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# AN ESR INVESTIGATION OF SOME PARAMAGNETIC SPECIES DERIVED FROM AROYLSILANES, AROYLGERMANES AND AROYLSTANNANES

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## Summary

The spin adducts between Group IVB organometallic radicals ($\dot{M}R_3$, M = Si, Ge, Sn) and benzoyltriphenylsilane, benzoyltriphenylgermane and benzoyltriphenylstannane have been investigated by ESR spectroscopy. Secondary radical species were detected when acetyltrimethylsilane was used, and their nature and origin are discussed. The radicals formed upon reduction with alkali alkoxides in polar solvents have also been investigated.

## Introduction

Acylsilanes are very reactive compounds which can easily give rise to radical species, although their behaviour is strongly dependent on the nature of the reaction medium. Thus, upon photolysis in apolar solvents they undergo homolytic cleavage of the carbon–metal bond with formation of acyl and silyl radicals [1], whereas in alcoholic solutions the intermediacy of a siloxy-carbene can be inferred from the products [2].

Homolytic fragmentation of aroylsilanes has also been postulated in the thermal or photoreaction of these compounds with triethylphosphite and tetraethylpirophosphite [3]. In addition, there is evidence for the formation of silicon-centered radicals in the photodecomposition of acylsilanes, not only from product analysis [1,2], but also from ESR detection of spin adducts of the radicals with the unreacted

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ketone [4], thus indicating that acylsilanes behave as good spin traps for silicon-centered radicals.

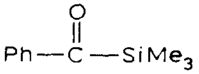
Other organometallic radicals such as $\cdot GePh_3$, $\cdot SnR_3$ [5], and $\cdot PPh_2$ [3] have also been found to add readily to the carbon–oxygen double bond of these compounds, whose behaviour therefore parallels that of other carbonyl derivatives, such as aryl alkyl ketones [6], although the lifetime of the organometallic adducts of the latter substrates is generally shorter. The presence of a silyl group near the ketyl carbon seems to stabilize the radical adducts more than an alkyl group, and only a very weak ESR spectrum could be observed at room temperature in an attempt to add $\cdot SiR_3$ radicals to phenyl t-butyl ketone.

It is to be expected that similarly substituted germanium and tin compounds behave analogously. The trimethylsilyl adducts of benzoyltriphenylgermane and benzoyltriphenylstannane have, indeed, been generated and their ESR spectral parameters measured [5].

Acylsilanes can also be reduced to the corresponding radical anions by treatment with alkali metals in ethereal solvents and an ESR investigation of the ketyls derived from acetyltrimethylsilane and isobutyryltrimethylsilane has been reported [7]. We report here the results of a thorough ESR investigation on the organometallic adducts of, and the radical anions derived from, a series of aroylsilanes. The study has also been extended to the organometallic adducts of $PhC(O)MPh_3$ ($M = Ge, Sn$) and to the rotational barriers of the phenyl ring of the benzoyl group in the observed paramagnetic species.

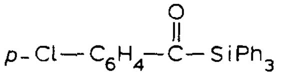
## Results and discussion

The organometallic ketones investigated were benzoyltriphenylsilane (I), *p*-chlorobenzoyltriphenylsilane (II), 2-thenoyltrimethylsilane (III), benzoyltriphenylgermane (IV) and benzoyltriphenylstannane (V).



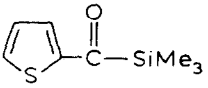
$$Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SiMe_3$$

(I)

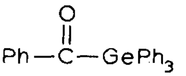


$$p\text{-}Cl{-}C_6H_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SiPh_3$$

(II)

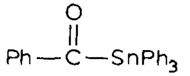


(III)



$$Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}GePh_3$$

(IV)



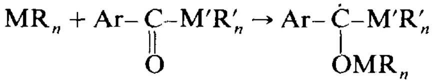
$$Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SnPh_3$$

(V)

For the sake of simplicity we will discuss the results for the adducts obtained by addition of transient organometallic radicals to these ketones separately from those of the paramagnetic anions observed upon alkaline reduction.

*Group IVB adducts. Nature of the observed radicals*

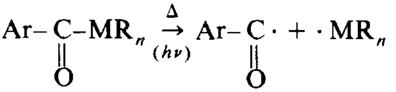
The addition of photolytically generated silicon, germanium and tin centered organometallic radicals to the carbonyl oxygen of the title compounds occurs readily over a wide temperature range (200–450 K) and leads to rather persistent adducts:



$$MR_n + Ar{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}M'R'_n \rightarrow Ar{-}\underset{\underset{\displaystyle OMR_n}{|}}{\dot{C}}{-}M'R'_n$$

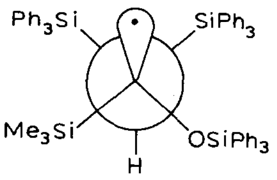
(VI)

The radicals VI with $MR_n = M'R'_n = SiR_3$ or $GeR_3$ can also be obtained by thermolysis of the appropriate ketones in high boiling solvents such as t-butylbenzene (BB) or biphenyl, the intensity of the ESR signal being greatly enhanced by UV irradiation. This is in line with the known thermal [8] and photolability [1,2] of aroyl-silanes and -germanes, which decompose with formation of aroyl and $\cdot MR_n$ radicals. The latter species can then attack the unreacted ketone to give the observed adducts VI.



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}MR_n} \xrightarrow[(h\nu)]{\Delta} \mathrm{Ar{-}\underset{\underset{O}{\|}}{C}\cdot} + \cdot \mathrm{MR}_n$$

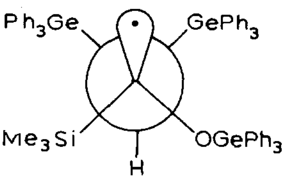
On the other hand, in the case of benzoyltriphenylstannane, under similar conditions we were only able to detect a rather weak ESR signal, which could be interpreted in terms of the hyperfine splitting constants *a*(6H) 1.09, *a*(4H) 0.48 G and assigned to the $\cdot SnPh_3$ adduct of benzyl $PhC(O)\dot{C}(OSnPh_3)Ph$ [9]. In order to compare the relative stabilities of the adducts from aroylsilanes with those from acylsilanes we treated acetyltrimethylsilane with $\cdot SiPh_3$ or $\cdot GePh_3$ radicals at room temperature in t-butylbenzene. The observed ESR spectra indicated the presence of several paramagnetic species. However, upon prolonged irradiation, only two radicals were detectable, one possibly being the expected adduct $Me\dot{C}(OMR_3)SiMe_3$, giving a 1/3/3/1 quartet of ca. 22 G. The second radical gives a much more intense spectrum consisting only of a doublet, which is further split into a small decet when $MR_n = SiPh_3$. In this latter case, three different sets of satellite lines were also detected and, on the basis of their relative intensities with respect to the main spectrum, assigned to two equivalent $^{29}Si$ nuclei and to two different $^{29}Si$ nuclei. We attribute these spectra to the radicals VIIa and VIIb shown below, the silicon bound to the oxygen atom being responsible for the 11.40 G splitting in VIIa.



(VIIa)

$a(^1H)$ 30.12 G
$a(9H)$ 0.28G

$a(2\,^{29}Si)$ 32.20 G
$a(^{29}Si)$ 13.85 G
$a(^{29}Si)$ 11.40 G
$g$ = 2.00309



(VII b)

$a(^1H)$ 25.02 G
$g$ = 2.00290

A possible reaction sequence leading to the formation of VIIa and VIIb is depicted in Scheme 1.

The structure proposed for radicals VIIa and VIIb is consistent with the rather long lifetime of the observed species, and also with the results of Brook and Duff who recovered substantial amounts of 1,2-di(triphenylsilyl)-1-triphenylsilyloxyethy-

*(Continued on p. 296)*

TABLE 1

HYPERFINE SPLITTING CONSTANTS AND *g*-FACTORS FOR RADICALS OF GENERAL STRUCTURE VI [$Ar\dot{C}(OY)X$] (Values in Gauss)

| Radical | Ar | X | Y | *a*(H(Aromatic ring)) | | | *a*($^{13}$C) | *a*(X) | *a*(Y) | *g* | *T* (K) | Solvent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VIa | Ph [a] | $SiPh_3$ | $SiPh_3$ | 4.06($H_o$)<br>4.41($H_o$) | 1.46($2H_m$) | 4.91($H_p$) | – | 10.81($^{29}$Si) | 8.89($^{29}$Si) | – | 243 | BB |
| VIa | Ph | $SiPh_3$ | $SiPh_3$ | 3.88($2H_o$) | 1.45($2H_m$) | 4.44($H_p$) | 27.08 | 10.61($^{29}$Si) | 6.79($^{29}$Si) | 2.0030 | 453 | Biphenyl |
| VIb | Ph [b] | $SiPh_3$ | $GePh_3$ | 3.83($H_o$)<br>4.21($H_o$) | 1.42($2H_m$) | 4.60($H_p$) | – | 11.05($^{29}$Si) | 6.12($^{73}$Ge) | – | 253 | BB |
| VIb | Ph | $SiPh_3$ | $GePh_3$ | 3.90($2H_o$) | 1.41($2H_m$) | 4.45($H_p$) | 25.00 | 11.00($^{29}$Si) | 5.74($^{73}$Ge) | 2.0029 | 298 | Toluene |
| VIc | Ph [c] | $SiPh_3$ | $SnBu_3$ | 3.55($H_o$)<br>3.93($H_o$) | 1.28($2H_m$) | 4.40($H_p$) | – | – | – | – | 253 | BB |
| VIc | Ph | $SiPh_3$ | $SnBu_3$ | 3.88($2H_o$) | 1.37($2H_m$) | 4.55($H_p$) | 21.73 | 10.50($^{29}$Si) | 78.10($^{117}$Sn)<br>81.80($^{119}$Sn) | – | 298 | Toluene |
| VId | Ph | $SiPh_3$ | $SnMe_3$ | 4.02($2H_o$) | 1.39($2H_m$) | 4.74($H_p$) | 21.60 | 10.60($^{29}$Si) | 98.00($^{117}$Sn)<br>102.50($^{119}$Sn) | 2.0024 | 298 | Toluene |
| VIe | Ph | $SiPh_3$ | $SnPh_3$ | 3.90($2H_o$) | 1.36($2H_m$) | 4.51($H_p$) | – | – | 112.50($^{Avg}$Sn) | 2.0025 | 298 | Toluene |
| VIf | Ph | $SiPh_3$ | H | 4.08($2H_o$) | 1.41($2H_m$) | 4.81($H_p$) | – | – | 2.41($H_{OH}$) | – | 330 | Tol/HMPA |
| VIg | Ph | $GePh_3$ | $SiPh_3$ | 4.10($H_o$)<br>4.40($H_o$) | 1.42($2H_m$) | 5.07($H_p$) | – | – | – | – | 298 | BB |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| VIg | Ph | $GePh_3$ | $SiPh_3$ | 4.22($2H_o$) | 1.52($2H_m$) | 4.90($H_p$) | – | 4.98($^{73}Ge$) | 7.90($^{29}Si$) | 2.0024 | 423 | Neat[e] |
| VIh | Ph[d] | $GePh_3$ | $GePh_3$ | 4.13($H_o$)<br>4.49($H_o$) | 1.49($2H_m$) | 5.07($H_p$) | – | – | – | – | 258 | BB |
| VIh | Ph | $GePh_3$ | $GePh_3$ | 4.08($2H_o$) | 1.46($2H_m$) | 4.72($H_p$) | – | – | 6.00($^{73}Ge$) | 2.0024 | 398 | Neat |
| VIi | Ph | $SnPh_3$ | $SiPh_3$ | 4.32($2H_o$) | 1.60($2H_m$) | 5.23($H_p$) | – | 86.51($^{117}Sn$)<br>90.50($^{119}Sn$) | – | – | 398 | BB |
| VIl | Ph | $SnPh_3$ | $GePh_3$ | 4.33($2H_o$) | 1.51($2H_m$) | 5.11($H_p$) | – | 91.20($^{117}Sn$)<br>95.80($^{119}Sn$) | – | – | 383 | BB |
| VIm | 4-Cl-Ph | $SiPh_3$ | $SiPh_3$ | 4.16($2H_o$) | 1.53($2H_m$) | 0.36($^{35}Cl$)<br>0.26($^{37}Cl$) | – | 10.66($^{29}Si$) | 7.48($^{29}Si$) | 2.0035 | 373 | BB |
| VIn | 4-Cl-Ph | $SiPh_3$ | $GePh_3$ | 4.00($2H_o$) | 1.53($2H_m$) | 0.32($^{35}Cl$)<br>0.23($^{37}Cl$) | – | 11.22($^{29}Si$) | 5.52($^{73}Ge$) | 2.0033 | 343 | BB |
| VIo | 4-Cl-Ph | $SiPh_3$ | $SnBu_3$ | 3.99($2H_o$) | 1.52($2H_m$) | 0.28($^{35}Cl$)<br>0.20($^{37}Cl$) | | – | 75.30($^{117}Sn$)<br>78.60($^{119}Sn$) | 2.0030 | 373 | BB |
| VIp | 2-Thienyl | $SiMe_3$ | $SiPh_3$ | 6.99($H_3$) | 1.51($H_4$) | 6.32($H_5$) | – | – | – | 2.0034 | 403 | BB |
| VIq | 2-Thienyl | $SiMe_3$ | $GePh_3$ | 6.79($H_3$) | 1.46($H_4$) | 6.14($H_5$) | – | – | 5.48($^{73}Ge$) | 2.0033 | 323 | BB |
| VIr | 2-Thienyl | $SiMe_3$ | $SnBu_3$ | 6.68($H_3$) | 1.49($H_4$) | 6.19($H_5$) | – | – | 75.00($^{117}Sn$)<br>78.10($^{119}Sn$) | 2.0029 | 298 | BB |

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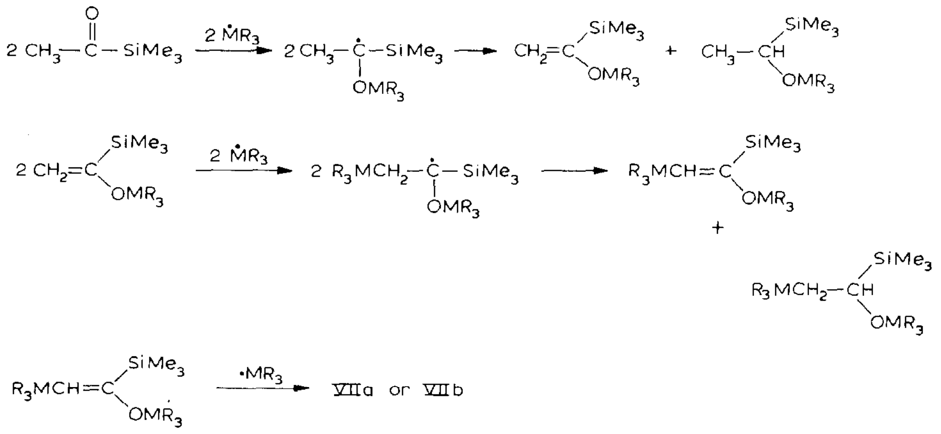
[a] Hindered rotation of Ar: $E_a$ 7.30 ± 0.15 kcal mol$^{-1}$, log $A = 12.09 \pm 0.13$. [b] Hindered rotation of Ar: $E_a = 7.82 \pm 0.42$ kcal mol$^{-1}$, log $A = 12.42 \pm 0.36$. [c] Hindered rotation of Ar: $E_a = 8.27 \pm 0.30$ kcal mol$^{-1}$, log $A = 12.45 \pm 0.28$. [d] Hindered rotation of Ar: $E_a = 8.96 \pm 0.24$ kcal mol$^{-1}$, log $A = 12.51 \pm 0.20$. [e] In neat triphenylsilane.



SCHEME 1

lene $Ph_3SiCH{=}C(SiPh_3)OSiPh_3$ in the photolysis of acetyltriphenylsilane in cyclohexane [1b].

The greater persistency of the organometallic adducts of aroylsilanes compared to that of the analogous adducts of acylsilanes can thus be attributed to the fact that disproportionation reactions only can occur with the latter paramagnetic species.

*Spectral parameters*

The ESR parameters for radicals VIa–VIr are listed in Table 1. The spectra of all adducts VI with Ar = Phenyl showed rather similar features, indicating the coupling of the unpaired electron with two *meta* protons, two *ortho* protons and a *para* proton. In most cases there were additional satellite lines on the two wings of the main spectrum arising from the naturally abundant nuclei having nuclear spin quantum number different from zero, namely $^{13}C$ (*n.a.* 1.1%, $I = 1/2$), $^{29}Si$ (*n.a.* 4.7%, $I = 1/2$), $^{73}Ge$ (*n.a.* 7.61%, $I = 9/2$), $^{117}Sn$ (*n.a.* 7.67%, $I = 1/2$), and $^{119}Sn$ (*n.a.* 8.68%, $I = 1/2$).

The spectral pattern of radicals VIa–VIo was found to be temperature dependent owing to hindered rotation of the phenyl ring close to the ketyl carbon atoms, and the activation energies for this process have been determined for some of these species by a detailed analysis of the spectral shape variation with temperature. In the spectra of the adducts of the chloro derivatives, VIm–VIo, the larger doublet splitting due to *para* proton was replaced by a small 1/1/1/1 quartet ($^{35/37}Cl$, $I = 3/2$).

In the case of radicals VIp–VIr the spectra consisted of only eight lines, due to the interaction of the unpaired electron with three different protons. The assignment of the different splittings was made by analogy with that reported for structurally related radicals [10]. Although in principle one would expect to detect two different rotational isomers for radicals VIp–VIr, we only observed a single species in each case; however the relatively high temperatures at which the spectra of these adducts had to be recorded rule out speculation on the height of the barrier to rotation of the heterocyclic ring.

From the data collected in Table 1 it appears that the couplings of the aryl protons increase on changing the $\alpha$ substituent in the sequence t-Bu < $SiR_3$ < $GePh_3$ < $SnPh_3$. This suggests that the average deviation of the aromatic ring from the plane of the $sp^2$ hybrid centred on the ketyl carbon decreases in the same order, possibly reflecting the decrease of steric hindrance of the Group IVB substituent with increasing atomic number. This conclusion is also supported by the increase in activation energy for the internal rotation of the phenyl ring when passing from $Ph(Ph_3GeO)\dot{C}SiPh_3$ (7.82 kcal $mol^{-1}$) to $Ph(Ph_3GeO)\dot{C}GePh_3$ (8.96 kcal $mol^{-1}$). A definite, although smaller enhancement of the rotational barrier is also observed on changing the organometalloxy group from $OSiPh_3$ to $OSnPh_3$. However a still higher barrier can be predicted for the radical anion of I for which a lower limit of 10.2 kcal $mol^{-1}$ was estimated by assuming the frequency factor (12.4) measured for the adducts VIa–VIc.

A second point to be noted is the reasonable constancy of the silicon splittings when they are $\alpha$ to the ketyl carbon ($a(^{29}Si) \simeq 11$ G) or $\beta$ to it and bonded to the oxygen atom ($a(^{29}Si) \simeq 8$ G). This feature can be valuable in the identification of silicon-containing radicals of unknown structure [3].

From the variation of $^{13}C$ hyperfine splitting, which is 27.08 in VIa, 25.0 in VIb and ca. 21.7 G in VIc, it appears that in these adducts the radical carbon centre is slightly pyramidal, the substitution of Ge and Sn for Si rendering it more planar. This is possibly the result of the decrease in electronegativity experienced by the $OMR_3$ group when the metallic character of the Group IVB element is increased.

### *Reduction of aroylsilanes*

The ESR data for the radicals obtained upon reduction of a number of aroylsilanes are listed in Table 2.

The most thoroughly investigated compound was benzoyltriphenylsilane (I) whose reduction was performed with a variety of methods. The corresponding radical anion

TABLE 2

HYPERFINE SPLITTING CONSTANTS FOR THE RADICALS OBSERVED BY REDUCTION OF AROYLSILANES (ACYLSILANES)

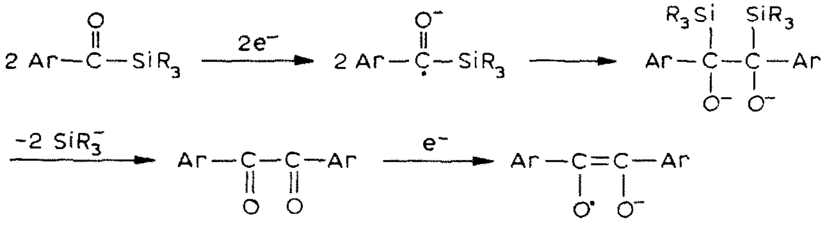
| Compound | Solvent Reducing agent | Observed radical (rad. anion) | Hyperfine splitting constants (G) | | |
|---|---|---|---|---|---|
| $C_6H_5C(O)SiPh_3$ | DMF/Electrolysis | Benzil | $1.00(4H_o)$ | $0.37(4H_m)$ | $1.11(2H_p)$ |
| $C_6H_5C(O)SiPh_3$ | DMSO/NaSMe<br>HMPA/NaSMe<br>HMPA/t-BuOK | Benzil | $0.98(4H_o)$ | $0.37(4H_m)$ | $1.09(2H_p)$ |
| $C_6H_5C(O)SiPh_3$ | DMSO/t-BuOK | Benzophenone | $2.51(4H_o)$ | $0.80(4H_m)$ | $3.47(2H_p)$ |
| $4\text{-Cl-}C_6H_4C(O)SiPh_3$ | DMSO/NaSMe<br>DMSO/t-BuOK | $4,4'\text{-}Cl_2$-benzil | $1.04(4H_o)$ | $0.38(4H_m)$ | |
| 2-Thienyl-$C(O)SiMe_3$ | DMSO/t-BuOK | 2,2′-Thenyl | $1.62(2H_3)$ | $0.41(2H_4)$ | $2.03(2H_5)$ |
| $CH_3C(O)SiMe_3$ | DMSO/t-BuOK | *cis*-Biacetyl | 7.19(6H) | | |
| | | *trans*-Biacetyl | 5.84(6H) | | |
| t-$BuC(O)SiMe_3$ | DMSO/t-BuOK | Bipivaloyl | 0.27(18H) | | |
| $C_6H_5C(O)SiPh_3$ | THF/K/Crown$^{a,b}$ | Benzoylsilane | $3.09(H_o)$ | $0.88(H_m)$ | $4.86(H_p)^c$ |
| | | | $3.97(H_o)$ | $1.18(H_m)$ | |

[a] Hindered rotation of Ar: $E_a > 10.2$ if $\log A = 12.4$ is assumed. [b] Dibenzo-18-Crown-6 ether. [c] Additional splittings are observed due to $^{39}K$ ($a$ 0.10 G) and to $^{29}Si$ ($a$ 8.56 G).

was observed by ESR only when I was treated with potassium in THF containing a small amount of the cyclic ether dibenzo-18-Crown-6 below room temperature. The inequivalence of the two *meta* and the *ortho* splittings indicates restricted rotation of the phenyl ring about the $Ph-\dot{C}(O^-)SiPh_3$ bond. Attempts to determine the rotational barrier by studying the temperature dependence of the ESR spectrum were unsuccessful, since above room temperature the initial spectrum is contaminated by the signals from other unidentified paramagnetic species.

The reduction of I with NaSMe in DMSO or in HMPTA, or electrolytically in DMF, results in the formation of the radical anion of benzil ($PhC(O^-)C(O^{\cdot})Ph$), while the treatment with t-BuOK in DMSO unexpectedly gives a clean and perfectly resolved ESR spectrum of benzophenone ketyl ($Ph_2\dot{C}O^-$). Benzoyltriphenylsilane is unique in this respect, since all other silanes in DMSO give the semidiones analogous to that of benzyl. Thus, upon reduction $p$-$ClC_6H_4C(O)SiPh_3$ the spectrum of $p$-$ClC_6H_4C(O^-)C(O^{\cdot})C_6H_4$-$p$-$Cl$ is observed, and in a few hours this gradually changes to that of the benzil radical anion as the result of the fragmentation of the Ar–Cl bond. The reduction of benzoyltrimethylsilane also gives the benzil radical anion, while 2-thenoyltrimethylsilane under similar conditions gives the radical anion from 2,2′-thenyl.

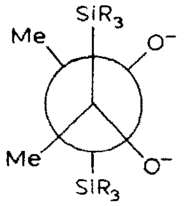
The formation of semidiones from aroylsilanes can be explained in terms of a mechanism involving dimerization of the initially formed ketyl, followed by elimination of the organometallic groups:



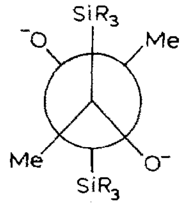
An analogous mechanism was postulated by Tordo et al. to explain the formation of similar semidiones in the metal redution of α-ketophosphonates [11].

The same type of reaction is also shown by acetylsilane, which when reduced in DMSO at room temperature gives an ESR spectrum indicative of the presence of the *trans* and *cis* isomers of the radical anion from biacetyl, in a ca. 2/1 intensity ratio. This was presumably the species observed by Jones and West, and not $Me(Me_3Si)C(O^-)C(O^{\cdot})(SiMe_3)Me$ as they postulated [7].

Similarly the reduction with t-BuOK of pivaloylsilane in DMSO results in the



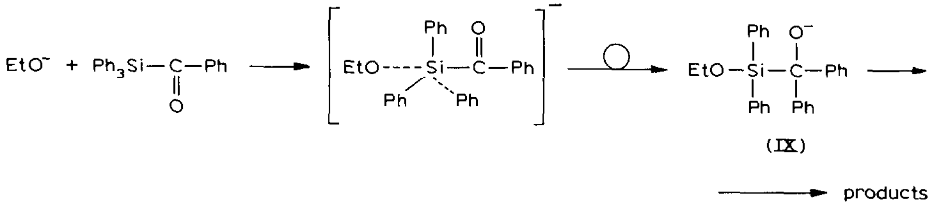
(VIII a)



(VIII b)

appearence of the ESR spectrum of the semidione t-Bu(O$^-$)C–C(O$^\bullet$)-t-Bu. The 2/1 ratio of the *trans* and *cis* isomers of the semidione from biacetyl differs considerably from the equilibrium value of ~ 15/1 reported by Russel et al. [12]. This may reflect the relative conformational stability of the two dimeric intermediates VIIIa and VIIIb, which by elimination of the silyl groups would lead to *cis*- and *trans*-biacetyl, respectively.

The formation of benzophenone ketyl from benzoyltriphenylsilane, on the other hand, is not easy to explain. An impurity of benzophenone in I seems unlikely, especially in view of the fact that we were not able to generate the corresponding radical anion by treating $Ph_2CO$ alone with t-BuOK in DMSO. A possible mechanism can be suggested on the basis of the results by Brook et al. [13] for the reaction between I and alkoxide ions in ethanol. According to these authors the reaction can proceed by two alternative pathways, one of which involves the nucleophilic attack of RO$^-$ on the silicon atom followed by a rearrangement in which a phenyl group migrates from silicon to carbon with formation of the intermediate IX. Thus the observed benzophenone radical anion may possibly come from IX by a homolytic cleavage of the carbon–silicon bond.



## Experimental

The aroylsilanes were prepared by standard procedures, as well as benzoyl-triphenylgermane and benzoyl-triphenylstannane. All other reagents were commercially available. The ESR spectra were recorded on a Bruker ER 200 spectrometer equipped with an NMR gaussmeter (calibration of the field), a frequency counter (*g*-factor determination), and a standard variable temperature device. A 1 kW high pressure mercury lamp was used as UV light source.

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