ly to **5** (mp >300° from xylene, 40% overall yield):[16] uv, λ_{max} (CH_2Cl_2) 234 (log ϵ 4.79), 260 s (4.42), 285 s (4.18), 304 s (4.09), and 398 nm (4.19). Compound **6** (mp >300°)[16] was prepared analogously (22% overall yield): uv, λ_{max} (CH_2Cl_2) 268 (log ϵ 4.50), 290 s (4.29), and 392 (4.21). Compound **7** (mp >300° from bromobenzene)[16] was synthesized by a biomolecular Zn-HCl reduction of 6-chloro-2-methoxy-*N*-methylacridone[18] in ethanol (98% yield): uv, λ_{max} (CH_2Cl_2) 241 (log ϵ 4.71), 302 (4.24), and 446 (4.20). Each compound (**5**, **6**, and **7**) exists in two geometrical forms, *Z* and *E*, as revealed by the NMR spectra: two singlets (in approximately equal population) in the appropriate region, ascribed to the *Z* and *E* isomers (in each geometrical isomer, symmetry causes both substituents to be isochronous). In **5**, the two ^{19}F NMR CF_3 singlets[19] (δ ($CDBr_3$, 298 K) 7.46, 7.72 ppm, $\nu(Z\text{-}\mathbf{5})-\nu(E\text{-}\mathbf{5}) = 21.0 \pm 0.1$ Hz) coalesced at 414 ± 4 K. The process proved to be reversible, characteristic of a dynamic exchange process. The application of the usual coalescence approximation[20,21] leads to the low value of $\Delta G^{\ddagger}_{414K} = 21.3 \pm 0.2$ kcal/mol. Likewise, in **6**, the two ^1H NMR CH_3 singlets (δ($CDBr_3$, 298 K) 2.08, 2.10 ppm, $\nu(Z\text{-}\mathbf{6})-\nu(E\text{-}\mathbf{6}) = 1.9 \pm 0.1$ Hz) coalesced at 357 ± 4 K with $\Delta G^{\ddagger}_{357K} = 20.0 \pm 0.5$ kcal/mol. A similar phenomenon has been revealed in the biacridan derivative (**7**). The ^1H NMR of **7** in 1-bromonaphthalene displayed in the aliphatic region a broad $N\text{-}CH_3$ singlet at 2.57 ppm and two sharp OCH_3 singlets at 3.11 and 3.15 ppm, in the ratio of 1:1. For comparison, the corresponding $N\text{-}CH_3$ signal in *N*,*N'*-dimethylbiacridan appeared at 2.73 ppm. The two OCH_3 singlets ($\nu(Z\text{-}\mathbf{7})-\nu(E\text{-}\mathbf{7}) = 4.2 \pm 0.1$ Hz at 298 K) coalesced at 373 ± 4 K with $\Delta G^{\ddagger}_{373K} = 20.3 \pm 0.2$ kcal/mol.

The remarkably low barriers associated with the *Z*,*E* isomerizations of **5**, **6**, and **7**, are interpreted *predominantly* in terms of ground-state destabilization due to steric strain, rather than to a stabilization of diradical transition states. This interpretation is supported by our recent observation on the thermal behavior of 3,3′-dimethyl[$\Delta^{5,5'(12H,12H')}$-binaphthacene]-12,12′-dione (**8**): the linear annelation of **6** (in contrast to **2**[22]) did not lead to faster *Z*,*E* isomerizations, in spite of the more effective stabilization of a possible diradical transition state.[3] In order to reduce steric interactions, the bianthrone molecule adopts a folded geometry in its ground-state A isomer, and a twisted geometry (about the "pinch") with the two anthrone halves in planar configuration in its B isomer.[4,5] The transition state for the *Z*,*E* isomerization may be structurally related to B, but with a 90° twist.[23] However, such a transition state should not be located in the free energy diagram too far away from the relatively strained ground-state A isomer. The unusually fast true *Z*,*E* isomerizations of **5**, **6**, and **7**, are indeed intrinsic properties of the bianthrone and biacridan systems. The low barriers to *Z*,*E* isomerization reported here are consistent with the contention that the thermochromism, displayed by these systems (in solution or in adsorbed state[13]), is associated with conformational changes.[5]

Acknowledgment. We thank Mr. M. Grinberg of the Weizmann Institute of Science, Rehovot, for the FT ^{19}F NMR determinations.

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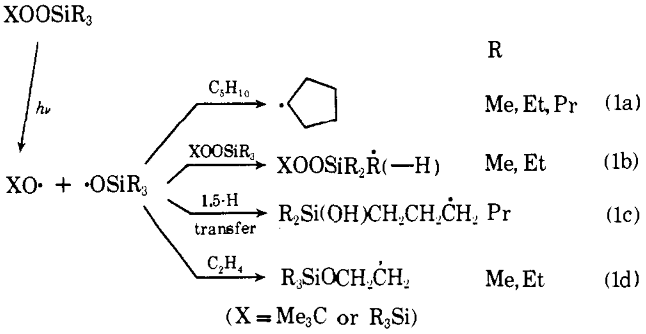
Electron Spin Resonance Studies of the Photolysis of Trialkylsilyl Peroxides

Sir:

The photolysis and thermolysis of dialkyl peroxides (R_3COOCR_3) have been investigated extensively, but little work has been reported on the corresponding metallic peroxides $R_3COOMR'_3$ and R_3MOOMR_3 (M = Si, Ge, Sn, or Pb). We now report a preliminary ESR study of the photolysis of some *tert*-butyl trialkylsilyl peroxides ($Me_3COOSiR_3$) and bis(trialkylsilyl) peroxides ($R_3SiOOSiR_3$).[1,3]

The *tert*-butyl trialkylsilyl peroxides and bis(trialkylsilyl) peroxides show in common the behavior which may be attributed to trialkylsiloxyl radicals (eq 1a–d).



Photolysis of *tert*-butyl trimethylsilyl peroxide and of *tert*-butyltriethylsilyl peroxide ($Me_3COOSiR_3$, R = Me and Et) in cyclopentane showed only the spectrum of the cyclopentyl radical resulting from abstraction of hydrogen by the *tert*-butoxyl and trialkylsiloxyl radicals (reaction 1a); *tert*-butyl tripropylsilyl peroxide under the same conditions showed also the spectrum of the γ-silylpropyl radical $Pr_2Si(OH)CH_2CH_2\dot{C}H_2$ (reaction 1c). In cyclopropane as solvent (which undergoes hydrogen abstraction less readily), the attack occurs mainly on the alkyl group bonded to silicon (reaction 1b); *tert*-butyltrimethylsilyl peroxide showed the formation of the radical $\mathrm{Me_3COOSi(Me_2)\dot{C}H_2}$[5] ($a$ (Hα) 20.9 (2 H), a (Hγ) 0.75 G (6 H) at −120°) (and of $\mathrm{C_3H_5\cdot}$), and *tert*-butyl triethylsilyl peroxide showed the presence of both the radicals $\mathrm{Me_3COOSi(Et_2)\dot{C}HCH_3}$ (a (Hα) 20.7 (1 H), a (Hβ) 25.7 G (3 H) at −120°) and $\mathrm{Me_3COOSi(Et_2)CH_2\dot{C}H_2}$ (a (Hα) 21.0 (2 H), a (Hβ) 18.0 G (2 H) at −120°, but *tert*-butyl tripropylsilyl peroxide now showed almost exclusive formation of the radical $\mathrm{Pr_2Si(OH)CH_2CH_2\dot{C}H_2}$ (a (Hα) 21.7 (2H), a (Hβ) 27.6 (2H), a (Hγ) 0.7 G (2H) at −40°). If the photolysis was carried out in the presence of ethylene, addition occurred to give the β-siloxyethyl radical (reaction 1d), as described by Edge and Kochi.[2]

The photolysis of bis(trimethylsilyl) peroxide followed this simple pattern and, over the range −120 to −20 °C it showed the presence of radicals resulting from the reactions 1a (in cyclopentane solvent), 1b (in cyclopropane solvent),[6] or 1d (in the presence of ethylene). The higher bis(trialkylsilyl) peroxides, $\mathrm{R_3SiOOSiR_3}$, however, deviated from this behavior in that at low temperature they showed the presence of the appropriate *alkyl radical R·* (eq 2).

$$\mathrm{R_3SiOOSiR_3} \xrightarrow{h\nu} \mathrm{R\cdot} + \ ? \tag{2}$$

Photolysis of bis(triethylsilyl) peroxide at −120 to −80 °C showed principally a strong spectrum of the *ethyl* radical, together with a relatively small concentration of the cyclopentyl radical (in cyclopentane) or of the radicals $\mathrm{Et_3SiOOSi(Et_2)\dot{C}HCH_3}$ (a (Hα) 20.5 (1 H), a (Hβ) 25.7 G (3 H)) and $\mathrm{Et_3SiOOSi(Et_2)CH_2\dot{C}H_2}$ (a (Hα) 21.0 (2 H), a (Hβ) 18.1 G (2 H)) (in cyclopropane). As the temperature was increased, the intensity of the spectrum of the ethyl radical diminished, until at −50° it was approximately equal in intensity to the spectra of the radicals resulting from hydrogen abstraction.

Bis(tripropylsilyl) peroxide at −120 °C similarly gave a strong spectrum of the *propyl* radical, together with that of the species $\mathrm{Pr_2Si(OH)CH_2CH_2\dot{C}H_2}$, in approximately equal concentration. As the temperature was increased, the intensity of the signal of the propyl radical diminished, but it was still detectable at −35°.

Photolysis of trialkylsilyl *tert*-butyl peroxides or bis(trialkylsilyl) peroxides in cyclopentane, isopentane, or toluene in the presence of oxygen gave rise to the spectra of alkylperoxyl radicals formed from alkyl radicals derived by hydrogen abstraction from the solvent.[7]

The reactions involving intermolecular hydrogen abstraction illustrate the expected parallel between the behavior of the alkoxyl and siloxyl radicals, and the addition of the siloxyl radicals to ethylene has been demonstrated previously by Edge and Kochi in the photolysis of *tert*-butyl trimethylsilyl peroxide.[2] The rearrangement of tripropylsiloxyl radical to the radical $\mathrm{Pr_2Si(OH)CH_2CH_2\dot{C}H_2}$ provides another example of a 1,5-hydrogen transfer from carbon to oxygen,[8] which is a familiar process in the chemistry of alkoxyl radicals[9] although it does not appear to have been demonstrated there by ESR spectroscopy.

The two remaining reactions, however, need special comment.

The Formation of the ROO· Radicals. Edge and Kochi observed the formation of a broad (1.5 G) singlet, g 2.01502,[2] in the photolysis of *tert*-butyl trimethylsilyl peroxide, which they assigned to the radical $\mathrm{Me_3COO\cdot}$, formed by $\mathrm{S_H2}$ displacement by the trimethylsiloxyl radical at the silicon center (eq 3).

$$\mathrm{Me_3SiO\cdot} + \mathrm{Me_3SiOOCMe_3} \longrightarrow \mathrm{Me_3SiOSiMe_3} + \mathrm{\cdot OOCMe_3} \tag{3}$$

We find that ESR signals of alkylperoxyl radicals may be detected during photolysis of both *tert*-butyl trialkylsilyl peroxides *and* bis(trialkylsilyl) peroxides, but *only* when oxygen or *tert*-butyl hydroperoxide is also present in the system. In particular, photolysis of $\mathrm{Me_3SiOOCMe_3}$, purified by trap to trap distillation from 1,4-diazabicyclo[2.2.2]octane (to remove $\mathrm{Me_3COOH}$[10]), in cyclopropane gave rise, immediately photolysis was commenced, only to the spectrum of $\mathrm{Me_3COOSi(Me_2)\dot{C}H_2}$ (see above) and no signal from $\mathrm{Me_3COO\cdot}$ could be detected. If the peroxide was contaminated with $\mathrm{Me_3COOH}$, a strong spectrum of $\mathrm{Me_3COO\cdot}$ was detected which persisted for a time dependent upon the concentration of hydroperoxide and the light intensity, before being replaced by the spectrum of $\mathrm{Me_3COOSi(Me_2)\dot{C}H_2}$. These results strongly suggest that the $\mathrm{S_H2}$ reaction at silicon proposed by Edge and Kochi (eq 3) is not occurring under these conditions.

Photolysis of $\mathrm{Me_3SiOOSiMe_3}$ in oxygen-free cyclopentane gave rise to the spectrum of the cyclopentyl radical (see above), but in the presence of a trace of oxygen this was replaced by a strong signal from the cyclopentylperoxyl radical[11] (a (H) 7.4 G (1 H) at −120 °C).

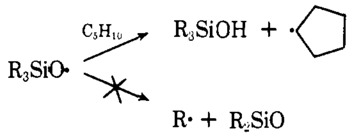
The Formation of the R· Radicals. The β-scission of trialkylmethoxyl radicals (eq 4) is a familiar process,[12] and it is usually rationalized in terms of the similarity in the strength of the σ C–C bond, which is broken, and the π C=O bond, which is formed.

$$\mathrm{R_3CO\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{R_2CO} \tag{4}$$

$$\mathrm{R_3SiO\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{R_2SiO} \tag{5}$$

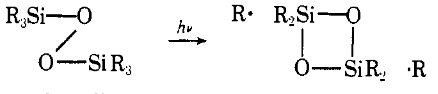
On this basis, the unimolecular β-scission of a trialkylsiloxyl radical (eq 5) would appear to be rather unlikely because the process would be strongly endothermic ($DH°$ (CSi) ca. 76 kcal mol^{-1}, $DH°$ (πSiO) ⩾ 38 kcal mol^{-1} [13]), and indeed the formation of the alkyl radicals was observed only from the photolysis of the bis(trialkylsilyl) peroxides and not from the *tert*-butyl trialkylsilyl peroxides, although both systems involve the formation of trialkylsiloxyl radicals.[14,16]

The relative intensities of the spectra of the ethyl and cyclopentyl radicals were therefore monitored during the photolysis of bis(triethylsilyl) peroxide in a mixture of cyclopentane and cyclopropane, where the concentration of the cyclopentane was varied by a factor of 12. The relative concentrations of the two radicals remained constant over this range, implying that they are not the result of competing unimolecular and bimolecular reactions of the trialkylsiloxyl radical (eq 6).



(6)

One interesting possibility, which avoids the endothermic reaction 5, is the concerted process shown in eq 7. It may



(7)

also be that the alkyl and the siloxyl radicals are derived from excited peroxide molecules of different spin multiplicity.

Acknowledgment. We wish to thank Imperial Chemical Industries, Ltd., and the C. Mahlon Kline Memorial Foundation for the award of Fellowships to P.G.C. and N.A.F., respectively.

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photolysis of *tert*-butyl trimethylsilyl peroxide.[2]

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(6) Between −120 and −40 °C, a second triplet was apparent with a slightly higher g value ($\Delta g = 0.0006$) and showing only a 19.4 G (2 H); this is probably to be ascribed to an $-O\dot{C}H_2$ radical.

(7) We are grateful to Dr. J. A. Howard for discussions concerning the origin of these peroxyl radicals.

(8) Intermolecular abstraction of hydrogen by the photolysis of di-*tert*-butyl peroxide in the presence of hexapropyldisiloxane in cyclopropane at −120° showed the spectra of only the radicals $Pr_3SiOSi(Pr_2)\dot{C}HCH_2CH_3$ (a (Hα) 20.0 (1 H), a (Hβ) 25.3 G (2 H)) and $Pr_3SiOSi(Pr_2)CH_2\dot{C}HCH_3$ (a (Hα) 21.0 (1 H), a (Hβ) 16.7 (2 H), a (CH_3) 24.2 G (3 H)), but no radical resulting from abstraction of hydrogen from the methyl group.

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(14) The relative reactivity of the methyl and ethyl silicon compounds (MeSi < EtSi) by reaction 2 correlates with the relative ease of homolysis of the Me–H and Et–H, or Me–Sn and Et–Sn bonds,[15] and can be related to the higher bond dissociation energy in the methyl compounds.

(15) A. G. Davies and J. C. Scalano, *J. Chem. Soc., Perkin Trans. 2*, 1777 (1973).

(16) Preliminary results show that the behavior of the germyl peroxides is similar to that of the silyl peroxides. When bis(triethylgermyl) peroxide is photolyzed in cyclopentane at −120 °C, a strong spectrum of the ethyl radical is observed; in cyclopropane at −120 °C, the ethyl radical is still present but the radical $CH_3\dot{C}HGeEt_2OOGeEt_3$ is the dominant species (a (CH_3) 26.1, a (CH) 20.7 G). The peroxide $Et_3GeOOCMe_3$ at −120 °C in cyclopropane gave no evidence for the formation of the ethyl radical.

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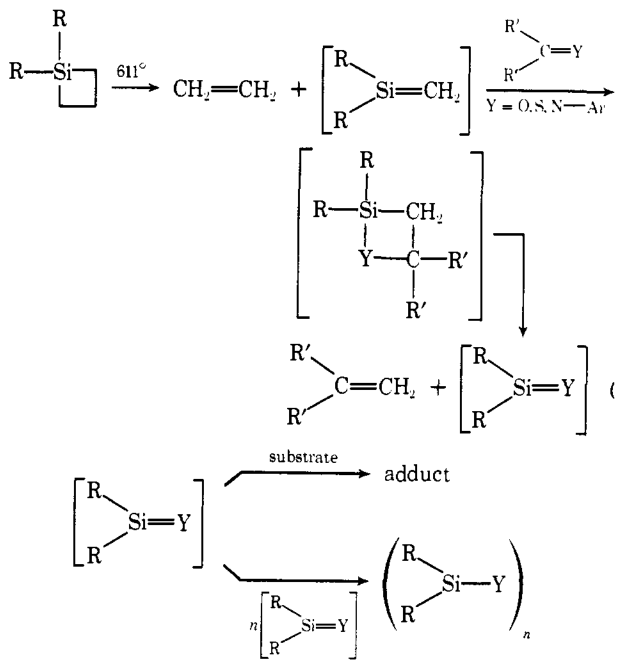
Photolysis of Silyl Azides. Generation and Reactions of Silicon–Nitrogen (p_π–p_π) Doubly Bonded Intermediates. [$R_2Si{=}NR$]

Sir:

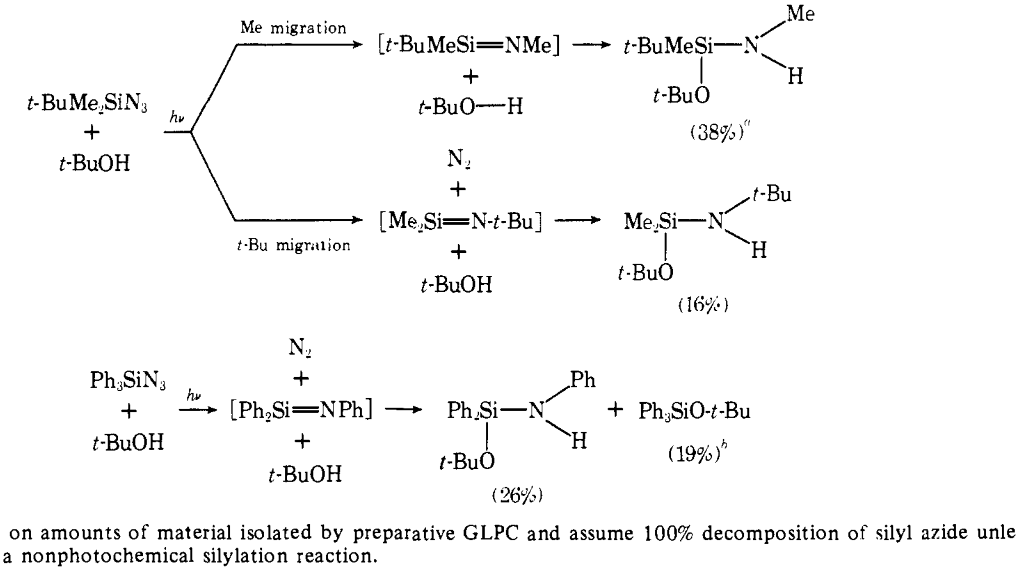
Much interest has been expressed recently in multiply bonded silicon species.[1,2] Silicon has been shown to form (p_π–p_π) double bonds with carbon,[2a] silicon,[2b] oxygen,[2c,2d] nitrogen,[2e] and sulfur.[2f] The usual mode of generation involves *gas phase* copyrolysis of a silacyclobutane, solvent, and substrate (eq 1). Thermolysis of the silacyclobutane forms a silicon–carbon doubly bonded intermediate which then reacts with the desired π-bonded heteroatom. The newly formed multiply bonded silicon species then further reacts either with substrate or with itself in a head to tail manner to give dimer or polymer. The first definitive evidence for thermally generated silicon–nitrogen (p_π–p_π) doubly bonded species, silaimines, [$R_2Si{=}NR$] was obtained via this method.[2e]



(1)

We would like to report the first conclusive evidence for the photochemical generation of silaimines and their reactions in the *condensed phase*. The generation involves irradiation of a silyl azide in the presence of a trapping reagent and solvent (when desired) in a quartz tube under a nitrogen atmosphere. The photolyses were carried out in a Rayonet reactor using Rayonet RPR-2537 lamps. Photolysis of silyl azides in *tert*-butyl alcohol afforded the products shown in Scheme I. These adducts are believed to be the first clear evidence of a silaimine insertion into a σ bond. The products obtained are in accord with analogous ther-

Scheme I



[a] All yields were based on amounts of material isolated by preparative GLPC and assume 100% decomposition of silyl azide unless otherwise noted. [b] From a nonphotochemical silylation reaction.