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Alkoxymesitylchlorogermanes and aryloxymesitylchlorogermanes

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Abstract

New alkoxymesitylchlorogermanes and hindered aryloxymesitylchlorogermanes were synthesized either by intermolecular dehydrohalogenation between mesityltrichlorogermane and the corresponding alcohols or phenols, or by transmetallation. Both methods are limited by the steric hindrance of the organic moieties. Transmetallation from lithium fluorenol yields the corresponding aryloxymesityldichlorogermane in poor yields; by contrast the compound is easily formed by dehydrohalogenation in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. From dimesityldichlorogermane, regardless of the method used, mesitylchlorofluorenoxygermane is always formed in a mixture with the bis(fluorenoxy)dimesitylgermane; from the dilithium derivative of fluorenol the five-membered 2,2-dimesityl-4,5-difluorenyl-1,3-germoxolane is formed which is explained by a further addition on fluorenone formed as by-product of the reaction, along with hexamesitylcyclotrigermane.

Keywords: Aryloxy compounds; Alkoxy compounds; Germane compounds; Mesityl compounds

1. Introduction

With the aim of preparing new starting materials for the preparation of germylpolymers or stable unsaturated germyl species, we have been interested in the synthesis of new germyldichlorides and have tried to prepare compounds of the type $MesGe(OR)Cl_2$ in which R is an alkoxy or a very bulky aryloxy functional group. We also prepared the corresponding monochlorides $Mes_2Ge(OR)Cl$ and we now present our results.

2. Experimental

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

NMR spectra were recorded on Brücker AC 80 (^1H) and AC 200 (^{13}C) spectrometers, IR spectra on a Perkin-Elmer 1600 FT-IR 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). Melting points were measured on a Leitz microscope. Elemental analyses were performed by the microanalysis center of the Ecole Nationale Supérieure de Chimie de Toulouse.

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2.1. Methoxymesityldichlorogermane 1

2.1.1. Preparation by dehydrohalogenation

To $MesGeCl_3$ (0.60 g, 2.00 mmol) dissolved in benzene (4 ml) was added at room temperature under stirring a solution of methanol (0.064 g, 2.00 mmol) and triethyl amine (0.200 g, 2 mmol) in benzene (4 ml). After 1.5 h stirring at room temperature, triethylamine chlorohydrate was removed by centrifugation. The remaining solution concentrated under vacuum led to 0.44 g of a white powder identified as pure $MesGe(OMe)Cl_2$ **1**. Yield 76%. M.p. 44–46°C. ^1H NMR ($CDCl_3$) δ: 2.28 (s, 3H, *p*-CH_3); 2.59 (s, 6H, *o*-CH_3); 6.90 (s, 2H, C_6H_2); 3.80 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$) δ: 21.20 (*p*-CH_3); 23.52 (*o*-CH_3); 143.30 (C2); 129.95 (C3); 142.74 (C4); 52.70 (OMe). MS (EI) *m/z*: 294 ((M^+), 84%); 262 ((M–MeOH), 76%). *Anal.* Found: C, 40.42; H, 4.67; O, 5.38. Calc. for ($C_{10}H_{14}GeCl_2O$): C, 40.89; H, 4.80; O, 5.44%.

2.1.2. Preparation by transmetallation

A solution of lithium methanolate, prepared by the addition of 1.6 M *n*-BuLi in hexane (0.41 ml, 0.67 mmol) to methanol (0.021 g, 0.67 mmol) in benzene (4 ml) at room temperature and under stirring, was added dropwise at room temperature to $MesGeCl_3$ (0.201 g, 0.670 mmol) dissolved in benzene (3 ml). After 2 h stirring at room temperature, LiCl was centrifugated and the solvent evaporated under vacuum lead-

ing to 0.14 g of a white powder analyzed by ^{1}H NMR: MesGe(OMe)Cl_2 **1** 48%; MesGe(Cl)$(OMe)_2$ 19%; MesGe$(OMe)_3$ 3%; unreacted $MesGeCl_3$ 30%.

2.2. *o-t-butylphenoxymesityldichlorogermane* 2

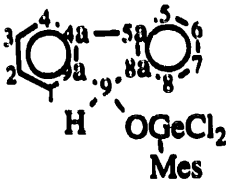
2.2.1. *Preparation by dehydrohalogenation*

Following a method similar to that used to obtain **1**, $MesGeCl_3$ (0.20 g, 0.67 mmol), 2-t-butylphenol (0.10 g, 0.67 mmol), and Et_3N (0.067 g, 0.67 mmol) led to 0.192 g of a sticky white compound identified as **2**. Yield 70%. ^{1}H NMR ($CDCl_3$) δ: 2.33 (s, 3H, *p*-CH_3); 2.66 (s, 6H, *o*-CH_3); 1.41 (s, 9H, tBu); 7.40–6.77 (m, 6H, C_6H_2 and C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 21.29 (*p*-CH_3); 23.49 (*o*-CH_3); 140.80 (C1); 142.82 (C2); 129.54 (C3); 143.07 (C4); 34.75 (C *tBu*); 30.08 (CH_3 *tBu*). Phenoxy: 154.29 (C1′); 137.53 (C2′); 126.91 (C3′); 122.14 (C4′); 127.41 (C5′); 119.85 (C6′). MS (EI) *m/z*: 412 ((*M*$^+$), 8%); 397 ((M–Me), 8%); 361 ((M–Me–HCl), 4%).

2.2.2. *Preparation by transmetallation*

Following a method similar to that used for the preparation of **1** by transmetallation, 2-t-butylphenol (0.10 g, 0.67 mmol) in THF (4 ml), *n*-BuLi in hexane (0.67 mmol), and $MesGeCl_3$ (0.20 g, 0.67 mmol) in THF (3 ml), after centrifugation of LiCl in benzene solution, led to 0.23 g of **2**. Yield 83%.

2.3. *Fluorenoxymesityldichlorogermane* 3



2.3.1. *Preparation by dehydrohalogenation*

To a mixture of fluorenol (0.18 g, 0.99 mmol) and mesityltrichlorogermane (0.29 g, 0.99 mmol) in THF (4 ml), at 0°C under stirring, was added diazabicyclo-undecene (0.15 g, 0.99 mmol). The mixture was then allowed to warm to room temperature and after 1.5 h stirring, DBU,HCl was eliminated by centrifugation. Evaporation of the solvents led to a pale yellow sticky compound; 0.31 g of **3**. Yield 72%. ^{1}H NMR ($CDCl_3$) δ: mesityl 2.28 (s, 3H, *p*-CH_3), 2.61 (s, 6H, *o*-CH_3), 6.91 (s, 2H, C_6H_2); fluorenyl 6.28 (s, 1H, CH(9)), 7.74–7.27 (m, 8H, $C_{13}H_8$). ^{13}C NMR ($CDCl_3$) δ: mesityl 21.24 (*p*-CH_3), 24.06 (*o*-CH_3), 143.43 (C2), 130.08 (C3), 142.97 (C4); fluorenyl 125.91 (C1+8), 127.77 (C2+7), 129.04 (C3+6), 119.97 (C4+5), 145.04 (C4a+5a), 140.33 (C8a+9a), 77.29 (C9). MS (EI) *m/z*: 444 ((*M*$^+$), 20%); 408 ((M–HCl), 2%).

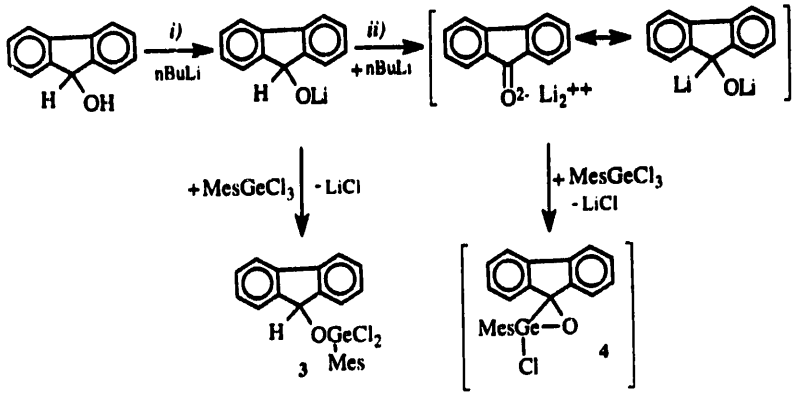
2.3.2. *Preparation by transmetallation*

Lithium fluorenolate was prepared at 0°C by addition of 1.6 M *n*-BuLi in hexane (1.55 ml, 2.47 mmol) to fluorenol (0.45 g, 2.47 mmol) dissolved in 7 ml of benzene and kept in the dark. After 3 h further stirring at 0°C, the suspension of lithium fluorenolate was added at 20°C to $MesGeCl_3$ (0.73 g, 2.47 mmol) in benzene (4 ml) and kept in the dark. After 2 h stirring at room temperature, LiCl was filtered. The solvents evaporated under vacuum led to a sticky residue whose ^{1}H NMR analysis showed **3** as the main compound (61%) and fluorenyl by-products (39%). MS (EI) *m/z*: 444 ((*M*$^+$), 35%); 408 ((M–HCl), 18%); 429 (M–Me), 18%); 289 ((M–Mes–HCl), 32%).

2.4. *Characterization of* 4

In mass spectrometry of **3** prepared by transmetallation (fluorenol/*n*-BuLi in a 1:1 ratio), *M*$^+$ = 408 (18%) is a fragment of **3**.

From a similar experiment, but with fluorenol/*n*-BuLi in a 1:2 ratio (Scheme 1, (ii)), an attempt at recrystallization in ether led to a sticky powder whose mass spectrometry analysis showed only one germylated compound at *M*$^+$ = 408 (25%) characteristic of **4**, and fluorenone *M*$^+$ = 180 (100%).



Scheme 1.

2.5. Attempts at preparation of the more sterically hindered 2,6-di-t-butyl,4-methylphenoxymesityldichlorogermanes and 2,4,6-trinitrophenoxymesityldichlorogermanes

2.5.1. Preparation by dehydrohalogenation

Similar to the preparation of **3**, $MesGeCl_3$ (0.21 g, 0.67 mmol), 2,6-di-t-butyl-4-methylphenol (0.15 g, 0.67 mmol) in ether (4 ml) and DBU (0.10 g, 0.67 mmol) do not give any reaction.

2.5.2. Preparation by transmetallation

Similar to the preparation of **1**, 2,6-di-t-butyl-4-methylphenol (0.15 g, 0.67 mmol) reacted with t-BuLi (0.67 mmol) added to $MesGeCl_3$ (0.20 g, 0.67 mmol) does not give any reaction.

Sodium picrate prepared from 2,4,6-trinitrophenol (0.25 g, 1.09 mmol), in THF (4 ml) and sodium (0.025 g, 1.09 mmol) does not react with $MesGeCl_3$ (0.33 g, 1.09 mmol) in THF (3 ml).

2.6. Preparation of difluorenoxydimesitylgermane 6

2.6.1. Preparation by dehydrohalogenation

Mes_2GeCl_2 (0.25 g, 0.66 mmol), fluorenol (0.24 g, 1.32 mmol) in THF (3 ml) and DBU (0.20 g, 1.32 mmol) were heated for 24 h at 100°C in a Carius tube. After decanting DBU,HCl and evaporation of the solvents, the pale yellow residue treated in ether led to 0.23 g of a white powder of **6** separated by filtration. Yield 51%. M.p. 204–206°C. ^{1}H NMR ($CDCl_3$) (80 MHz) δ: mesityl 2.25 (s, 6H, *p*-CH_3), 2.61 (s, 12H, *o*-CH_3), 6.87 (s, 4H, C_6H_2); fluorenyl 5.68 (s, 2H, CH(9)), 6.87–7.83 (m, 16H, $C_{13}H_8$). ^{1}H NMR ($CDCl_3$) (250 MHz) δ: mesityl 2.26 (s, 6H, *p*-CH_3), 2.61 (s, 12H, *o*-CH_3), 6.87 (s, 4H, C_6H_2); fluorenyl 5.67 (s, 2H, CH(9)), 7.50 (d, 4H, H1+H8, $^3J_{HH}$ 7.5 Hz), 6.99 (t, 4H, H2+H7, $^3J_{HH}$ 7.5 Hz), 7.25 (t, 4H, H3+H6, $^3J_{HH}$ 7.5 Hz), 7.54 (d, 4H, H4+H5, $^3J_{HH}$ 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ: mesityl 21.13 (*p*-CH_3), 24.14 (*o*-CH_3), 130.10 (C1), 143.77 (C2), 129.63 (C3), 140.36 (C4); fluorenyl 126.20 (C1+C8), 121.07 (C2+C7), 128.02 (C3+C6), 119.37 (C4+C5), 146.70 (C4a+5a), 139.89 (C8a+9a), 77.62 (C9) (attributed by selective heteronuclear decoupling). MS (EI, 30 eV) *m/z*: 674 ((*M*$^+$), 2%); 554 ((M–MesH), 2%); 492 ((M–$C_{13}H_9O$), 5%). *Anal.* Found: C, 77.99; H, 5.82. Calc. for ($C_{44}H_{40}GeO_2$): C, 78.48; H, 5.99%. ^{1}H NMR analysis of the remaining solution shows the presence of **5**.

2.7. Characterization of fluorenoxydimesitylchlorogermane 5 in the mixture of 5 and 6

2.7.1. Preparation by dehydrohalogenation

Following the same method as for the other dehydrohalogenation, from Mes_2GeCl_2 (0.25 g, 0.66 mmol), fluorenol (0.12 g, 0.66 mmol) in THF (7 ml) and DBU (0.10 g, 0.66 mmol), after 1.5 h stirring, chlorohydrate centrifugation led to 0.25 g of a white residue whose NMR analysis showed **5** (46%) and **6** (14%) with unreacted Mes_2GeCl_2 (40%).

2.7.2. Preparation by transmetallation

Following a method similar to that used for the preparation of **3**, lithium fluorenolate (0.66 mmol) in benzene/hexane was added to Mes_2GeCl_2 (0.26 g, 0.66 mmol) in THF (4 ml). After 2 h stirring and LiCl centrifugation, the reaction led to 0.24 g of a white residue whose analysis showed **5** (28%), **6** (17%) and Mes_2GeCl_2 (55%).

Spectroscopic characteristics of **5**. ^{1}H NMR ($CDCl_3$) δ: mesityl 2.29 (s, 6H, *p*-CH_3), 2.47 (s, 12H, *o*-CH_3), 6.87 (s, 4H, C_6H_2); fluorenyl 5.97 (s, 1H, CH(9)), 6.86–7.65 (m, 8H, $C_{13}H_8$). ^{13}C NMR ($CDCl_3$) δ: mesityl 21.16 (*p*-CH_3), 23.75 (*o*-CH_3), 133.35 (C1), 142.85 (C2), 129.96 (C3), 140.77 (C4); fluorenyl 125.74 (C1+C8), 127.44 (C2+C7), 128.30 (C3+C6), 119.60 (C4+C5), 146.28 (C4a+5a), 140.04 (C8a+9a), 77.16 (C9). MS (EI) *m/z*: 528 ((*M*$^+$), 2%); 493 ((M–Cl), 2%); 408 ((M–MesH), 25%).

2.8. Preparation of 2,2-dimesityl-4,5-difluorenyl-2,1,3-germadioxolane 7

2.8.1. Reaction of Mes_2GeCl_2 with the fluorenone dianion

A solution of 1.38 mmol of the dilithiated compound of the fluorenone [3] in 10 ml of Et_2O was added to Mes_2GeCl_2 (0.52 g, 1.37 mmol) in 4 ml of benzene. After 2 h at reflux, the solvents were evaporated under vacuum and 5 ml of THF was added. After 3 h at 70°C, the mixture was concentrated and the residue extracted with CH_2Cl_2. After filtration, the precipitate obtained was recrystallized in a mixture of CH_2Cl_2/petroleum ether (3 days at −30°C) giving 0.30 g of white crystals identified as **7**. Yield 32%. M.p. 350°C. These crystals were nearly insoluble in organic and chlorinated solvents. The ^{1}H NMR spectrum can only be obtained in hot C_6D_6. ^{1}H NMR δ: mesityl 2.10 (s, 6 H, *p*-CH_3), 2.71 (s, 12H, *o*-CH_3), 6.75 (s, 4H, C_6H_2); fluorenyl 6.80–7.10 (m, 12H, $C_{13}H_8$), 7.57–7.67 (m, 4H, $C_{13}H_8$). MS (CI, CH_4) *m/z*: 701 ((*M*+29), 1%), 673 ((*M*+1), 11%), 492 ((M–$C_{13}H_8O$), 8%). *Anal.* Found: C, 78.67; H, 5.76. Calc. for ($C_{44}H_{38}GeO_2$): C, 78.72; H, 5.70%.

The ^{1}H NMR analysis of the filtrate shows the presence of $(MesGe)_3$ (19%) [7] which was partially isolated in a low yield after several recrystallizations from CH_2Cl_2.

2.8.2. Reaction of Mes_2GeCl_2 with 9,9′-bisfluorenol

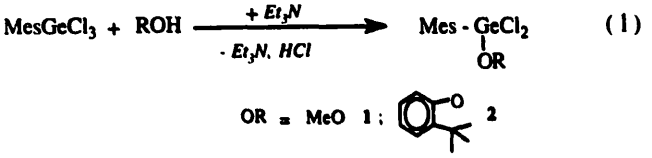
A solution of Mes_2GeCl_2 (0.39 g, 1 mmol), 9,9′-bisfluorenol (0.36 g, 1 mmol, synthesized as described in [4]) and DBU (0.31 g, 2 mmol) in 1.5 ml of benzene was heated in a Carius tube at 100°C for 3 days. After cooling at 20°C, white crystals appeared and were isolated by decanting. They were washed with benzene and $CHCl_3$ to eliminate the chlorohydrate DBU,HCl. After drying in vacuo, white crystals were isolated and identified as **7**: 0.11 g (16%).

3. Results and discussion

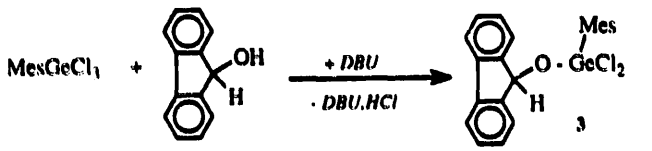
To obtain alcoxymesityldichlorogermanes and aryloxymesityldichlorogermanes, we used classical routes to the formation of oxygen–germanium bonds [1]. We mainly tried two methods: (i) intermolecular dehydrohalogenation between germylchloride and hydroxy compounds, (ii) the transmetallation reaction from a lithium-alkoxy or aryloxy compound. Both methods were optimized on the preparation of mesitylmethoxydichlorogermane.

Intermolecular dehydrohalogenation between methanol and mesityltrichlorogermane led to methoxymesityldichlorogermane **1** with high selectivity and in very good yields (Eq. (1)).

The same reaction starting from the more stencally hindered *o*-t-butylphenol led to the corresponding aryloxymesityldichlorogermane **2** (Eq. (1)).

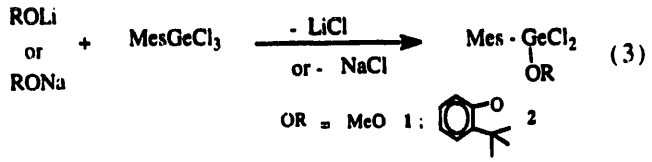


With increasing steric hindrance, a more nucleophilic tertiary amine is needed and dehydrohalogenation between mesityltrichlorogermane and fluorenol only occurs in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (Eq. (2)). However, the reaction (Eq. (2)) is limited by steric effects. With the more sterically hindered di-*o*-t-butyl-*p*-cresol, no reaction occurs.



The same result is observed with the transmetallation reaction (Eq. (3)).

Lithium (or sodium) methanolate reacts readily with mesityltrichlorogermane, although the reaction is slightly less selective than dehydrohalogenation; **1** is obtained in good yields but with small amounts of the other mesitylmethoxy compounds. **2** is readily obtained in very good yields and high purity from *o*-t-butylphenoxy-lithium (Eq. (3)).

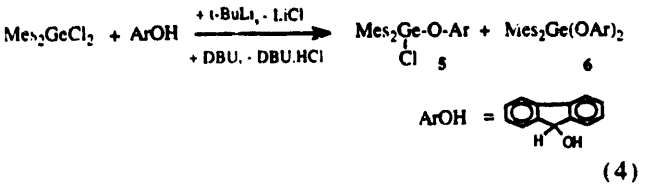


By contrast, the reaction from the sodium derivative of 2,3,5-trinitrophenol does not lead to the aryloxygermyl compound. There are two possible explanations for this result: (i) the inductive attractor effects of the NO_2 groups render the phenoxy oxygen a poor nucleophile, thus not favoring the transmetallation reaction; (ii) the steric hindrance of the same NO_2 groups in ortho position prevents the approach of mesityltrichlorogermane.

Steric hindrance is certainly a determinant factor since di-*o*-t-butyl-*p*-cresol, which presents two bulky groups in the ortho positions, does not lead to the desired compound, neither by dehydrohalogenation (Eq. (2)), nor transmetallation (Eq. (3)).

With fluorenol, transmetallation led partially to **3**, but the well known rearrangement of the lithium derivative of fluorenol [2,3] (Scheme 1) led to secondary reactions, from which we identified compound **4** in mass spectroscopy (Scheme 1). **4** is the only germylated compound detected by mass spectroscopy when 2 equiv. of butyllithium are used in the reaction (Scheme 1, (ii)). Therefore, the transmetallation reaction is not a good route to fluorenoxymesityldichlorogermane which should be prepared by dehydrohalogenation.

If dimesityldichlorogermane is used instead of mesityltrichlorogermane (Eq. (4)), whether the reaction is performed by dehydrohalogenation or transmetallation, the corresponding aryloxydimesitylchlorogermane **5** is formed always in a mixture with the bis-aryloxylated derivative **6**.

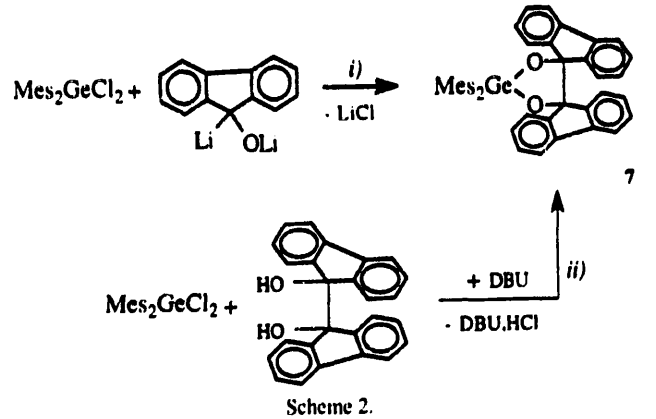


Compound **6** can be obtained as a pure sample from dehydrohalogenation between 2 equiv. of fluorenol and dimesityldichlorogermane in the presence of DBU.

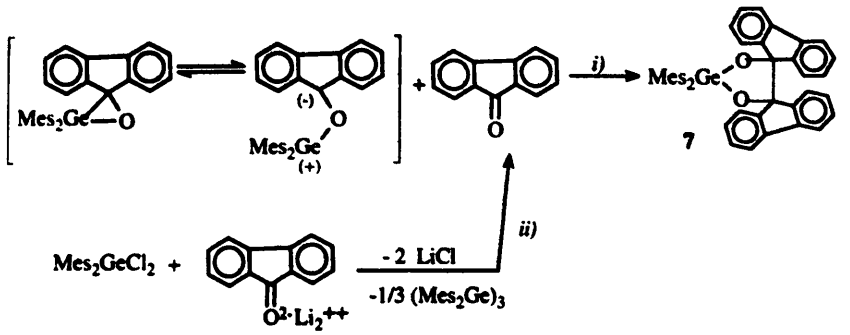
With the fluorenone dianion, prepared with 2 equiv. of *n*-BuLi [3], the transmetallation reaction gave mainly the 2:1 cycloadduct **7** (Scheme 2, (i)).

The same compound **7** was obtained from dehydrohalogenation reaction between the α-diol [4] and dimesityldichlorogermane in the presence of DBU at 100°C for 3 days (Scheme 2, (ii)).

The formation of **7** (Scheme 2, (i)) can be explained by the transient formation of an unstable three-membered ring similar to **4**, which would react in its zwitterionic form on



Scheme 2.



Scheme 3.

fluorenone according to what was observed within the silicon series [5] (Scheme 3, (i)). The formation of fluorenone can be explained by the elimination of lithium chloride between dimesityldichloride and fluorenone dilithium (Scheme 3, (ii)) as in the reaction between metal naphthalenide and dihalogenogermanes [1,6]. This hypothesis is confirmed by the formation of hexamesityltrigermane characterized in the reaction (Scheme 3, (ii)). The fluorenoxy groups stabilize the formation of the five-membered rings like **7**, as previously observed in the silicon series [4].

From this study, we can conclude that the best way to obtain alkoxymesitylgermane or aryloxymesitylgermane is the dehydrohalogenation reaction in the presence of a powerful nucleophile hydrochloride abstractor such as DBU. The transmetallation reaction in most cases is less selective and induces secondary reactions which can become predominant in the case of fluorenol derivatives.

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