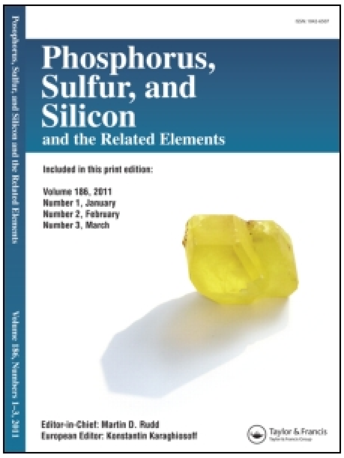

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PHOTOCHEMISTRY OF DI(9-ANTHRYL)- AND BENZYL-SUBSTITUTED SILANES AND RELATED COMPOUNDS[1]

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By irradiation, both di(9-anthryl)dimethylsilane and germane afforded a new type of [4 + 2] intramolecular addition product that underwent quantitative cycloreversion by thermolysis. The photoproduct from the former was converted to a novel naphthotriptycene derivative. A phosphorus analogue, di(9-anthryl)phenylphosphine, however did not undergo the reaction. Photochemical reactions of benzyltrimethylsilane and acyloxymetyl(benzyl)dimethylsilanes ($RC(O)OCH_2SiMe_2CH_2Ph$: $R = CH_3$ and $R = t-Bu$) are also reported for the first time. The mechanisms of these new photochemical reactions are discussed.

INTRODUCTION

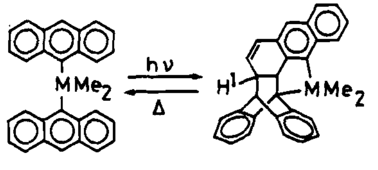
Photochemistry of organosilicon compounds is a relatively new but rapidly growing field of chemistry.[2a] Its importance is recognized not only from the theoretical point of view but from the industrial one, since organosilicon compounds find many new applications in high-technology industries such as photo-image processing and electronics based on the unique photochemical reactivities. We have been working in this field since our discovery of the interesting electronic absorption of certain organosilicon compounds.[2b] In this paper, special attention will be paid to the new photochemistry of di(9-anthryl)-substituted silanes as well as of benzyl-substituted compounds. In the latter, we also discuss an interesting free radical 1,2-acyloxy rearrangement associated with the photoreactions.

RESULTS AND DISCUSSION

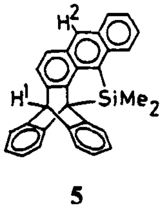
Di(9-Anthryl)-Substituted Silane, Germane, and Phoshorus. Anthracene is known to give a photodimer (para-dianthracene) on irradiation.[3–5] Also, intramolecular reactions are known. For example, di(9-anthryl)methane gave an intramolecular [4 + 4] addition compound (**1**) with a cyclopropane structure. In view of the known high reactivity of silacyclopropane,[6] we have been interested in the photochemistry of the corresponding silicon and germanium compounds and, consequently, we have found an entirely new type of intramolecular photochemical dimerization of anthracene for di(9-anthryl)silanes.[7]

The reaction of 9-anthryllithium, prepared by the reaction of 9-bromoanthracene and *t*-butyllithium, with dimethyldichlorosilane and dimethyldichlorogermane afforded di(9-anthryl)dimethylsilane (**2**) and -germane (**3**) in 35 and 68% yields, respectively.

Irradiation of a benzene solution of **2** with a high-pressure mercury arc lamp with a Pyrex filter gave a photoproduct **4** in 90% yield.[7] The formation of **4** is formally due to the photochemical [4 + 2] reaction which may require mechanistic scrutiny.[8] The reaction may occur from the triplet states of the anthracene derivative but the details of the reaction mechanism are now under investigation. Expectedly, thermolysis of **4** at 250°C for 1 h gave the starting **2** quantitatively by cycloreversion.



2: M = Si **4**: M = Si
3: M = Ge **6**: M = Ge



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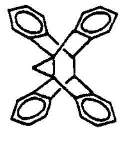

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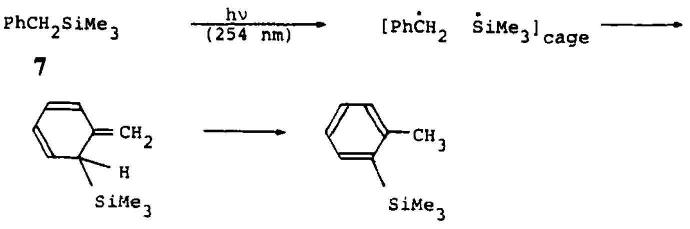
Existence of three methine and two vinylic protons is characteristic of the structure of **4**. The proton H^1 couples with all those protons as evidenced by a decoupling experiment. Correspondingly, four sp^3 carbons other than those of SiCH$_3$ were observed as three doublets and one singlet in ^{13}C NMR. These data indicate unequivocally the structure shown in the equation.

Dehydrogenation of **4** with DDQ in refluxing chloroform gave a new naphthotriptycene derivative **5** in 70% yield. Structure of **5** is verified by ^{1}H NMR, especially by signals characteristic of triptycene (H^1) and anthracene (H^2).

Irradiation of the germanium analog (**3**) under similar conditions gave **6** in 71% yield as colorless crystals, mp 194°C. Similarly to **4**, thermal cycloreversion of **6** at 200°C for 1 h afforded **3** quantitatively.

A phosphorus analogue, di(9-anthryl)phenylphosphine, was prepared similarly by the reaction of *t*-butyllithium and phenyldichlorophosphine but did not undergo the same photochemical reaction.

Benzyl-Substituted Silanes.[9] Whereas benzyltrimethylsilane (**7**) has been described as photochemically inert,[10] the detailed study in our hands revealed that **7** actually isomerized to *o*-tolyltrimethylsilane (**8**) but with very low efficiency.[15] We then speculated that the primary photochemical process of the photolysis of benzylsilane must be the homolysis of a benzyl carbon-silicon bond affording a benzyl-silyl radical pair in the solvent cage and that **8** is formed through recombination of the radical pair, while the major pathway of the reaction is the reproduction of **7**.



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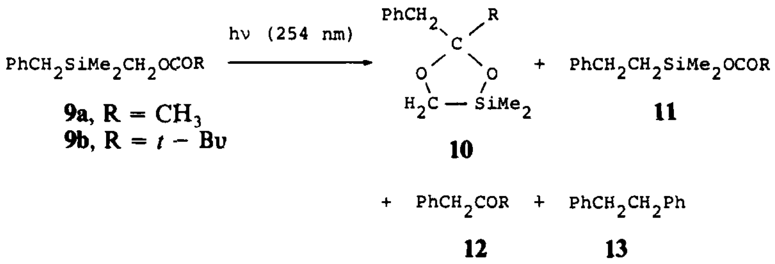
8

We have then designed acyloxymethyl-substituted benzylsilanes, which bear effective intramolecular silyl radical traps, in order to obtain evidence for the formation of the radical pair intermediate in the photoreaction. Intramolecular trapping of a silyl radical by an acyloxy carbonyl group, i.e. free-radical 1,2-(C → Si)-acyloxy migration,[16] may intercept the radical pair formed initially.

Irradiation of acyloxymethyl(benzyl)dimethylsilanes (**9a** and **b**) afforded mainly the corresponding isomers **10** and **11**, benzyl ketones **12**, and bibenzyl (**13**). The reaction conditions, products,[17] and the yields are shown in Table I.



9a, R = CH_3
9b, R = *t* − Bu
10
11
12
13

The formation of these products may well be interpreted as shown in the Scheme involving the initial homolysis of the benzyl carbon-silicon bond followed by the 1,2-(C → Si)-acyloxy migration of the acyloxylmethyldimethylsilyl radical **15**.

Detection of a dioxasilolane (**10a** and **b**) is particularly interesting since the results indicate involvement of the dioxasilolanyl radical (**16**) as an important intermediate of free radical 1,2-(C → Si)-acyloxy migration. In contrast, the corresponding (C → C)-acyloxy migration reportedly does not involve such a cyclic intermediate.[18]

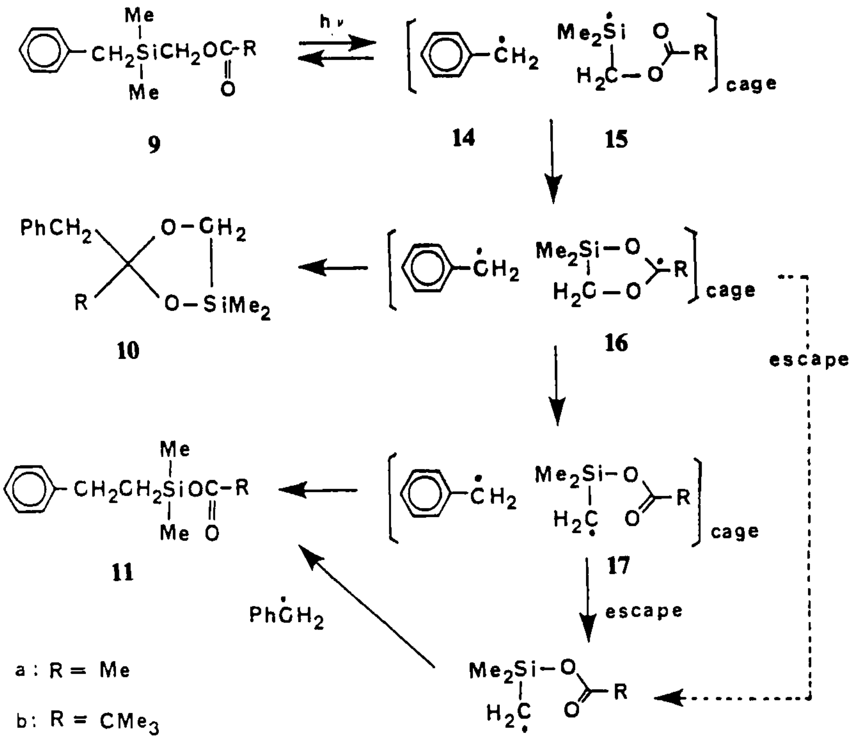
In order to determine whether **10** and **11** were cage or escape products, a 49 : 51 mixture of **9a** and **b**, where the latter was labeled with deuterium at the para-position (89% deuterium content),[19] was irradiated in benzene for 5 h; the conversion of **9a** and **9b** was found by glc analysis to be 76 and 87%, respectively. The deuterium contents of the products were determined by the standard procedure.[19]

Expectedly, the observed $d_0 : d_1 : d_2$ ratio in **13** is compared with a calculated ratio based on the random encounter of the generated benzyl radicals, $d_0 : d_1 : d_2 = 30 : 50 : 20$. Whereas cross products were produced in significant amounts in **9a** and **9b**, no scrambling of deuterium was observed in **10a** and **10b** as well as in recovered **9a** and **9b** within experimental errors. Therefore, it can be concluded that the

TABLE I

Product Distributions of the Photolysis of Benzyl(acyloxymethyl)dimethylsilanes (**9**)

		Products and Yields (%)			
9	Conversion (%)	**10**	**11**	**12**	**13**
a (R = CH_3)	88	11 (0)	13 (0)	4 (14)	13 (14)
b (R = *t* − Bu)	67	21 (0)	24 (0)	0 (21)	16 (16)



formation of **10** occurred only in the solvent cage, but **11** arises as both cage and escaped products. These results imply that **16** is formed in the cage as a transient species during the acyloxy migration. The success of detecting **10** in the present case may be a result of the concurrent generation of an effective radical trap such as **14** in the vicinity of **16**.

We have obtained ESR evidence for supporting the mechanism shown here but the details will be published elsewhere.

Di(9-anthryl)silanes and benzylsilanes are only two examples of interesting photoreactive silicon compounds. Elucidation of the mechanism and extension to sulfur and phosphorus compounds will be a fruitful future new area of photochemistry.

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