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# Photo-induced single electron transfer addition of triphenylgermane to conjugated carbonyl compounds: competitive radical addition

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**Conjugated ketones are poorly reactive towards triphenylgermane under radical conditions, but in their excited state they can undergo single electron transfer (SET) reactions. The SET reaction, through the formation of a germanium-centred radical, initiates a competitive and divergent radical addition. In the case of carvone, the SET adduct was isolated pure from the reaction of triphenylgermyllithium with the same ketone. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** radical reactions; SET reactions; carvone; germane

## INTRODUCTION

We showed recently[1] that 2,6-diethyl-4,8-dimethyl-1,5-dioxo-*s*-hydrindacene, on account of its fundamental lowest unoccupied molecular orbital (LUMO) energy level, was unable to give single electron transfer (SET) additions with triphenylgermane. On the contrary, the same diketone in its excited state ($h\nu$), and consistent with a lowering of its LUMO level, was able to initiate an SET reaction with triphenylgermane and subsequently a photo-induced competitive radical hydrogermylation (Scheme 1(b)).[1]

The work presented here deals with the competition between radical chain and SET addition of triphenylgermane on conjugated ketones, carvone being used as an example, in their fundamental and excited electronic states.

## RESULTS AND DISCUSSION

Compared with limonene, carveol and hydrocarvone, carvone is less reactive towards hydrometallation by metal 14 hydrides.[2–9] Under radical initiation sequence (RIS)[10] from 20 to 150 °C, we observed regiospecific 1, 4 addition of triphenylgermane to the conjugated endocyclic system of carvone (Scheme 2).

Under these experimental conditions, the SET addition, observed mainly in the case of hydrogermylation of quinones or other conjugated compounds,[11] was not detected (see below). This unexpected quasi-absence of a thermally induced SET reaction can be analyzed by theoretical calculations of the highest occupied molecular orbital (HOMO)–LUMO carbonyl gap offered to the germanium derivative by carvone or quinone (Tables 1 and 2). These results lead to the following comments:

- Among the reagents (Table 1), carvone **1** presents a higher LUMO to the electron coming from $Ph_3GeH$ and therefore, a less favorable transition.
- In the excited state **1*** of the carvone (s* excited singlet state), the LUMO is lower than that of the starting quinone in the fundamental state (Table 1). Thus, the SET reaction should be favored under UV irradiation for transitions $n\pi^*$ or $\pi\pi^*$ of ketone **1**.

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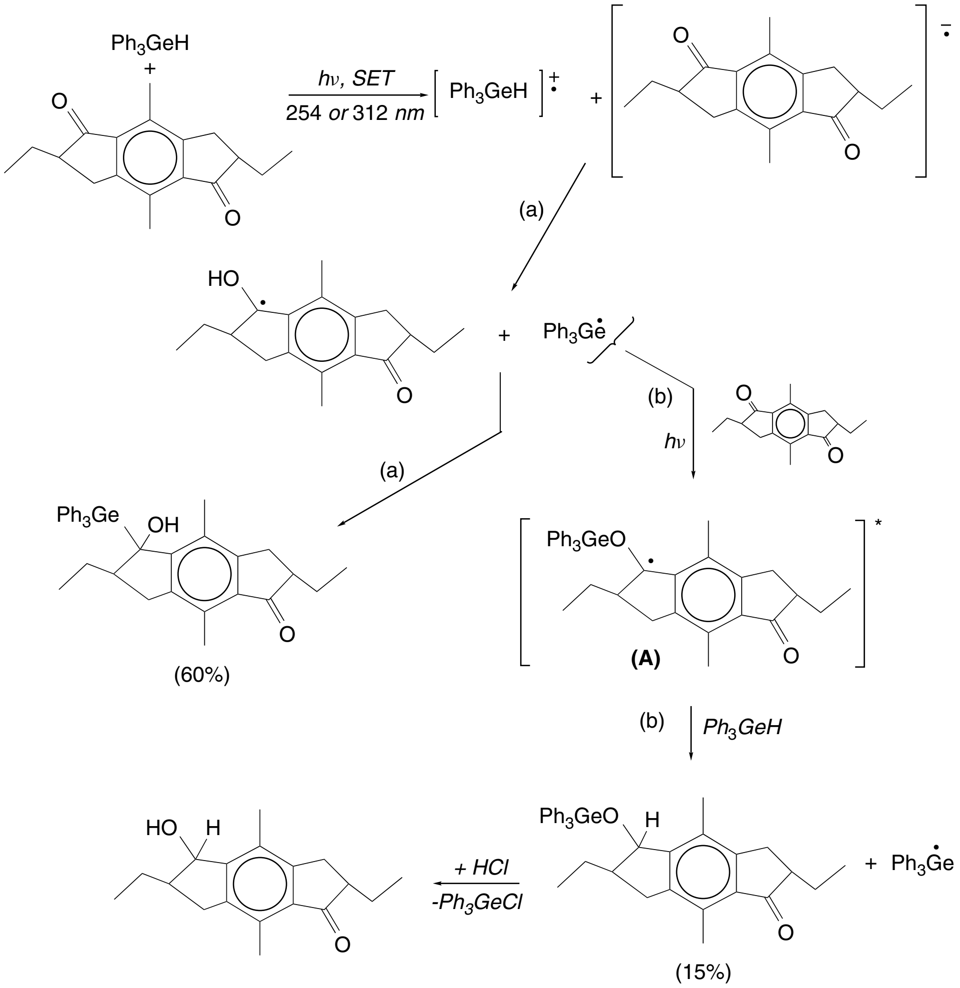
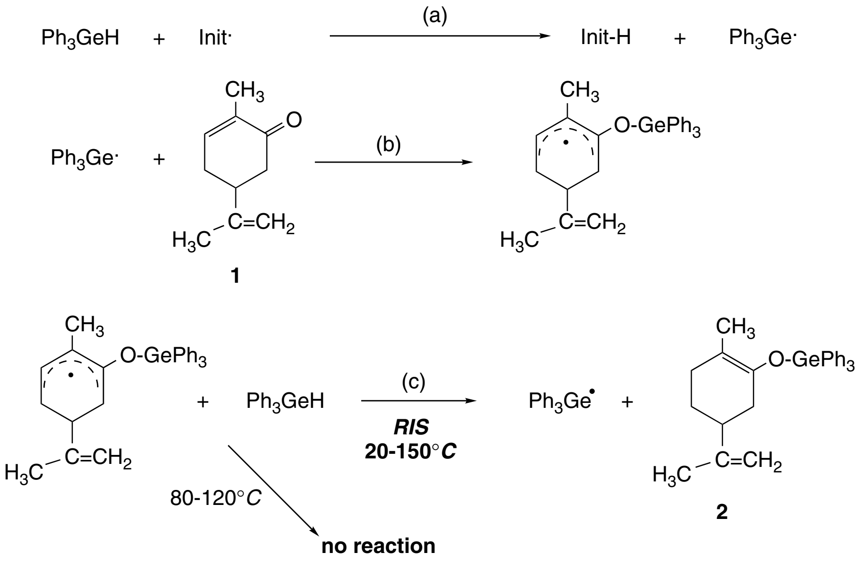


**Scheme 1.**



**Scheme 2.**

**Table 1.** Relative-scale HOMO–LUMO for carvone **1, 1*** (excited state of the carvone), quinone **3** and $Ph_3GeH$ (computational study PM3)

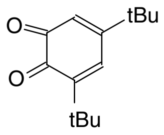
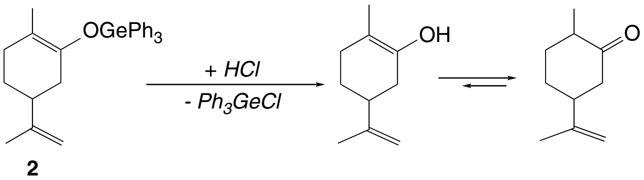
| | $Ph_3GeH$ | Carvone **1** | **1*** |  <br>3 |
|---|---|---|---|---|
| LUMO (L) (eV) | −0.37 | −0.109 | −3.33 | −1.35 |
| HOMO (H) (eV) | −9.54 | −9.97 | −7.07 | −9.84 |

**Table 2.** Relative-scale HOMO–LUMO in the case of radical ions of carvone **1**, quinone **3** and $Ph_3GeH$ (computational study PM3)

| | (Quinone **3**)$^{-\bullet}$ | (Carvone **1**)$^{-\bullet}$ | $(Ph_3GeH)^{+\bullet}$ |
|---|---|---|---|
| LUMO (L) (eV) | +5.64 | +4.24 | −4.07 |
| HOMO (H) (eV) | +0.36 | +2.43 | −11.27 |

- Considering the radical anions (Table 2), note that the electron coming from the germane goes to the quinone at an energy level lower (+0.36 eV) than that of the carvone (+2.43 eV). Therefore, the quinonic radical anion should be more stable. Actually, this is more easily observed by electron spin resonance (ESR) at 20 °C[11] than that formed from carvone **1**.

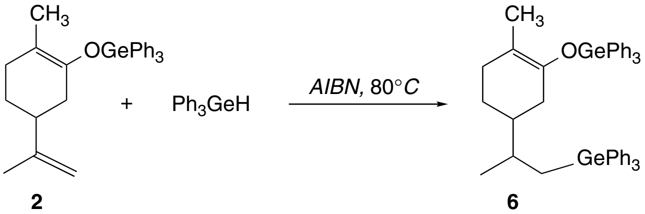
As it was also observed that carvone in its excited state (*hν*) reacted with silylated amines by an SET reaction, which had not occurred in the absence of UV irradiation,[12] we treated triphenylgermane with carvone **1** in its excited state by irradiation either at 254 nm ($\pi\pi^*$) or at 312 nm ($n\pi^*$). In both cases we observed (Scheme 3) a competition between the products expected from the SET reaction (Scheme 3(a)) and the chain radical addition (Scheme 3(b)). The addition products observed in the reaction mixture were identified by chemical and physicochemical means. Compound **4** was also synthesized by reacting triphenylgermyllithium with **1** (see Scheme 4). The alkoxygermane **2** was also identified by acid hydrolysis, which led to $Ph_3GeCl$ and the corresponding dihydrocarvone (Eqn (1)).



**2**

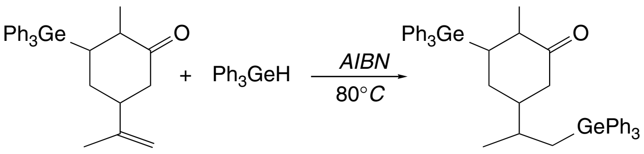
(1)

The monoaduct **4** reacted *in situ* with $Ph_3GeH$ to give the diadduct **5** (Scheme 3(c)), and **2** gave the digermylated compound **6** (Scheme 3(d)). These radical hydrogermylations of **2** and **4** by $Ph_3GeH$ were produced directly (Eqns (2) and (3)).



**2** **6**

(2)



**4** **5**

(3)

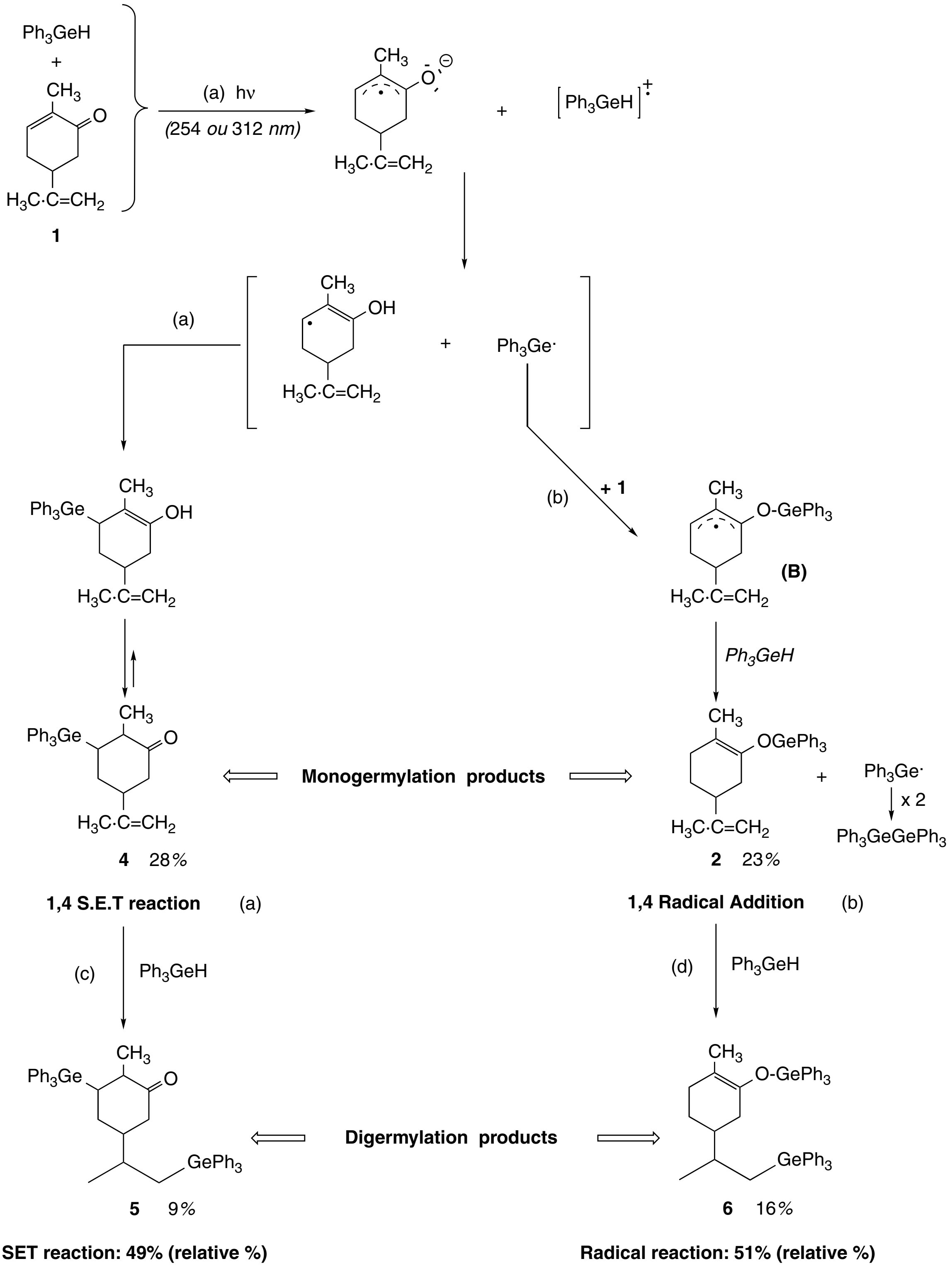
In the case of triphenylgermylithium reacting with carvone (Scheme 4), the reaction is sufficiently rapid at low temperature (−60 °C) to make the reaction intermediate (**C**) observable (Fig. 1). This was identified by comparison with the *O*-germylated radical (**B**; Scheme 3) prepared in the ESR cavity irradiating $Ph_3GeH$, $t\text{-}Bu_2O_2$ in the presence of carvone (Fig. 1).

## CONCLUSION

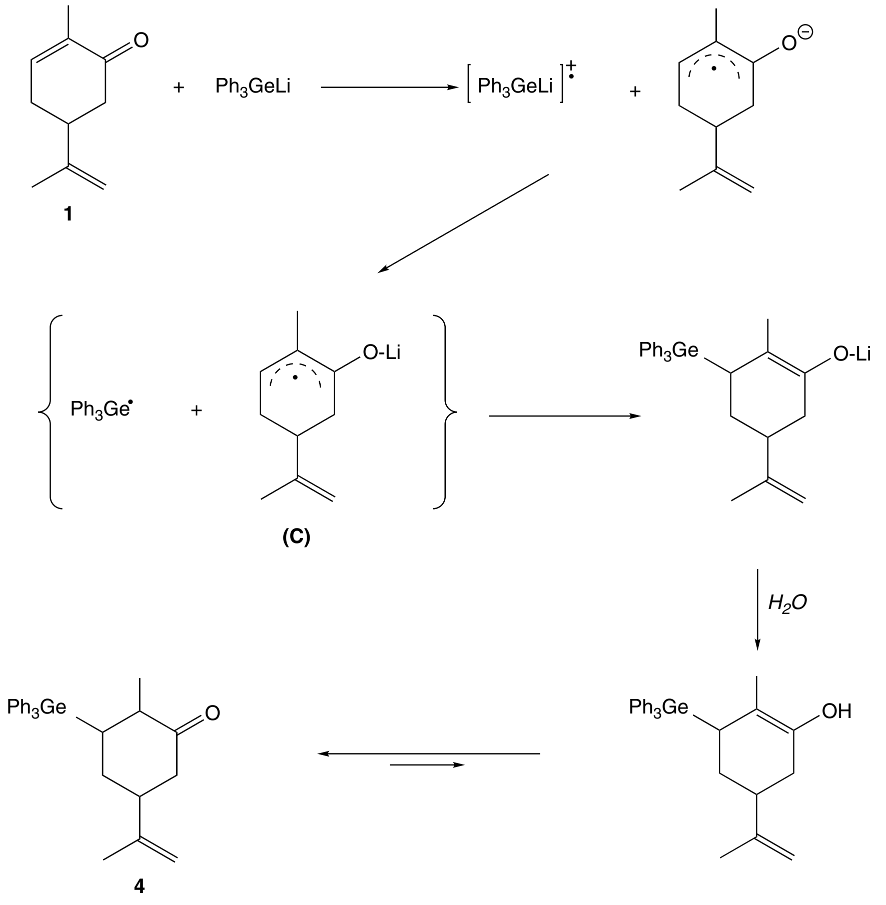
Conjugated ketones, which are poorly reactive towards hydrogermylation in their fundamental state (as in carvone), can undergo competitive and divergent SET and radical additions in their excited state.

## EXPERIMENTAL

All reactions were performed under nitrogen using standard Schlenk tube techniques, Carius tubes and dry solvents. NMR spectra were recorded on Bruker AC 80 ($^1H$, 80 MHz) and AC 200 ($^1H$ and $^{13}C$ in the sequence J mod, 50.3 MHz) spectrometers. Gas chromatography (GC) was undertaken on a Hewlett Packard HP6890 and mass spectra were recorded with a Hewlett Packard HP5989 instrument in the electron impact (EI) mode (70 eV) or with a Rybermag R10-10 spectrometer operating in the EI mode. IR spectra were recorded with a Perkin Elmer 1600FT spectrometer. Elemental analyses were done by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse. Molecular calculations were performed with Hyperchem at the PM3 level. ESR spectra were recorded on a Bruker ER200 instrument with an EIP frequency meter. Radical initiators were used in 10% concentration relative to organic reagents.

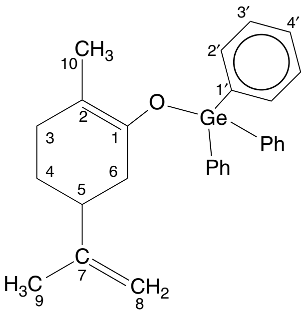

Ph3GeH
+
CH3
O
H3C·C=CH2
1
(a) hν
(254 ou 312 nm)
CH3
O
+
[Ph3GeH]+·
(a)
CH3
OH
H3C·C=CH2
+
Ph3Ge·
(b)
+ 1
CH3
Ph3Ge
OH
H3C·C=CH2
CH3
O-GePh3
(B)
H3C·C=CH2
Ph3GeH
CH3
Ph3Ge
O
H3C·C=CH2
4 28%
Monogermylation products
CH3
OGePh3
H3C·C=CH2
2 23%
+
Ph3Ge·
x 2
Ph3GeGePh3
1,4 S.E.T reaction (a)
1,4 Radical Addition (b)
(c) Ph3GeH
(d) Ph3GeH
CH3
Ph3Ge
O
GePh3
5 9%
Digermylation products
CH3
O-GePh3
GePh3
6 16%
SET reaction: 49% (relative %)
Radical reaction: 51% (relative %)

**Scheme 3.**



Scheme 4.

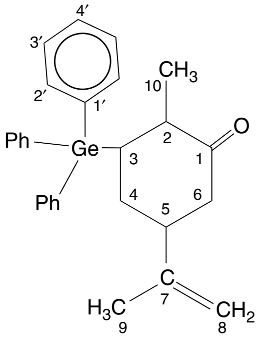
## Preparation of 2



To avoid the formation of the digermylated adduct, an excess of carvone was used (2.0 g, 13.31 mmol) together with $Ph_3GeH$ (3.0 g, 9.83 mmol) in a Carius tube, using RIS[10] from 20 °C up to 150 °C for 48 h. Distillation led to 3.69 g of **2**. Yield: 82%; b.p. 163 °C/3 × $10^{-3}$ mmHg. IR ($CDCl_3$) $\nu$ cm$^{-1}$: 1645 and 1654 (C=C). $^1H$ NMR: ($CDCl_3$) $\delta$ ppm: 7.53 (m, 15H, Ph); 1.62 (b, s, 6H, $CH_3$ in 9, 10); 4.62 (m, 2H, $CH_2$ in 8); 1.30–2.5 (m, 7H, in 3, 4, 5, 6). $^{13}C$ NMR ($CDCl_3$) $\delta$ ppm: 149.58 (C1); 112.05 (C2); 30.50 (C3); 27.94 (C4); 42.55 (C5); 36.71 (C6); 135.01 (C7); 108.49 (C8); 20.70 (C9); 16.55 (C10); 145.66 (C′1); 134.66 (C′2); 128.45 (C′3); 129.07 (C′4). Mass (EI): $M^{+\bullet} = 456$ (25%); $M^{+\bullet} - Ph = 379$ (35%), $M^{+\bullet} - 2Ph = 302$ (100%); $M^{+\bullet} - 3Ph = 225$ (75%). Anal. Found: C, 74.32; H, 6.71. Calc. for $C_{28}H_{30}GeO$: C, 73.89; H, 6.64%.

A sample of **2** (0.1 g, 0.22 mmol) in ether solution (2 ml) was treated by 1 ml of 6 M HCl and then analyzed by GC. $Ph_3GeCl$ and dihydrocarvone were identified by comparison with pure samples.

## Preparation of 4



$Ph_3GeLi$ (5 mmol; from $Ph_3GeH$ (1.52 g, 4.9 mmol) and 3.13 ml *n*-BuLi in 1.6 M hexane) in 5 ml of an ether–tetrahydrofuran solution, was added dropwise at 0 °C to an ether

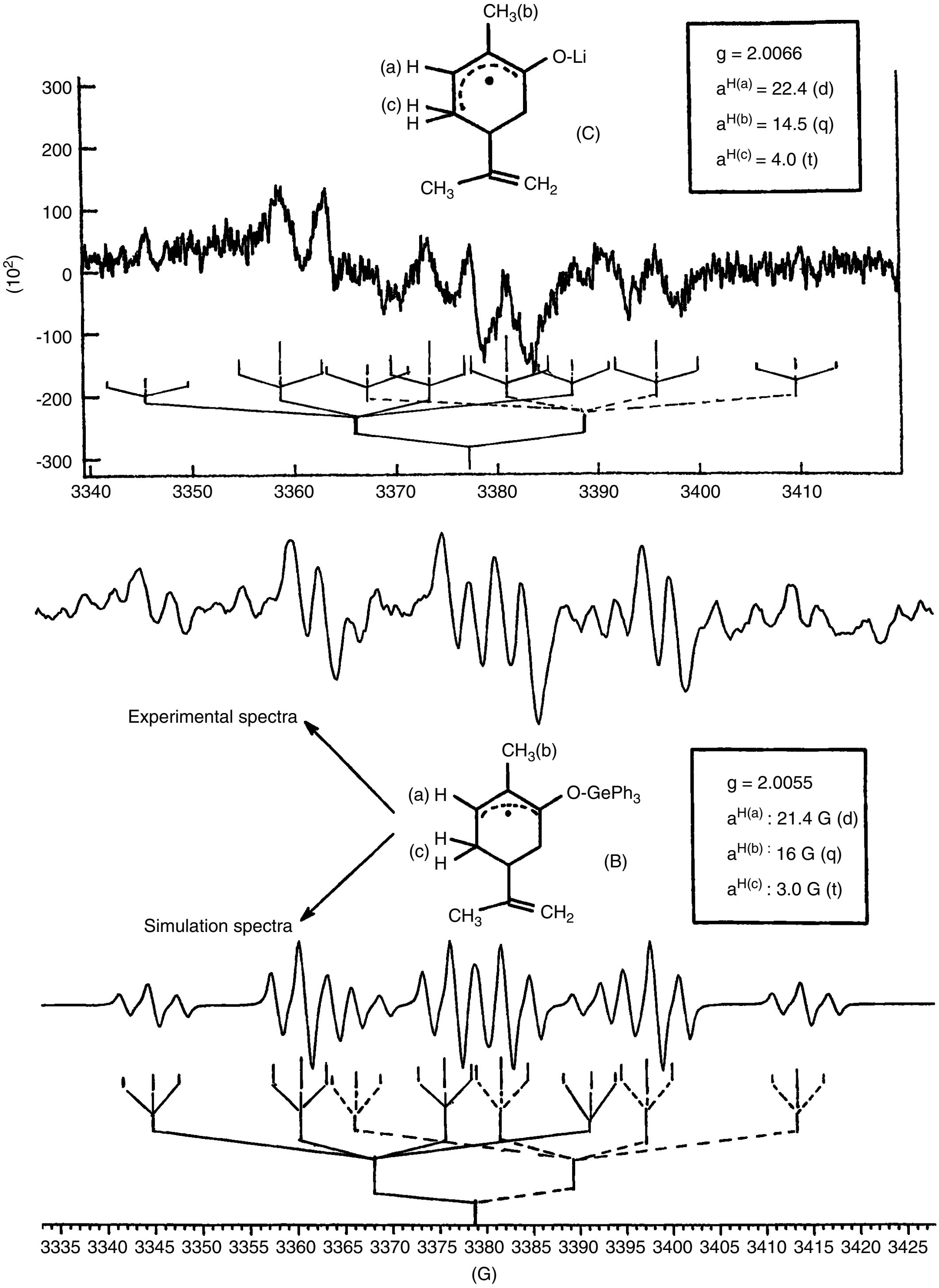
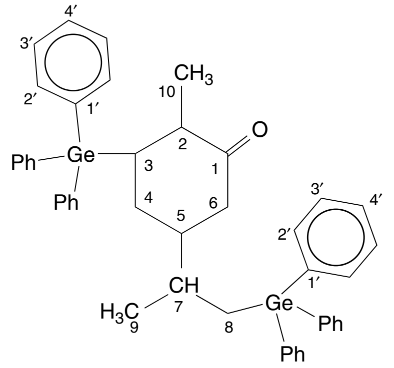


**Figure 1.** ESR spectra for the reaction intermediate **C** and the *O*-germylated radical **B**.

(3 ml) solution of carvone (0.75 g, 5 mmol). After 4 h at 0 °C, the mixture was heated 1 h at ether reflux, then cooled and hydrolyzed ($H_2O$, 1 ml), extracted twice with ether (2 ml), dried over $CaCl_2$, concentrated *in vacuo* and distilled, leading to 1.64 g of **4**. Yield: 72%; b.p. 168–172 °C/5 × $10^{-3}$ mmHg (mixture of diastereoisomers). IR ($CDCl_3$) $\nu$ cm$^{-1}$: 1646 (C=C), 1712 (C=O). $^{1}H$ NMR ($CDCl_3$) $\delta$ ppm: 7.45, 7.62 (m, 15H, Ph); 4.96 (m, 2H in 8); 1.70 (s, 3H, $CH_3$ in 9); 1.30 (s, 3H, $CH_3$ in 10); 2.70–2.00 (m, 3H in 2, 6); 0.90–2.00 (m, 4H in 3, 4, 5). $^{13}C$ NMR ($CDCl_3$) $\delta$ ppm: 214.50, 214.33, 214.19 (C1); 46.29, 46.70, 46.95 (C2); 29.32 (C3); 26.99, 28.34, 27.68 (C4); 44.41, 43.99, 42.25 (C5); 40.83,

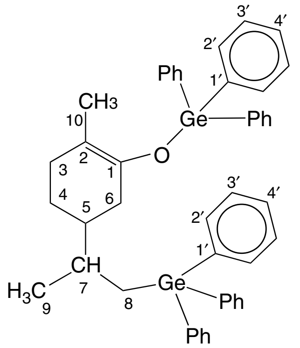
42.25, 42.57 (C6); 136.73, 136.50, 136.18 (C7); 110.17, 113.11, 113.88 (C8); 22.65, 22.18 (C9); 16.49, 16.17, 16.00 (C10); 144.82, 145.69, 147.32 (C′1); 135.87, 135.69, 135.38 (C′2); 128.29, 128.57, 128.66 (C′3); 128.86, 129.07, 129.32 (C′4). Mass (EI): $M^{+\bullet} = 456$ (80%), $M^{+\bullet} - Ph = 379$ (11%); $M^{+\bullet} - 2Ph = 302$ (50%); $M^{+\bullet} - 3Ph = 227$ (30%); $M^{+\bullet} - Ph_3Ge = 151$ (55%); $Ph_3Ge = 305$ (100%). Anal. Found: C, 73.64; H, 6.58. Calc. for $C_{28}H_{30}GeO$: C, 73.89; H, 6.64%.

## Preparation of 5



**5** was prepared according to the procedure used for **6** (but at 80 °C), from **4** (0.97 g, 2.13 mmol) and $Ph_3GeH$ (0.65 g, 2.13 mmol); 0.94 g was isolated by distillation. Yield: 58%; b.p. 243–245 °C/2 × $10^{-2}$ mmHg (mixture of diastereoisomers). IR ($CDCl_3$) $\nu$ cm$^{-1}$: 1714 (C=O). $^1$H NMR ($CDCl_3$) $\delta$ ppm: 8.20–7.02 (m, 30H, Ph); 1.29 (m, 6H in 9, 10); 2.61–2.00 (m, 3H in 2, 6); 1.02–2.01 (overlap of m, 7H in 3, 4, 5, 7, 8). $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 198.35, 198.28, 197.57 (C1); 47.30, 47.23 (C2); 31.25, 31.17 (C3); 26.66 (C4); 27.30 (C5); 43.22 (C6) 43.64 (C7); 20.03, 19.59 (C8); 19.05, 18.74 (C9); 15.91 (C10); 137.65, 137.58, 137.27 (C′1); 134.99, 134.20 (C′2); 130.69, 130.61 (C′3); 133.79, 131.67 (C′4). Mass (EI): $M^{+\bullet} = 760$ (5%); $M^{+\bullet} - Ph = 683$ (11%), $M^{+\bullet} - 2Ph = 606$ (17%); $M^{+\bullet} - Ph_3Ge = 457$ (25%), $Ph_3Ge = 305$ (100%). Anal. Found: C, 72.27; H, 6.12. Calc. for $C_{46}H_{46}Ge_2O$: C, 72.68; H, 6.10%.

## Preparation of 6



A mixture of **2** (1.09 g, 2.39 mmol) and $Ph_3GeH$ (0.73 g, 2.39 mmol) was heated in a Carius tube for 24 h at 80 °C, in the presence of azobisisobutyronitrile (AIBN). By distillation, 1.23 g of **6** was isolated. Yield: 68%; b.p. 234–237 °C/2 × $10^{-2}$ mmHg (mixture of diastereoisomers). IR ($CDCl_3$) $\nu$ cm$^{-1}$: 1653 (C=C). $^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.50 (m, 30H, Ph); 1.55 (s, 3H, $CH_3$ in 10); 1.07 (d, 3H, $CH_3$ in 9, $J^3$ CH–$CH_3$ = 6 Hz); 0.58–2.21 (m, 10H, $CH_2$ in 3, 4, 6, 8 and CH in 5, 7). $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 146.07, 145.96 (C1); 112.18, 111.97 (C2); 30.57, 30.74 (C3); 27.52, 29.21 (C4); 32.80, 34.50 (C5); 36.71, 35.06 (C6); 43.07, 45.05 (C7): 19.35, 19.01 (C8); 18.70, 19.01 (C9); 16.35 (C10); 137.40, 137.90 (C′1); 135.25, 134.68 (C′2); 128.87, 129.09 (C′3); 129.71, 130.18 (C′4). Mass (EI): $M^{+\bullet} = 760$ (22%); $M^{+\bullet} - Ph = 683$ (10%), $M^{+\bullet} - 2Ph = 606$ (15%); $M^{+\bullet} - Ph_3Ge = 457$ (100%). Anal. Found: C, 72.42; H, 6.06. Calc. for $C_{46}H_{46}Ge_2O$: C, 72.68; H, 6.10%.

## Reaction of 1 with $Ph_3GeH$ under UV irradiation

A solution of $Ph_3GeH$ (0.15 g, 0.49 mmol) and carvone (0.07 g, 0.47 mmol) in $C_6D_6$ (0.5 ml) was irradiated in an NMR quartz tube at 254 nm. The reaction was followed hour by hour by $^1$H NMR and stopped after 6 h of irradiation, which corresponded to a maximum of reaction (76%) with a minimum of decomposition. $C_6D_6$ was changed by $CDCl_3$ and $^1$H NMR analysis of the reaction mixture gave its composition as: **2** (23%) from $\delta$ $H^8$, 4.62 (m); **4** (28%) from $\delta$ $H^8$, 4.96 (m); **5** (9%) from $\delta$ $H^{9,10}$, 1.30 (m of d); and **6** (16%) from $\delta$ $H^9$ 1.07 (d). Similar results were obtained with irradiation at 312 nm.

## Reaction of 1 with $Ph_3GeH$, t-$Bu_2O_2$ under UV irradiation, ESR study

A toluene solution of a stoichiometric mixture $Ph_3GeH$/**1** (10%) and t-$Bu_2O_2$ (20%) was irradiated at 203 K in the ESR cavity. The ESR spectra of **C** were recorded and analyzed from computational calculation (PM3) of the density of spin localization. This study shows spin localization on a, b and c positions (Fig. 1).

## Acknowledgements

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