Tetrahedron Vol 46, No 11, pp 3963-3972, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

ADDITION OF TRIS(TRIMETHYLSILYL)SILYL RADICALS TO THE CARBONYL GROUP

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(*Received in UK* 10 *January* 1990)

Abstract - The reactions of tris(trimethylsilyl)silyl radicals with some compounds containing the carbonyl function (dialkyl or diaryl ketones and quinones) have been studied in solution by means of laser flash photolysis and ESR spectroscopy. The reactivities vary significantly with the nature of the substrate and the rate constants cover a range of four orders of magnitude. Overall tris(trimethylsilyl)silane is found to be an effective hydrosilylating agent for dialkyl ketones, operating through a free radical mechanism.

INTRODUCTION

Recently one of us has discovered that organic halides can be reduced in excellent yields to the corresponding dehalogenated compounds by tris(trimethylsilyl)silane.[1,2] The procedure is straightforward and involves a two step free radical chain process, *viz.*,

$$R\cdot + (Me_3Si)_3SiH \longrightarrow RH + (Me_3Si)_3Si\cdot \qquad (1)$$

$$(Me_3Si)_3Si\cdot + RX \longrightarrow (Me_3Si)_3SiX + R\cdot \qquad (2)$$

In this respect absolute rate constants[3,4] for reactions 1 and 2, as well as the bond dissociation energy of the Si-H bond,[5] have been obtained. The use of this reagent as a mediator in the formation of carbon-carbon bonds *via* radicals has also been described.[6] All these results, together with the fact that silanes are more acceptable than organotin compounds from an ecological and toxicological perspective,[7,8] point to $(Me_3Si)_3SiH$ as to an attractive alternative to Bu_3SnH in radical chain reactions.

In the present work we have employed optical absorption techniques and electron spin resonance (ESR) spectroscopy to study the addition of tris(trimethylsilyl)silyl radicals to the carbonyl function (reaction 3), which is conceivably one of the steps in the free radical hydrosilylation of ketones (reactions 3 and 4); we believe that our approach should provide the basis for the investigation of such process as in organic synthesis.

$$(Me_3Si)_3Si\bullet + R'RC{=}O \longrightarrow R'RC\text{-}OSi(SiMe_3)_3 \qquad (3)$$

$$R'RC\text{-}OSi(SiMe_3)_3 + (Me_3Si)_3SiH \longrightarrow R'RCH\text{-}OSi(SiMe_3)_3 + (Me_3Si)_3Si\bullet \qquad (4)$$

Although a large body of data are available for the addition of trialkylsilyl radicals[9] to carbonyl compounds, in our knowledge only one ESR study referring to very few substrates[10] is available for tris(trimethylsilyl)silyl radicals.

RESULTS

The experimental techniques employed in this investigation are laser flash photolysis and ESR spectroscopy. Products studies have also been carried out in some instances.

Tris(trimethylsilyl)silyl radicals are conveniently generated by photodecomposition of di-*tert*-butyl peroxide in the present of the silane, *viz.*,[11]

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2\ Me_3CO\bullet \qquad (5)$$

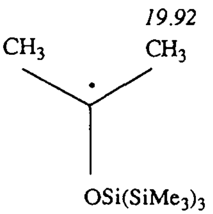
$$Me_3CO\bullet + (Me_3Si)_3SiH \longrightarrow Me_3COH + (Me_3Si)_3Si\bullet \qquad (6)$$

Reaction 6 is a very fast process, its rate constant being $1.0\times10^8\ M^{-1}s^{-1}$ at 300 K.[11]

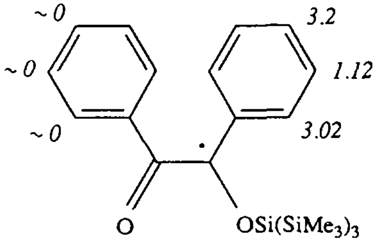
ESR studies - In Table I are collected the ESR parameters for the radical adducts obtained by reaction of $(Me_3Si)_3Si\bullet$ radicals with a variety of carbonyl compounds. In all cases the detected species had *g*-values and hfs constants typical of ketyl radicals (**1**);[12] the adducts to quinones may also be viewed as aryloxyl radicals (**2**).[12]

A comparison of the measured hyperfine splitting constants of the tris(trimethylsilyl)silyl adducts with those of the trialkyl- or triarylsilyl adducts of the same substrates[9] shows that substitution of $SiMe_3$ for alkyl or aryl groups in SiR_3 only leads to very small variations of the spin density distribution in the adducts, despite the substantial difference in steric requirements. Likewise their simpler silyl analogs, the $Si(SiMe_3)_3$ adducts to dialkyl or diaryl ketones exhibit a rather low kinetic stability at ordinary temperature, dimerization being their more likely decay pathway. In fact, UV irradiation of solutions of the ketones and $HSi(SiMe_3)_3$ at room temperature leads to rather weak ESR spectra of the adducts; intense signals are instead observed in the case of the adducts with diaryl ketones by heating solutions of the reactants, which have previously been irradiated at room temperature, above *ca.*393 K in the absence of UV light.

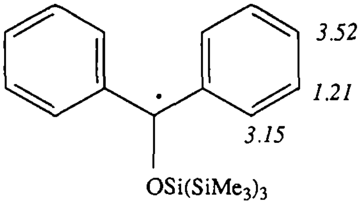
TABLE I - Hyperfine splitting constants (10^{-4} T) for the investigated •Si(SiMe$_3$)$_3$ radical adducts.[a]



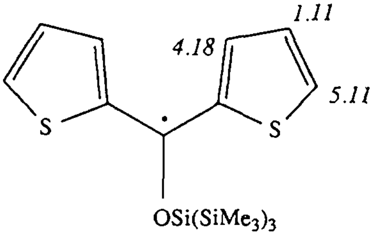
$g = 2.0032$



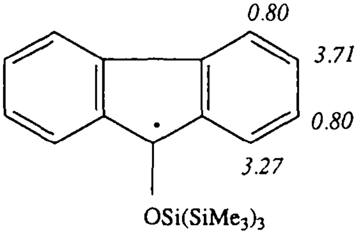
$g = 2.0039$ [b]



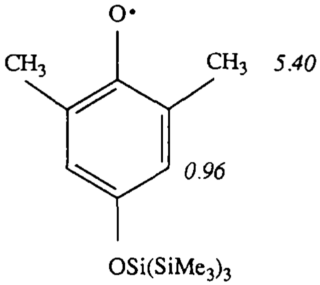
$g = 2.0030$ [c]



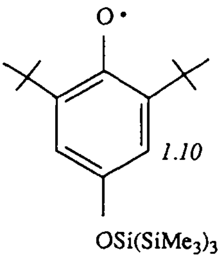
$g = 2.0038$ [c]



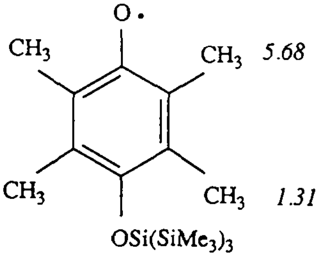
$g = 2.0030$ [d]



$g = 2.0048$



$g = 2.0048$



$g = 2.0047$

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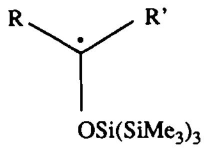
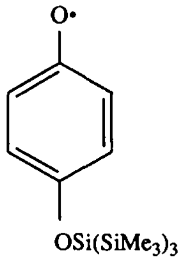
[a] At 298K; [b] in the slow exchange region; [c] at 343K; [d] at 423K.

Coupling constants to atoms in equivalent positions are equal.



R,R' = Alkyl, Aryl

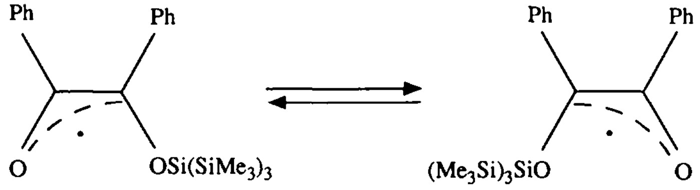
(1)



(2)

Although it is known that silyl radicals preferentially attack unsaturated carbonyl compounds at the carbon-carbon double bonds,[13] in the reactions of $\bullet Si(SiMe_3)_3$ with 2,6-dimethyl-, 2,6-di-*tert*-butyl-*para*-benzoquinone and duroquinone only the adducts resulting from addition to a carbonyl oxygen could be observed over the temperature range $213 < T < 393K$.

In order to investigate the behaviour of $\bullet Si(SiMe_3)_3$ towards α-diones, we have studied its reaction with benzil. At room temperature the observed adduct is characterized by the magnetic inequivalence of the two aromatic rings, significant spin density being observed only on the ring directly bonded to the radical carbon (cf. Table I). As the temperature is raised, significant linewidth alternation effects become apparent, which are believed to arise from the intramolecular migration of the $Si(SiMe_3)_3$ between the oxygen atoms of the two carbonyl moieties outlined in eq. 7. This fluxional behaviour can be monitored up to 398K, at which temperature other unidentified species are formed. Since the spectral parameters at the slow exchange limit are known, spectra at temperatures in the range $348 < T < 398K$ were satisfactorily computer simulated by means of a program based on a two-jump exchange model. It was assumed that the hfs constants of a given phenyl ring of the benzil adduct exchanged between the values given in Table I and zero. The resulting kinetic data for this process can be described by the Arrhenius equation characterized by $\log(A/s^{-1}) = 12.00 \pm 0.10$ and $E_a = 8.81 \pm 0.17$ kcal mol^{-1}.



(7)

Kinetic ESR spectroscopy - The kinetic ESR spectroscopic technique allows the measuring of rate constants for radical-molecule reactions in the range 10^3 to 10^5 $M^{-1}s^{-1}$, provided that both the attacking silyl radical and the resulting radical adduct can be observed simultaneously.[14] This is found to be the case for samples containing 1:1:1:4 (v/v) tris(trimethylsilyl)silane:di-*tert*-butyl peroxide:acetone:benzene at 318 K. Under these conditions the radical adducts is formed through reactions 5, 6 and 8. The rate constant for dimerization of

$$(\mathrm{Me_3Si})_3\mathrm{Si}\bullet \quad + \mathrm{Me_2C{=}O} \longrightarrow \mathrm{Me_2C\text{-}OSi(SiMe_3)_3} \qquad (8)$$

$$2\ (\mathrm{Me_3Si})_3\mathrm{Si}\bullet \longrightarrow \text{non radical products} \qquad (9)$$

$$(\mathrm{Me_3Si})_3\mathrm{Si}\bullet \ + \mathrm{Me_2\overset{\bullet}{C}\text{-}OSi(SiMe_3)_3} \longrightarrow \text{non radical products} \qquad (10)$$

$$2\ \mathrm{Me_2\overset{\bullet}{C}\text{-}OSi(SiMe_3)_3} \longrightarrow \text{non radical products} \qquad (11)$$

$\bullet\mathrm{Si(SiMe_3)_3}$ radicals has been found to be controlled by diffusion, as described in the following section. As to termination reactions 10 and 11, they can be safely assumed to be also diffusion controlled processes in view of the unhindered hydrocarbon radicals involved.[15] Under conditions of steady photolysis, where the radical concentrations do not change with time, we can write:[14]

$$\frac{k_8\,[\mathrm{Me_2C{=}O}]}{2\,k_t} = [\mathrm{Me_2\overset{\bullet}{C}\text{-}OSi(SiMe_3)_3}]\left(1 + \frac{[\mathrm{Me_2\overset{\bullet}{C}\text{-}OSi(SiMe_3)_3}]}{[(\mathrm{Me_3Si})_3\mathrm{Si}\bullet]}\right) \qquad (12)$$

The measured concentrations of the $\mathrm{Me_2C\text{-}OSi(SiMe_3)_3}$ and $\bullet\mathrm{Si(SiMe_3)_3}$ were 8.450×10^{-6} M and 3.276×10^{-6} M, respectively, at full light intensity. Since the concentration of acetone was 1.946 M, from eq. 12 we obtain $k_8/2k_t = 1.55\times10^{-5}$. Taking for $2k_t$ a value of $5\times10^{9}\ \mathrm{M^{-1}s^{-1}}$, the resulting value of k_8 is $7.8\times10^{4}\ \mathrm{M^{-1}s^{-1}}$ at 348K.

Laser Flash Photolysis - The employed laser flash photolysis apparatus had a time resolution covering the range 0.1 to 10 μs; the lowest rate constants that could be conveniently measured were *ca.* $10^{6}\ \mathrm{M^{-1}s^{-1}}$.

Decay of tris(trimethylsilyl)silyl radicals. Tris(trimethylsilyl)silyl radical can be detected by optical absorption techniques. For example, when a 0.15 M solution of $(\mathrm{Me_3Si})_3\mathrm{SiH}$ in di-*tert*-butyl peroxide:isooctane (1:4 v/v) is irradiated either with a nitrogen (337 nm) or an excimer (308 nm) laser the formation of a transient species is observed which exhibits a weak spectrum with continuously increasing absorption below *ca.* 350 nm and no maximum above 280 nm.[11] We identify this transient species with the tris(trimethylsilyl)silyl radical formed *via* reactions 5 and 6 and decaying *via* reaction 9. The identification is substantiated by product studies indicating that dimerization is the only decay pathway of $\bullet\mathrm{Si(SiMe_3)_3}$ radicals.[16] The decay trace of this species proved to be clean second order and its analysis yielded $2k_t/\epsilon_{300\mathrm{nm}} = 5.0\times10^{6}\ \mathrm{cm\ s^{-1}}$ and $2k_t/\epsilon_{320\ \mathrm{nm}} = 6.1\times10^{6}\ \mathrm{cm\ s^{-1}}$ at 300K for the nitrogen and excimer laser experiment, respectively. As the values of ϵ_λ are needed in order to obtain absolute rate constants, the transient optical absorptions of $(\mathrm{Me_3Si})_3\mathrm{Si}\bullet$ at 300 and 320 nm were compared with that of $\mathrm{Ph_2COH}$ at 540 nm, both species being generated by hydrogen abstraction from the parent molecules with *tert*-butoxyl radicals. Taking $\epsilon_{540\ \mathrm{nm}} = 3220\ \mathrm{M^{-1}\ cm^{-1}}$,[17] we estimated the values $\epsilon_{300\ \mathrm{nm}} = 1300$ and $\epsilon_{320} = 650\ \mathrm{M^{-1}\ cm^{-1}}$ for $(\mathrm{Me_3Si})_3\mathrm{Si}\bullet$, which leads to values of 6.5×10^{9} and $4.0\times10^{9}\ \mathrm{M^{-1}s^{-1}}$ for $2k_t$.

Addition of $\bullet Si(SiMe_3)_3$ to carbonyl compounds. Generation of $(\mathrm{Me_3Si})_3\mathrm{Si}\bullet$ radicals in a 1:4 (v/v) mixture of tris(trimethylsilyl)silane[18] and di-*tert*-butyl peroxide containing either 2×10^{-5} - 6×10^{-3} M of duroquinone or 4×10^{-4} - 3×10^{-3} M of fluorenone led to transient absorption spectra strongly resembling those of the related

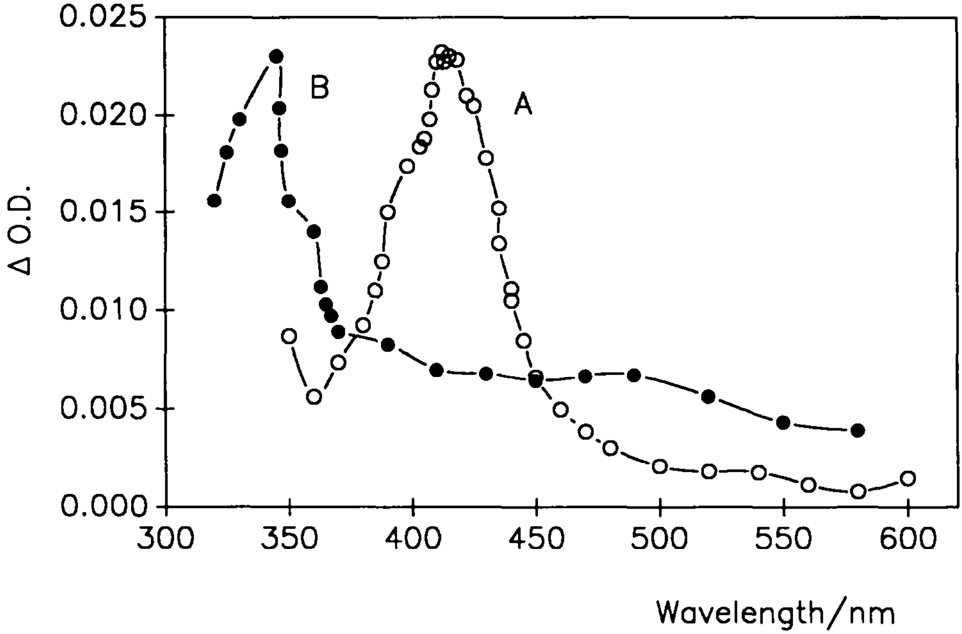


Figure 1 - Absorption spectra of the adducts obtained by reaction of tris(trimethylsilyl)silyl radicals with duroquinone (A) and fluorenone (B).

triethylsilyl adducts,[18] with maxima at 412 and 354 nm, respectively (see Figure1).

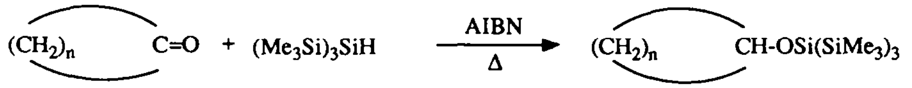
The rate constants were obtained from a study of the buildup traces for the tris(trimethylsilyl)silyl adducts at different concentrations of duroquinone or fluorenone. In these experiments the silyl radical adduct were monitored at the afore mentioned absorption maxima. Under these conditions, the pseudo-first-order rateconstant associated with the buildup, k_{expt}, is given by:

$$k_{expt} = k_0 + k\,[\text{Substrate}] \qquad (13)$$

where k_0 includes all pseudo-first-order modes of decay other than reaction with ketones. The value of k for duroquinone and fluorenone are $(1.0 \pm 0.1)\times10^8$ and $(3.8 \pm 0.7)\times10^7$ $M^{-1}s^{-1}$, respectively, at 296K. Since we were unable to observe any radical adduct in the presence of 0.01 M of benzil, we conclude that for this compound $k \leq 1\times10^7$ $M^{-1}s^{-1}$; at higher benzil concentration, the laser light was substantially absorbed by benzil itself, leading to interference by its triplet state.

Product studies - The above results suggest that tris(trimethylsilyl)silane, being a good hydrogen donor, should be capable of sustaining a radical chain hydrosilylation of dialkyl ketones (reactions 3 and 4). This expectation proved correct, and we report here some results on the use of tris(trimethylsilyl)silane as reducing agent for ketones.

When a mixture of $(Me_3Si)_3SiH$ (1.2 eq.) and a cycloalkanone (3) (1 eq.) is heated at 80-90°C for 1-2 hours in the presence of a catalytic amount of AIBN as radical initiator, addition of the silane across the carbonyl function occurs affording the hydrosilylated compound (4) in good yields.



(14)

n = 3, 4, 5

(3)

Yields > 70%

(4)

TABLE II - Absolute rate constants ($M^{-1}s^{-1}$) for the addition of $Et_3Si\cdot$, $(Me_3Si)_3Si\cdot$, and $Bu_3Sn\cdot$ radicals to some carbonyl compounds at *ca.* 298K.[a]

Substrate	$Et_3Si\cdot$[b]	$(Me_3Si)_3Si\cdot$	$Bu_3Sn\cdot$[c]
Duroquinone	$(2.5 \pm 0.5)x10^9$	$(1.0 \pm 0.1)x10^8$	$(1.4 \pm 0.1)x10^9$
Fluorenone	$(1.5 \pm 0.1)x10^9$	$(3.8 \pm 0.7)x10^7$	$(3.8 \pm 0.5)x10^8$
Benzil	$(3.3 \pm 0.3)x10^8$	$\leq 1x10^7$	$(1.3 \pm 0.1)x10^8$
Acetone	$(2.8 \pm 0.8)x10^5$	$\sim 8x10^{4}$[d]	[e]

[a]Using laser flash photolysis technique; [b]ref. 19; [c] ref. 20; [d]at 318K using kinetic ESR spectroscopy; [e]for cyclohexanone a limit value of $k < 5x10^4$ has been obtained.

DISCUSSION

The trends in reactivity for addition of $\cdot Si(SiMe_3)_3$ radicals across the carbonyl function are those expected on thermodynamic ground, the rate constants decreasing in the series quinones > diaryl ketones > dialkyl ketones. Our quantitative kinetic data reported in Table II indicate that $\cdot Si(SiMe_3)_3$ radicals are less reactive than triethylsilyl and tributyltin radicals towards addition to carbonyl compounds. It is known that silanes do not generally reduce carbonyl groups, although the reduction of a few carboxylic esters by triphenylsilane has been reported.[21] On the other hand, the reduction of ketones by trialkyltin hydride is believed to be a rather sluggish process.[22] The most striking feature of the present results is therefore to be found in the relatively high rate constant of addition of $\cdot Si(SiMe_3)_3$ radicals to dialkyl ketones; in fact, our product studies indicate that reactions 3 and 4 are fast enough to carry on radical reactions with long chain lengths.

It has been previously shown that for silyl radicals the kinetically controlled addition to the quinone ring is preferred over the thermodynamically more favourable addition to a carbonyl oxygen, the latter adducts being only formed in a second step *via* a 1,3 carbon to oxygen silicon shift, provided the temperature is high enough to promote this process.[13] This isomerization is a molecular rearrangement through a four-membered cyclic transition state, and does not involve free silyl radicals. In this respect the behaviour of $\cdot Si(SiMe_3)_3$ radicals towards *para*-quinones is substantially different from that of trialkyl- or triarylsilyl radicals, as they only add to a carbonyl moiety of quinones and not to the carbon-carbon double bonds of the quinonic ring. When comparing the rate constants for addition of tris(trimethylsilyl)silyl radicals to unsaturated carbonyl compounds with those of trialkyl or triarylsilyl radicals one must therefore bear in mind that different chemical processes may be involved.

Intramolecular migration of the silyl groups between the two carbonyl oxygens of benzil has already been reported for $\cdot SiEt_3$ and $\cdot SiPh_3$ radical adducts.[23] The activation energy for the analogous fluxional motion of $\cdot Si(SiMe_3)_3$ measured in this work (8.8 kcal mol^{-1}) is intermediate between those of the triethylsilyl and triphenylsilyl adducts. The negative activation entropy (-6 e.u.) suggests that also in this case the migration proceeds through a cyclic transition state, where the central silicon atom is bonded simultaneously to both oxygen atom of the substrate.

TABLE III - Activation parameters for the migration of silyl groups in benzil adducts.

MR_3	E_a/kcal mol^{-1}	log(A/s^{-1})	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/e.u.
[a]$SiEt_3$	9.43 ± 0.27	12.34 ± 0.15	8.67 ± 0.27	-4.57 ± 0.68
$Si(SiMe_3)_3$	8.81 ± 0.17	12.00 ± 0.10	8.08 ± 0.17	-6.03 ± 0.14
[a]$SiPh_3$	5.87 ± 0.47	11.62 ± 0.20	5.01 ± 0.47	-8.09 ± 0.13

[a]Ref. 23.

CONCLUSIONS

Although tributyltin hydride has found in recent years a wide application as reducing agent for a large number of chemical species, it is of little use for the reduction of dialkyl ketones *via* radicals. It has been previously shown that $(Me_3Si)_3SiH$ represents a valid substitute for tributyltin hydride in many reduction processes; our results now indicate that its use can be favourably extended to the reduction of carbonyl containing compounds.

EXPERIMENTAL

Materials - Tris(trimethylsilyl)silane was prepared by reaction of trichlorosilane with trimethylchlorosilane as described by Burger and Kilian,[24] and was purified by careful distillation. All other compounds used were commercially available, and were purified by standard methods.

Laser Flash Photolysis - The laser flash photolysis experiments were carried out under oxygen free conditions, using pulses (337.1 nm, ~ 8ns, up to 10 mJ) from a Molectron UV 24 nitrogen laser for excitation. The system was interfaced with a PDP/03L computer that controlled the experiment and provided data gathering, storage, and hard copy facilities.[25]

ESR measurements - ESR samples consisted of *ca.* 10^{-2} M *tert*-butylbenzene solutions of the ketone (quinone) containing equimolar amounts of tris(trimethylsilyl)silane and di-*tert*-butyl peroxide. The samples were carefully deoxygenated by prolongued nitrogen bubbling, then inserted inside the cavity of a Bruker ER 200 D ESR spectrometer and irradiated with the light from a Hanovia 1000 kW high pressure mercury lamp. Standard accessories for magnetic field calibration, frequency reading, and temperature control were employed. Radical concentrations were determined by double integration of the signals relative to a sample of DPPH, using the lowfield line from a ruby crystal as internal standard. Rate constants for migration of the organometallic moiety in benzil adducts were determined by fitting computer simulated spectra obtained using a program based on Bloch equations (two-jump model) to experimental spectra obtained at different temperatures.

ACKNOWLEDGMENT

We wish to express our gratitude to Mr. M. Ballestri (I.Co.C.E.A.-CNR, Italy) for his kind assistance and to Dr. J.C. Scaiano (NRC, Canada) for providing the Laser Flash Photolysis apparatus. We are also indebted to Progetto Finalizzato del CNR "Chimica Fine II" for financial support.

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