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PHOTOCHEMISTRY OF BICHROMOPHORIC SYSTEMS. SILICON GUIDED INTRAMOLECULAR 9,10 : 1', 2' ANTHRACENE PHOTODIMERIZATION IN BIS(9-ANTHRYL)DIMETHYLSILANE. ≠

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SUMMARY : Irradiation of bis(9-anthryl)dimethylsilane (1) generates a single photocyclomer formed by $(4_\pi + 2_\pi)$intramolecular 9,10 : 1',2'anthracene photodimerization. The influence of the silicon atom was investigated by reaction quantum yield determination and fluorescence study (stationary state and lifetimes).

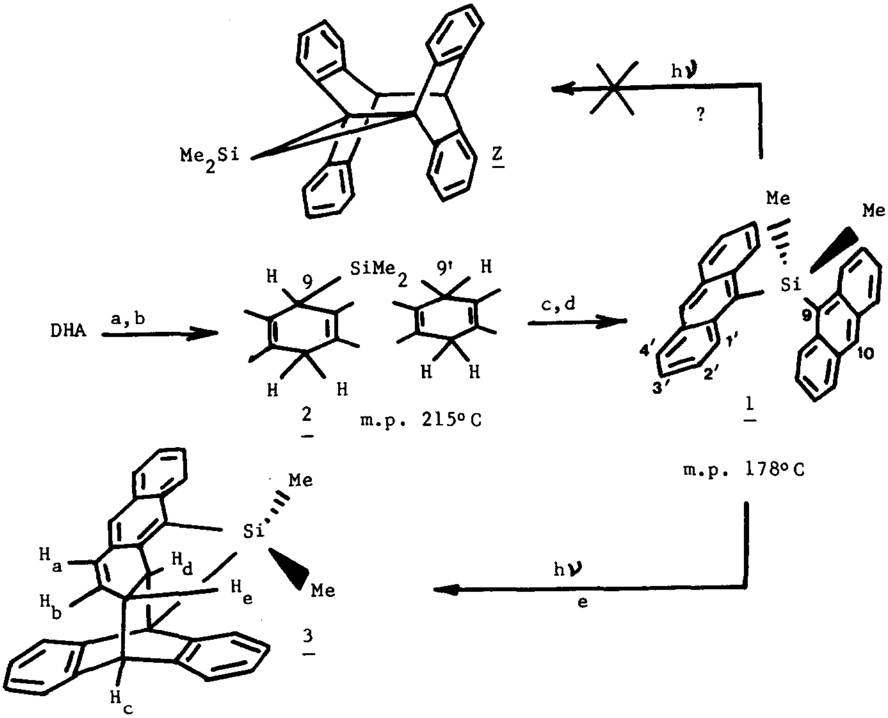
Isolation of stable compounds containing the silacyclopropane system was first achieved by Seyferth[1] by substituting the ring carbon atom with bulky groups. It occurred to us to take advantage of the easy photocyclomerization of 9,9'-bisanthracenes[2] to generate a crowded derivative of silacyclopropane by irradiation of bis(9-anthryl)dimethylsilane (1). The anticipated product (Z) was not actually isolated but a new compound (3) was obtained as a single photoproduct. Herein we report the synthesis and preliminary results of a photochemical study of 1 in different solvents. In parallel, 9-trimethylsilylanthracene (4) was examined as the monochromophoric reference compound.

Harvey's method[3], successful in the preparation of 4 was applied to the synthesis of 1 with an overall yield of 13% from 9,10 dihydroanthracene in pure isolated compound (see scheme). A noticeable feature of the ^1H n.m.r. spectrum of 1 is the deshielding of the protons of the $SiMe_2$ group (s, 6H at δ 1.26 ppm in $CHCl_3$ ref TMS) in comparison with the $SiMe_3$ 9 proton peak of 4 appearing at δ 0.63 ppm. In addition, a comparison of the u.v. absorption of 1 and 4 in methylcyclohexane[4] (MCH), CH_3CN and MeOH shows little solvent effect but a clear hypochromic effect for the ^1B_b band of the bichromophore and a bathochromic effect for the ^1L_a band ($\Delta\bar{\nu} \simeq 350\ cm^{-1}$). The latter is assigned to an interaction between the rings while the absence of significant effect for the ^1L_a transition indicates that the short axes tend to adopt an angle close to orthogonal. The other n.m.r. data are in agreement with this proposed ground state conformation (scheme).

Irradiation of 1 in MCH or ether (conc $\cong 10^{-4}$M at $\lambda \geqslant$ 320 nm) with a high pressure mercury lamp yields a single photoproduct identified as 3 by n.m.r. and u.v. spectroscopy.[5] Recording the u.v. spectra at different times during the irradiation shows the disappearance of the anthracene absorption and the formation of a new spectrum absorption maxima in MCH λ_{max} (nm) and (ε) : 390 (75) ; 370 (155) ; 356 (600) ; 340 (685) ; 310 (7375) ; 298.5 (9420) ; 263 (23,700) ; 254 (24,900) with an isosbestic point at 315 nm (fig.1). These data are consistent with those of a substituted 2-vinylnaphthalene[6]. The n.m.r. spectrum[7] is in full agreement with 9,10 : 1',2' intramolecular bounding between the two aromatic rings*.

This new type of cyclomerization in which the "1,2 bond of anthracene π system participate as a dienophile in a Diels-Alder reaction" has recently been observed by Becker as one of the possible photoreaction pathways of bis-9 anthryl ethylenes[8a] or bis-9 anthryl ethanes [8b]. But the present case is still more peculiar by the fact that a bis-9 anthracene with a one atom hinge yields the new photocyclomer as a single product. By contrast, bis-9 anthrylmethane readily photocyclomerizes at the 9,10 : 9',10' positions[9].

The fact that the photocyclomer Z was not observed may be explained by thermodynamic instability of Z or the absence of a favourable conformation in the excited state of 1; the latter would rather adopt a geometry leading to $4_\pi + 2_\pi$cycloaddition. If molecular models do not allow an obvious answer as regards the conformations, they show that the observed product (3) should be less strained than the anticipated Z. In order to gain deeper insight into the mechanism, we determined the reaction quantum yield in the three solvents used to examine the absorption spectra and studied the fluorescence under stationnary (see table) and transient kinetic conditions.



a) BuLi, THF . b) Cl_2SiMe_2 . c) BuLi, TMEDA . d) 2 $CdCl_2$. DHA = 9,10 dihydroanthracene .
e) Conc ≃ 10^{-4} in Et_2O or MCH, 500W high pressure mercury lamp, 17h, quantitative yield.

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* all other analytical data are in agreement with the proposed formula.

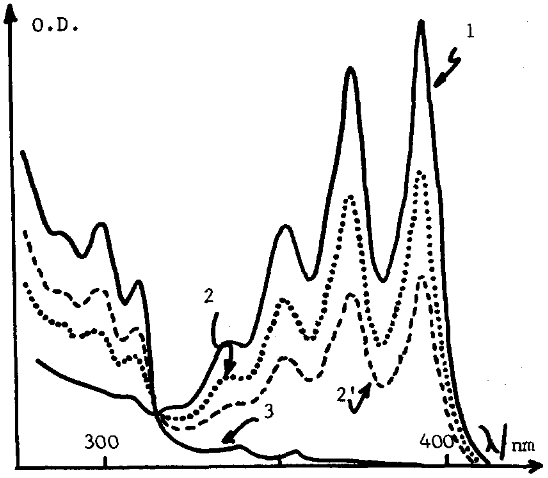

Fig. 1 - UV spectrum recording of the photochemical reaction : curve 1 : compound 1 before irradiation; curves 2 and 2' : after respectively 15 and 30 mn irradiation; curve 3 : photocyclomer 3.

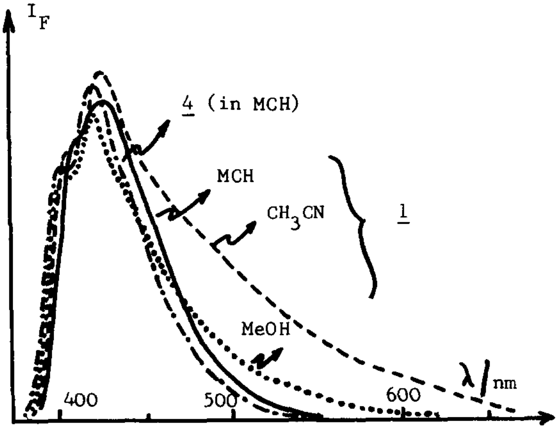

Fig. 2 - Fluorescence spectra of 1 in methylcyclohexane (MCH), CH_3OH and CH_3CN and of 4 in MCH.

As shown in figure 2, the fluorescence spectra of 1 are displaced towards long wavelengths compared to the spectrum of the reference compound 4, especially in polar solvents where the red shift is accompanied by fluorescence quenching (table); this denotes some polar character of the excited singlet state of 1. The fluorescence of the bichromophore displays a single exponential decay and the lifetimes[10a] increase in CH_3OH and CH_3CN contrary to Φ_F. This might be ascribed to a change of conformation in the excited state with the solvent characteristics. By comparison, the reference compound 4, exhibits higher fluorescence quantum yields in MCH and CH_3CN and an important quenching in CH_3OH (table). The same is true for 9-dimethylt-butyl silylanthracene[11] (5) whereas the fluorescence emission of 9-trimethylsilylmethylanthracene (6) is not quenched in CH_3OH. The quenching in CH_3OH is accompanied by a clear decrease of the single exponential fluorescence decay[10b-d] lifetimes in 4 and 5 in contrast to the behaviour of 6. These data suggest some specific interaction between methanol and the silicon

Table

Fluorescence (Φ_F) and reaction (Φ_R at 366 nm) quantum yields of degassed compounds 1 and 4 in methylcyclohexane (MCH) methanol and acetonitrile at R.T. in the conc. range 1-5 x 10^{-5}M. §A = 9-anthryl.

Quantum Yield	Φ_F	Φ_F	Φ_R 366 nm
Compound Solvent	$ASiMe_3$ 4 §	$ASiMe_2A$ 1 §	$ASiMe_2A$ 1 §
MCH	0.65	0.45	0.05
CH_3OH	0.27	0.10	0.08
CH_3CN	0.71	0.05	0.06

bonded to the π system.

The reaction quantum yields are similar and rather low for intramolecular processes and do not seem to be connected to the fluorescence properties. Other ($4\pi + 2\pi$) photocyclizations have been observed with anthracenes[8,12] but the excited state responsible for the reaction do not appear to have been well characterized. In view of testing the participation of the triplet state in the formation of 3, preliminary experiments were carried out with $HgMe_2$ known to increase intersystem crossing between S_1 and T_1 of anthracenes[13]; in the presence of $HgMe_2$ (2.5M), irradiation of 1 (5×10^{-5}M) in MCH resulted in lowering the rate of photocyclomerization by ca 2; the fluorescence was also quenched. Although this is not in favour of a triplet reaction, further investigation is needed to firmly establish the mechanism.

In conclusion, we have shown that the presence of a silicon atom as a hinge between two anthracene rings can induce an unusual reaction. Further studies on the photophysics of the aromatic silanes are in progress.

≠ Dedicated to Professor R. Calas on the occasion of his 70th birthday.

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11. Fluorescence quantum yield (Φ_F) in MCH, CH_3OH and CH_3CN respectively, at R.T. Bu^tMe_2SiA (5) : 0.79 ; 0.37 ; 0.80 : Me_3SiCH_2A (6) : 0.77 ; 0.80 ; 0.80.
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