stabilize germa-imines [4,5], and therefore searched for new substituents that can achieve the stabilization of unsaturated germanium–nitrogen species. We present here our results within the N-germylated compounds of p-toluene sulfonamide.

Within group 14, N-germylsulfonamides are un-

known compounds; only one germyldisulfonylamide, $Me_3GeN(SO_2Me)_2$, was published [6], and within the p-toluene sulfonyl series, only the cyclotrigermazane $(Cl_2GeNSO_2C_6H_4CH_3)_3$ is known [7], the corresponding monomer dichlorogermylidene p-toluene sulfonamide is not stable at room temperature [7]. A few stannyl compounds [7–9] or silicon compounds [10] of p-toluene sulfonamide are already known.
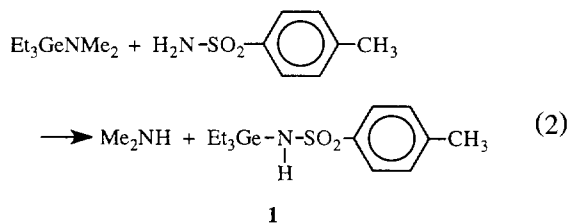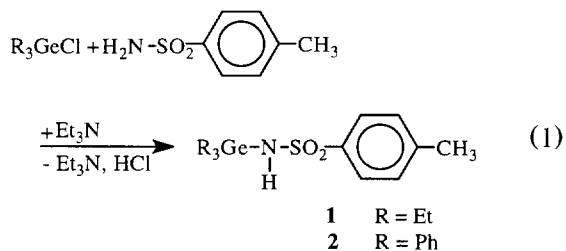
2. Result and discussion

First of all, we tested the most used methods for the synthesis of a Ge–N bond [1,2,11,12] on the p-toluene sulfonamide with trialkyl or triaryl chlorogermanes.
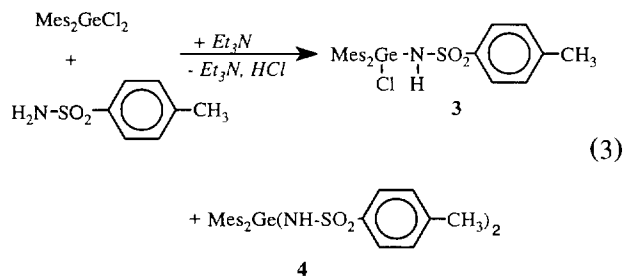
The dehydrochloration reaction (Eq. (1)) leads easily to the desired N-germyl p-toluene sulfonyl amide **1** or **2**. **1** was also obtained quantitatively from transamina-

* Corresponding author. Hétérochimie Fondamentale et Appliquée, UPRESA 5069, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex. Tel.: +33-05-61-55-83-48; fax: +33-05-61-55-82-34; e-mail: satge@iris.ups-tlse.fr.

tion between N-dimethylamino triethylgermylamine and *p*-toluene sulfonamide (Eq. (2)) [13].

$$R_3GeCl + H_2N-SO_2-\langle\bigcirc\rangle-CH_3$$

$$\xrightarrow[- Et_3N, HCl]{+Et_3N} R_3Ge-\underset{H}{N}-SO_2-\langle\bigcirc\rangle-CH_3 \quad (1)$$

$$\begin{array}{ll} \mathbf{1} & R = Et \\ \mathbf{2} & R = Ph \end{array}$$

$$Et_3GeNMe_2 + H_2N-SO_2-\langle\bigcirc\rangle-CH_3$$

$$\longrightarrow Me_2NH + Et_3Ge-\underset{H}{N}-SO_2-\langle\bigcirc\rangle-CH_3 \quad (2)$$
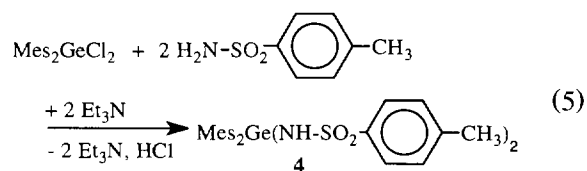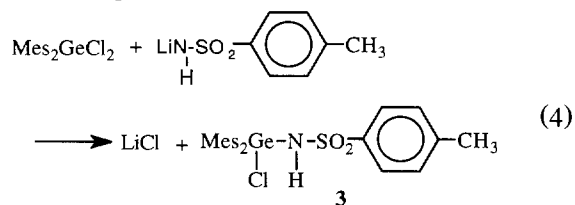
$$\mathbf{1}$$

By contrast, when we tried to prepare the corresponding N-dimesitylchlorogermyl *p*-toluene sulfonamide **3** (Eq. (3)), starting material for the iminocompound, we obtained mostly the bis-(*p*-toluene sulfonylamido) dimesitylgermane **4** beside nearly half of the starting dimesityldichlorogermane (Eq. (3)).

$$Mes_2GeCl_2$$
$$+$$
$$H_2N-SO_2-\langle\bigcirc\rangle-CH_3 \xrightarrow[- Et_3N, HCl]{+ Et_3N} Mes_2Ge-\underset{Cl}{\overset{}{\underset{H}{N}}}-SO_2-\langle\bigcirc\rangle-CH_3$$
$$\mathbf{3}$$
$$(3)$$

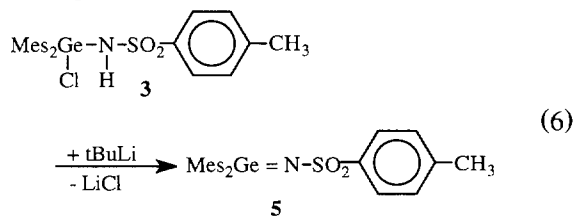$$+ Mes_2Ge(NH-SO_2-\langle\bigcirc\rangle-CH_3)_2$$
$$\mathbf{4}$$

As chlorogermylamine **3** has been found to be a

stable compound when prepared through transmetallation reaction (Eq. (4)), we therefore think that the formation of **4** from **3** is the result of a further dehydrochloration, the Ge–Cl bond in **3** being more reactive than in Mes_2GeCl_2. Moreover, diamine **4** is easily obtained in the presence of two equivalents of *p*-toluene sulfonamide (Eq. (5)).

$$Mes_2GeCl_2 + \underset{H}{LiN}-SO_2-\langle\bigcirc\rangle-CH_3$$

$$\longrightarrow LiCl + Mes_2Ge-\underset{Cl}{\overset{}{\underset{H}{N}}}-SO_2-\langle\bigcirc\rangle-CH_3 \quad (4)$$
$$\mathbf{3}$$

$$Mes_2GeCl_2 + 2 H_2N-SO_2-\langle\bigcirc\rangle-CH_3$$

$$\xrightarrow[- 2 Et_3N, HCl]{+ 2 Et_3N} Mes_2Ge(NH-SO_2-\langle\bigcirc\rangle-CH_3)_2 \quad (5)$$
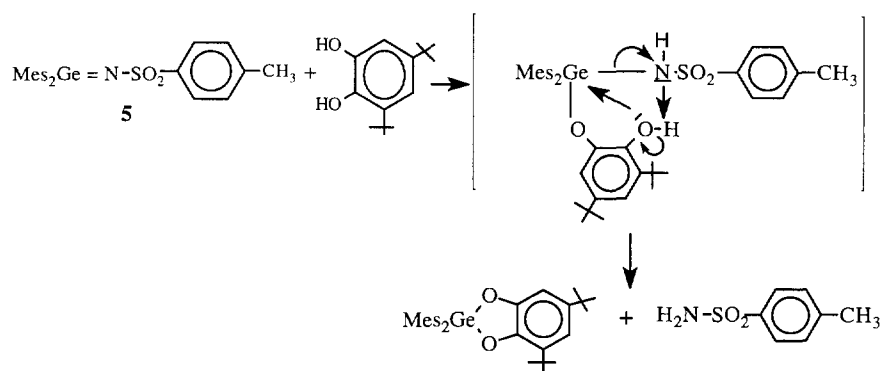$$\mathbf{4}$$

The dimesitylgermylidene *p*-toluene sulfonamide **5** is easily obtained at low temperatures through lithium chloride elimination of the transient N-lithium derivative of **3** (Eq. (6)).

$$Mes_2Ge-\underset{Cl}{\overset{}{\underset{H}{N}}}-SO_2-\langle\bigcirc\rangle-CH_3$$
$$\mathbf{3}$$

$$\xrightarrow[- LiCl]{+ tBuLi} Mes_2Ge = N-SO_2-\langle\bigcirc\rangle-CH_3 \quad (6)$$
$$\mathbf{5}$$

The same iminoderivative **5** is also obtained through a similar route (Eqs. (4) and (6)) starting from dimesityldibromogermane.
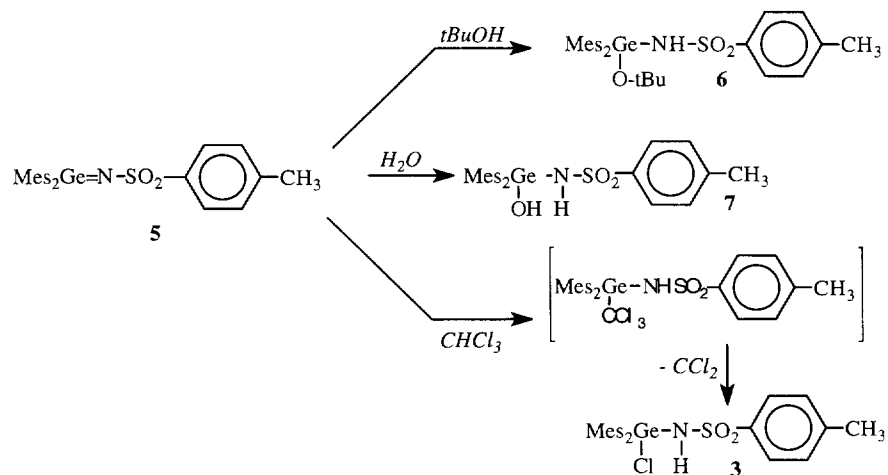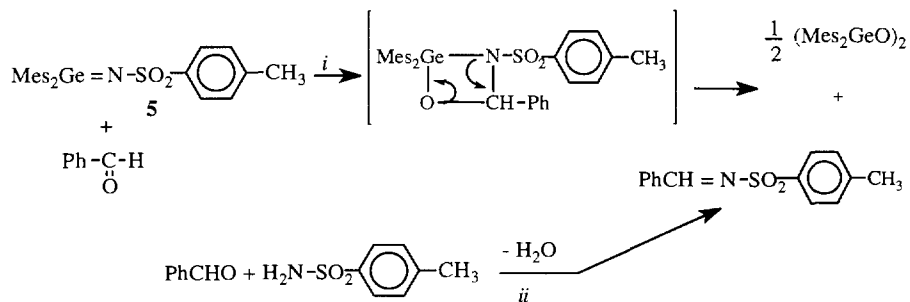

Scheme 1.

Scheme 2.

The unsatured dimesitylgermylidene *p*-toluene sulfonamide **5** is isolated as a white powder and is very stable at room temperature. The reaction never led to polymers contrary to what was observed in the case of the reaction between germylene and tosylazide which led to a polymer $\{[(Me_3Si)_2N]_2Ge-NSO_2-C_6H_4-pCH_3\}_n$ instead of the expected germa-imine [14]. In the same way, dichlorogermylidene *p*-toluene sulfonamide at room temperature, led to the corresponding trimer [7].

In a way similar to germa-imines [4,5,12,15], **5** reacts with protic species yielding the corresponding adducts (Scheme 1).

The adducts on *t*-butanol **6** and water **7** are thermally stable. By contrast, the adduct on chloroform leads to the dimesitylchlorogermylamine **3** in concordance with what was previously observed on a similar adduct on 2, 4, 6-trifluorophenyl dimesitylgerma-imine [4,5].

With 3,5-di-*t*-butyl *ortho*-diphenol, the adduct is also not stable. Because of the presence of the second phenol group in *ortho* position, the germanium nitrogen σ bond of the adduct is cleaved (Scheme 2) and the reaction leads to the corresponding dimesitylgermadioxolane with the elimination of *p*-toluene sulfonamide.
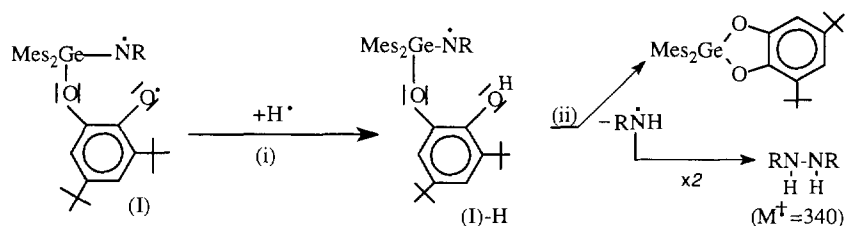
With benzaldehyde, the dimesitylgermylidene *p*-

Scheme 3.
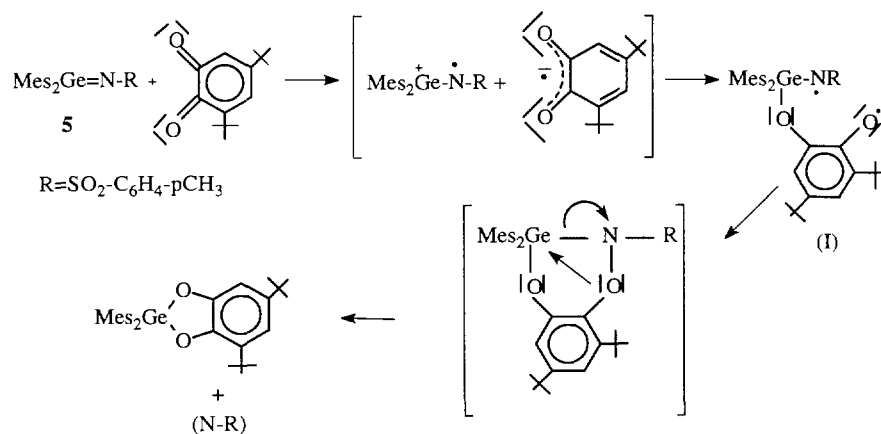
Scheme 4.

Scheme 5.

toluene sulfonamide 5 leads to a pseudo-wittig reaction yielding the corresponding germanium oxide and benzylidene p-toluene sulfonamide, probably through decomposition of the transient expected 1–2 adduct (Scheme 3, i). This imine was identified by comparison to a pure sample obtained by dehydration between benzaldehyde and p-toluene sulfonamide (Scheme 3, ii).

Contrary to germa-imines [4,5,12], dimesitylgermylidene p-toluene sulfonamide 5 does not react with the 1-3 dipole of N-t-butyl phenylnitrone (Eq. (7)), but like germa-imines reacts easily with 3,5-di-t-butyl ortho-quinone (Scheme 4).
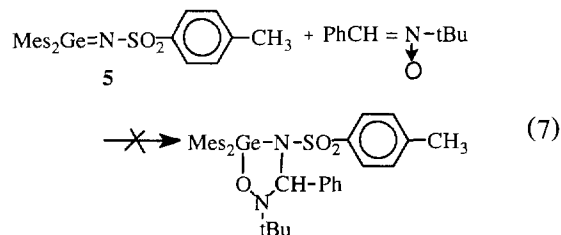
In a way similar to the other germanium nitrogen compounds [16,17], the reaction proceeds by a single electron transfer reaction in the first step evidenced by the RPE signal of the transient o-semiquinonic species ($g = 2.0047$; $a^H = 2.75$ G) (Scheme 4) and the characterization of isobutene in the reactional mixture. The SET in the initial step could lead to the unstable 1–4 adduct by recombination of the pair of radical ions in the solvent cage through intermediate (I) (Scheme 4).

As previously observed [1,2,12,16,17], the 1–4 adduct when formed (it could also be formed by 2 + 4 dipolar cycloaddition) leads to the expected decomposition in dimesitylgermadioxolane.

However, as the formation of p-toluene sulfonamidyl radicals in the reaction is evidenced by the characterization in mass spectroscopy of the corresponding hydrazine ($M^{+\cdot} = 340$) (Scheme 5, ii), germadioxolane formation can also be explained from (I)–H formed by hydrogen recombination with intermediate (I) (Scheme 5, i). The formation of isobutene is explained, as previously in reactions of the same type, by the homolytic cleavage of a C–t-Bu bond in the organic moieties after abstraction of hydrogen radicals from the quinone by intermediate (I) [16,17].

In the reaction between 5 and 3,5-di-t-butyl ortho-quinone, we never observed any competition between the 1–4 addition and the 1–2 dipolar addition on one of the carbonyl group which is sometimes observed [17], and would lead to the corresponding imine (Scheme 6).

2.1. Conclusion

The electron-withdrawing effect of the p-toluene sulfonyl group on nitrogen stabilise the dimesitylgermylidene p-toluene sulfonamide under its unsaturated monomeric form; the steric effects also probably play a role in the stabilisation. Dimesitylgermylidene p-toluene sulfonamide is easily obtained by elimination from the corresponding halolithium derivatives and is a very reactive compound. Addition reactions on protic species are a source of bifunctional germylated compounds and with benzaldehyde it leads to a pseudo-wittig reaction. Unlike germa-imines, 1 + 3 cycloaddition with nitrones does not take place, but 1–4 addition on di-t-butyl ortho-quinone, in a way similar to germa-imines, occurs by SET reaction in the first step, clearly evidenced by ESR spectroscopy and the characterisation of N,N'-bis-sulfonylhydrazine.
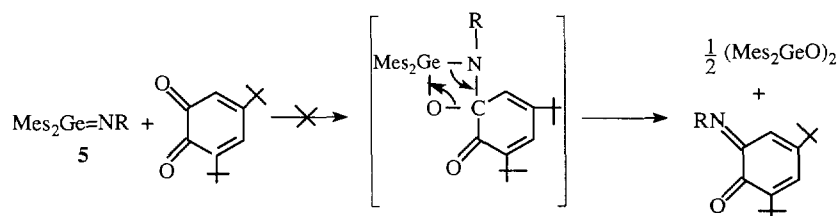

Scheme 6.

3. Experimental

All reactions were carried out under nitrogen or argon and with dry solvents.

NMR spectra were recorded on Brücker AC80 (^{1}H) and AC 200 (^{13}C) spectrometers; IR spectra on a Perkin-Elmer 1600 FTIR spectrometer; mass spectra on a HP 5989 in the electron impact mode (70 eV) or on a Rybermag R10-10 spectrometer operating in the electron impact mode or by chemical desorption (DCi/CH$_4$); RPE experiments on a Brüker ER 200 spectrometer with frequency meter EIP.

Melting points were measured on a Leitz microscope. Elemental analysis were performed by the microanalysis center of the Ecole Nationale Supérieure de Chimie de Toulouse.

For ^{13}C NMR the following numbering was used:
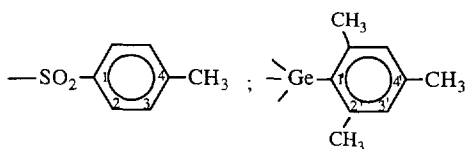
3.1. N-triethylgermyl p-toluene sulfonamide 1

3.1.1. By dehydrohalogenation

To p-toluene sulfonylamine (1.00 g; 5.8 10^{-3} mole) and Et$_3$N (2.5 ml; 17.8 10^{-3} mole) in THF, was added under stirring Et$_3$GeCl (1.14 g; 5.8 10^{-3} mole). After 4 h further stirring at room temperature, Et$_3$N · HCl was filtered and the solvent evaporated in vacuo leading to 1.62 g of a beige amorphous powder of 1: yield 85%. m.p.: 45–47°C. IR (CDCl$_3$) νNH: 3374 cm^{-1}, ν_sSO$_2$: 1153 cm^{-1}, ν_{as} SO$_2$: 1330 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ ppm: 0.98 (s, 15H, EtGe); 2.33 (s, 3H, CH$_3$); 4.44 (s, 1H, NH); 7.16 (d, 2H, CH(3)); 7.70 (d, 2H, CH(2), J_{2-3}: 8.4 Hz). ^{13}C NMR (CDCl$_3$) δ ppm: 7.9 (CH$_3$); 6.9 (CH$_2$); 21.4 (p-CH$_3$); 141.9 (C$_1$); 125.9 (C$_2$); 129.3 (C$_3$); 141.9 (C$_4$). Anal. C$_{13}$ H$_{23}$ Ge N SO$_2$ Found: C, 47.05; H, 6.91; N, 4.25. Calc.: C, 47.33.; H, 7.02; N, 4.24.MS (Ei): M$^+$: 331 (1%); M$^+$-Et: 302 (86%).

3.1.2. By transamination

p-toluene sulfonylamine (0.20 g; 18 10^{-3} mole) was added to triethylgermyl dimethylamine (0.24 g; 1.18 10^{-3} mole) in solution in 1.5 ml CDCl$_3$. The reaction followed by ^{1}H NMR, on the disappearance of the NMe$_2$ signal of the germylamine [13] led quantitatively to 1 with evolution of dimethylamine.

3.2. N-triphenylgermyl p-toluene sulfonamide 2

3.2.1. By dehydrohalogenation

In a way similar to the preparation of 1 p-toluene sulfonylamine (0.35 g; 2.1 10^{-3} mole), Et$_3$N (1.44 g; 14.2 10^{-3} mole), Ph$_3$GeCl (0.70 g; 2.1 10^{-3} mol) led to 0.80 g of 2: yield: 82%. m.p.: 176–178°C. IR (CDCl$_3$): νNH: 3369 cm^{-1}; ν_sSO$_2$: 1154 cm^{-1}; ν_{as} SO$_2$: 1335 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ ppm: 7.44 (m, 15H, PhGe); 2.33 (s, 3H, p-CH$_3$); 4.76 (s, 1H, NH); 7.01 (d, 2H, CH(3), J_{2-3}: 8.1 Hz); 7.44 (d, 2H, CH(2), J_{2-3}: 8, 1 Hz). ^{13}C NMR (CDCl$_3$) δ ppm: 21.5 (p-CH$_3$); 142.1 (C$_1$); 126.2 (C$_2$); 129.1 (C$_3$); 140.9 (C$_4$); 133.1 (C$_{1'}$); 134.9 (C$_{2'}$); 128.6 (C$_{3'}$); 130.4 (C$_{4'}$). Anal. C$_{25}$ H$_{23}$ Ge N SO$_2$ Found: C, 62.89; H, 4.86; N, 2.95. Calc.: C, 63.33.; H, 4.89; N, 2.96. MS (Ei): M$^+$: 475 (1%); M$^+$-Ph: 398 (100%).

3.3. N-dimesitylchlorogermyl p-toluene sulfonamide 3

3.3.1. Through lithium derivative of p-toluene sulfonamide

To a solution of p-toluene sulfonamide (0.40 g; 2.4 10^{-3} mole) in THF (6 ml) at −78°C, was added under stirring t-BuLi (1.7 M in pentane) (1.39 ml; 2.4 10^{-3} mole). After 15 min stirring at room temperature, the mixture was added dropwise to a solution of Mes$_2$GeCl$_2$ (0.90 g; 2.4 10^{-3} mole) in THF. After 2 h at room temperature, THF was replaced by benzene and LiCl centrifuged. The white amorphous residue obtained by evaporation of the solvent in vacuo was washed twice with pentane yielding 0.79 g of a white powder of 3. Yield 65%. m.p.: 127–129°C. IR (CDCl$_3$): νNH: 3368 cm^{-1}, ν_sSO$_2$: 1154 cm^{-1}, ν_{as}SO$_2$: 1339 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ ppm: 2.47 (s, 3H, p-CH$_3$); 5.11 (s, 1H, NH); 7.00 (d, 2H, CH(3)), 7.22 (d, 2H, CH(2), $^3J_{2-3}$ = 8.4 Hz); Mes: 2.33 (s, 12H, o-Me); 2.27 (s, 6H, p-Me); 6.79 (s, 4H, C$_6$H$_2$). ^{13}C NMR (CDCl$_3$) δ ppm: 21.49 (p-CH$_3$); 143.39 (C$_1$); 126.44 (C$_2$); 128.96 (C$_3$); 140.07 (C$_4$); Mes: 23.58 (o-Me); 21.10 (p-Me); 132.46 (C$_{1'}$), 142.88 (C$_{2'}$); 130.04 (C$_{3'}$); 140.83 (C$_{4'}$). Anal. C$_{25}$ H$_{30}$ Ge Cl N SO$_2$ Found: C, 57.75; H, 6.15; N, 2.51. Calc.: C, 58.13.; H, 5.85; N, 2.71. MS (Ei): M$^+$: 517 (8%); (DCi/CH$_4$): (M + 1)$^+$ = 518 (21%).

3.3.2. By dehydrochloration

To a mixture of p-toluene sulfonamide (0.4 g; 2.4 10^{-3} mole) and Mes$_2$GeCl$_2$ (0.90 g, 2.4 10^{-3} mole) in 10 ml THF, was added Et$_3$N (1.08 g; 10.7 10^{-3} mole). After 2 h stirring at room temperature, Et$_3$N · HCl was filtered. The residue (0.87 g) obtained by evaporation of the solvent in vacuo showed 3 (54%); 4 (24%); Mes$_2$GeCl$_2$ (22%) (^{1}H NMR analysis). This residue is washed four times with ether and dried in vacuo yield-

ing 0.15 g of pure **4**. The washing solvents were gathered in a Schlenk tube and evaporated in vacuo yielding 0.68 g of a mixture of Mes_2GeCl_2 (32%) and **3** (68%).

3.4. bis (p-toluene sulfonamide) dimesitylgermane 4

To a mixture of *p*-toluene sulfonamide (0.80 g; 4.7 10^{-3} mole) and Et_3N (2.59 g; 24.9 10^{-3} mole) in 12 ml THF was added a solution of Mes_2GeCl_2 (0.89 g; 4.7 10^{-3} mole) in 10 ml THF. After 3 h stirring at room temperature, half of the solvent is evaporated and Et_3N · HCl filtered out of the mixture at 0°C. Evaporation of the solvents at room temperature led to 1.4 g of a white residue identified to the diamine **4**. Yield: 92%. **4** is insoluble in benzene, ether, pentane and soluble in THF and chloroform. m.p.: 109–110°C. IR $(CDCl_3)$: νNH: 3353 cm^{-1}, $\nu_s SO_2$: 1153 cm^{-1}, $\nu_{as} SO_2$: 1335 cm^{-1}. ^{1}H NMR $(CDCl_3)$ δ ppm: 2.22 (s, 6H, *p*-CH_3); 5.37 (s, 2H, NH); 6.90 (d, 4H, CH(3), $^3J_{2-3}$: 8.4 Hz); 7.11 (d, 4H, CH(2), $^3J_{2-3}$: 8.4 Hz); Mes: 2.13 (s, 12H, *o*-Me); 2.30 (s, 6H, *p*-Me); 6.62 (s, 4H, C_6H_2). ^{13}C NMR $(CDCl_3)$ δ ppm: 21.5 (*p*-CH_3); 142.1 (C_1); 126.2 (C_2); 128.8 (C_3); 139.8 (C_4); Mes: 23.4 (*o*-Me); 21.1 (*p*-Me); 129.5 ($C_{1'}$); 143.3 ($C_{2'}$); 129.8 ($C_{3'}$); 140.06 ($C_{4'}$). Anal. $C_{32} H_{38}$ Ge $N_2 S_2 O_4$ Found: C, 58.84; H, 6.61; N, 4.32. Calc.: C, 59.02; H, 5.88; N, 4.30. MS (DCi/CH_4): $(M + 1)^+$: 653 (8%).

3.5. Dimesitylgermylidene p-toluene sulfonamide 5

3.5.1. From 3

To **3** (4.8 10^{-3} mole) prepared in situ in 14 ml THF, was added *t*-BuLi (1.7 M in pentane) (2.82 ml; 4.8 10^{-3} mole). The mixture is allowed to warm slowly to room temperature (1 h from −40°C to +2°C). Then, THF was replaced by pentane. After further stirring for 18 h at room temperature, LiCl is centrifuged. The solution by evaporation of pentane in vacuo, led to a white amorphous powder of **5**. Yield: 82%. m.p.: 73–75°C. IR $(CDCl_3)$: $\nu_s SO_2$: 1116 cm^{-1}, $\nu_{as} SO_2$: 1378 cm^{-1}. ^{1}H NMR $(CDCl_3)$ δ ppm = 2.23 (s, 3H, *p*-CH_3); 6.80 (d, 2H, CH(3), $^3J_{2-3}$: 7.4 Hz); 7.28 (d, 2H, CH(2), $^3J_{2-3}$: 7.4 Hz); Mes: 2.18 (s, 12H, *o*-Me); 2.23 (s, 6H, *p*-Me); 6.56 (s, 4H, C_6H_2). ^{13}C NMR $(CDCl_3)$ δ ppm: 21.35 (*p*-CH_3); 142.85 (C_1); 126.36 (C_2); 127.96 (C_3); 137.78 (C_4); Mes: 23.70 (*o*-Me); 21.06 (*p*-Me); 135.18 ($C_{1'}$); 142.61 ($C_{2'}$); 129.25 ($C_{3'}$); 136.67 ($C_{4'}$). Anal. $C_{25} H_{29}$ Ge N S O_2 Found: C, 61.94; H, 6.21; N, 2.70. Calc.: C, 62.53.; H, 6.08; N, 2.91. MS (DCi/CH_4): $(M + 1)^+$: 482 (30%).

3.5.2. from Mes₂GeBr₂

The *p*-toluene sulfonamide lithium (0.9 10^{-3} mole) in 3 ml THF is added to Mes_2GeBr_2 (0.41 g; 0.9 10^{-3} mole) in 3 ml THF. After 1 h stirring at room tempera-

ture, THF is replaced by Et_2O, the flask is cooled to −78°C and *t*-BuLi (1.7 M in pentane) (0.52 ml, 0.9 10^{-3} mole) added dropwise under stirring. The reactional mixture is slowly warmed to room temperature (4 h from −78°C to +4°C), then ether is replaced by C_6H_6 and LiBr removed by centrifugation. Evaporation of the solvent in vacuo, led to 0.69 g of **5**. Yield 80%.

3.6. Addition of t-BuOH on 5

5 (0.20 g; 0.42 10^{-3} mole) and *t*-BuOH (0.03 g; 0.42 10^{-3} mole) in 1 ml THF are heated in a sealed tube for 18 h at 100°C. The solvent was evaporated; the residue washed with pentane led to 0.21 g of **6** as an amorphous white powder. Yield: 91%. m.p.: 47–49°C. IR $(CDCl_3)$: νNH: 3399 cm^{-1}; $\nu_s SO_2$: 1152 cm^{-1}, ν_{as}: 1336 cm^{-1}. ^{1}H NMR $(CDCl_3)$ δ ppm: 2.31 (s, 3H, *p*-CH_3); 4.79 (s, 1H, NH); 6.92 (d, 2H, CH(3), $^3J_{2-3}$: 8.5 Hz); 7.13 (d, 2H, CH(2), $^3J_{2-3}$: 8.5 Hz); 1.21 (s, 9H, O-*t*-Bu); Mes: 2.26 (s, 12H, *o*-Me); 2.24 (s, 6H, *p*-Me); 6.70 (s, 4H, C_6H_2). ^{13}C NMR $(CDCl_3)$ δ ppm: 21.47 (*p*-CH_3); 143.36 (C_1); 128.77 (C_2); 126.25 (C_3); 139.79 (C_4); *t*-Bu: 32.30 (CH_3); 68.05 (C_{IV}); Mes: 23.47 (*o*-Me); 21.09 (*p*-Me); 132.75 ($C_{1'}$); 143.01 ($C_{2'}$); 129.68 ($C_{3'}$); 139.80 ($C_{4'}$).Anal. $C_{29} H_{39}$ Ge N S O_3 Found: C, 61.73; H, 7.17; N, 2.67. Calc.: C, 62.85.; H, 7.09; N, 2.53. MS (Ei): M^+-Mes: 435 (15%); M^+-Mes–*t*-Bu: 380 (30%).

3.7. Addition of H₂O to 5

To **5** (0.15 g; 0.3 10^{-3} mole) was added 0.3 10^{-3} mole of H_2O (0.06 ml of a 5.4 10^{-3} mole/l solution in THF) and the mixture heated at 100°C for 1 h in a sealed tube. Evaporation of the solvent in vacuo led to a white residue made up of a small amount of $Mes_2Ge(OH)_2$ (5%) and **7** (95%) (^{1}H NMR analysis). IR $(CDCl_3)$: νNH: 3351 cm^{-1}, νOH: 3623 cm^{-1}, $\nu_s SO_2$: 1152 cm^{-1}, $\nu_{as} SO_2$: 1332 cm^{-1}. ^{1}H NMR $(CDCl_3)$ δ ppm: 2.13 (s, 3H, *p*-CH_3); 5.43 (s, 1H, NH); 2.58 (s, 1H, OH); 7.12 (d, 2H, CH(3), $^3J_{2-3}$: 7.8 Hz); 7.87 (d, 2H, CH(2), $^3J_{2-3}$: 7.8 Hz); Mes: 2.31 (s, 12H, *o*-Me); 2.19 (s, 6H, *p*-Me); 6.66 (s, 4H, C_6H_2). ^{13}C NMR $(CDCl_3)$ δ ppm: 21.46 (*p*-CH_3); 143.37 (C_1); 126.20 (C_2); 128.62 (C_3); 138.25 (C_4); Mes: 21.06 (*o*-Me); 22.82 (*p*-Me); 134.41 ($C_{1'}$); 142.92 ($C_{2'}$); 129.03 ($C_{3'}$); 139.40 ($C_{4'}$). MS (Ei): M^+: 499 (2%); M^+-OH: 482 (30%).

3.8. Addition of chloroform on 5

A mixture of **5** (0.10 g; 0.2 10^{-3} mole) and dry $CHCl_3$ (0.02 g; 0.2 10^{-3} mole) in THF heated for 1 h at 100°C in a sealed tube gave after evaporation of the solvent 0.09 g of **3**. Yield 87%.

3.9. Reaction of 3,5-di-t-butyl ortho-catechol on 5

To **3** (0.04 g; 0.094 10^{-3} mole) placed in a NMR tube in 0.5 ml $CDCl_3$, was added a solution of 3,5-di-t-butyl $ortho$-catechol (0.02 g; 0.094 10^{-3} mole) in 0.5 ml $CDCl_3$. ^{1}H NMR analysis just after the addition, showed quantitative formation of dimesitylgermadioxolane identified to an authentic sample [18].

3.10. Addition of benzaldehyde on 5

A mixture of **5** (0.18 g, 0.37 10^{-3} mole) and PhCHO (0.04 g; 0.37 10^{-3} mole) in 1 ml THF was heated at 100°C for 3 h in a sealed tube. ^{1}H NMR and MS analysis showed the quantitative formation of $(Mes_2GeO)_2$ and $PhCH=N-SO_2-C_6H_4-CH_3$ identified to a pure sample prepared as follows.

3.11. Benzylidene p-toluene sulfonamide

p-toluene sulfonamide (2.00 g; 11.7 10^{-3} mole) in THF solution and benzaldehyde (1.24 g; 11.7 10^{-3} mole) in the presence of catalytic amounts of $AlCl_3$ were heated in a sealed tube for 4 h at 100°C. The solvent was evaporated and the residue washed with pentane, leading to 2.85 g of a light brown amorphous powder of $PhCH=N-SO_2-C_6H_4-CH_3$. Recrystallized in C_6H_6/hexane. m.p.: 107–109°C, conform to literature [19]. IR ($CDCl_3$): ν_sSO_2: 1162 cm^{-1}, $\nu_{as}SO_2$: 1324 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 2.38 (s, 3 H, p-CH$_3$); 7.29 (d, 2H, CH(3), $^3J_{2-3}$ 8.4 Hz); 7.88 (d, 2H, CH (2), $^3J_{2-3}$: 8.4 Hz); 7.50–7.81 (m, 5 H, C_6H_5); 8.98 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ ppm: 21.68 (p-CH$_3$); 144.68 (C$_1$); 128.12 (C$_2$) 129.19 (C$_3$); 135.5 (C$_4$); PhCH: 132.39 (C$_{1'}$); 131.34 (C$_{2'}$); 129.86 (C$_{3'}$); 135.00 (C$_{4'}$); 170.22 (=CH). MS (Ei): M$^+$ 259 (21%).

3.12. Reaction of 3,5-di-t-butyl ortho-quinone with 5

To a solution of **5** (0.04 g; 0.094 10^{-3} mole) in 1 ml C_6D_6 was added 3,5-di-t-butyl $ortho$-quinone (0.02 g; 0.094 10^{-3} mole). The mixture was heated for 13 h at 90°C in a sealed tube. ^{1}H NMR analysis showed the quantitative formation of dimesitylgermadioxolane and

the formation of isobutene (hept, CH_2). A GC/MS analysis allowed the characterization of N,N'-bis(p-toluene sulfonyl) hydrazine (M$^+$ = 340) besides dimesitylgermadioxolane (M$^+$ 532). The same mixture in toluene warmed up to 45°C, then irradiated in the cavity of the RPE spectrometer, led to a doublet characteristic of a semi-quinonic species (g = 2.0047, a^H = 2.75 G).

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