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PHOTOCHEMISTRY
AND MAGNETOCHEMISTRY

Photochemical Reactions of 9-Trimethylstannylanthracene in Various Solvents

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Abstract—9-Trimethylstannylanthracene (**1**) was synthesized and its photolysis by 365-nm light was studied. In aprotic solvents, the dimerization of **1** involves positions 9 and 10 and yields a head-to-tail dimer. The main route of the photolysis of **1** in alcohols is the cleavage of the C–Sn bond with the formation of anthracene. The quantum yields of the photoreaction and the lifetimes and quantum yields of **1** fluorescence were determined.

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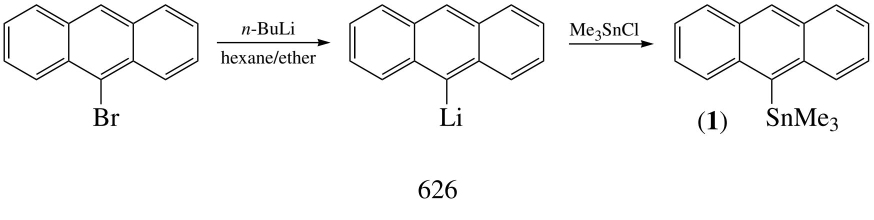
Photochemistry of anthracene derivatives has been extensively studied for many years. Irradiation of anthracene and its derivatives leads to its dimerization with the formation of a new carbon–carbon bond between positions 9 and 10 [1–3]. The loss of aromaticity in the central rings leads to the disappearance of the anthracene absorption band in the 300- to 400-nm range and the appearance of an absorption band near 270 nm. When irradiated in the 270-nm band or subjected to thermolysis, the photodimer decays to yield the initial molecule. This reversibility of photodimerization makes it possible to use anthracene derivatives as photochromic materials. In this work, we synthesized 9-trimethylstannylanthracene (**1**) and examined its photochemical behavior in various solvents.

EXPERIMENTAL

Proton NMR spectra were recorded on a Bruker AVANCE 600 spectrometer at 600 MHz in a THF-d_8 solution (Merk, 99.9% deuterium content, no additional purification). The absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. The fluorescence spectra were recorded on a Perkin-Elmer LS 50 spectrofluorimeter. The fluorescence lifetimes were measured with an Applied Optics SP-70 nanosecond spectrometer. The extinction coefficient of the last absorption band of **1** (at 385 nm) in methanol was found to be 11000 ± 500 M^{-1} cm^{-1}. Irradiation of 10^{-4} M solutions of **1** in various solvents was conducted in quartz glass cells (10 × 10 mm) using emission from a DRSh-500 mercury lamp with a filter isolating the 365-nm mercury line. The quantum yields of the photochemical reactions were calculated from the data on the changes in the absorption spectra during photolysis and the dose of absorbed light with the help of the Mathcad 2001i software.

The intensity of light absorbed by the sample was determined using an F-4 phototube calibrated with a ferrioxalate actinometer [4]. To determine the composition of the reaction mixture by ^{1}H and ^{13}C NMR, we conducted parallel experiments in which solutions of **1** in THF-d_8 (10 wt %) were irradiated in sealed evacuated ampules.

9-Trimethylstannylanthracene (**1**) was synthesized by the reaction of 9-lithioanthracene, prepared according to [5], with the equimolar amount of trimethylchlorostannane:



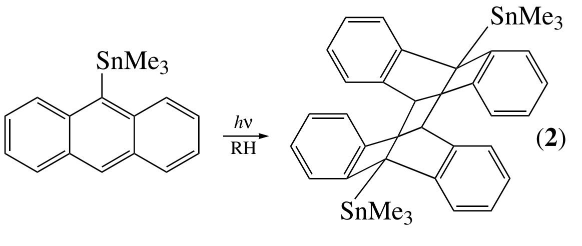
A solution of BuLi in hexane (1.79 M, 7 ml) was added to a solution of 9-bromoanthracene (3.15 g, 12.25 mmol) in diethyl ether (~70 ml, freshly distilled over sodium ketyl in an argon atmosphere) at ~20°C under conditions of incessant stirring. After a yellowish precipitate was formed, the mixture was stirred for 5 min and blended with a solution of Me_3SnCl (2.44 g, 12.25 mmol) in diethyl ether (15 ml), after which the resultant solution was left for ~8 h. The reaction mixture was stratified with water, the layers were isolated, and the organic layer was washed twice with water until neutral reaction and dried over Na_2SO_4. The solvents were removed in vacuum created by an oil pump. The residual was recrystallized from hexane (15 ml) at –12°C. As a result, we obtained 1.51 g (36.2%) of $C_{17}H_{18}Sn$ in the form of white crystals with a melting point of 70.7–71.5°C. The measured composition was 59.53% C and 5.24% H, as compared to the calculated composition 59.88% C and 5.32% H.

^1H NMR spectrum, δ(ppm): 0.658 (s. $\underline{Me_3}Sn$, $J_{(117Sn-1H)} = 52.2$ Hz, $J_{(119Sn-1H)} = 54.0$ Hz); 7.420 (t., $H_{2,7}$ or $H_{3,8}$); 7.496 (t., $H_{2,7}$ or $H_{3,8}$); 7.970 (d., $H_{1,8}$); 8.247 (d., $H_{4,5}$); 8.402 (s., H_{10}).

^{13}C NMR spectrum, δ (ppm): -4.55 (s. $\underline{Me_3}Sn$, $J_{(117Sn-13C)} = 332$ Hz, $J_{(119Sn-13C)} = 347.1$ Hz); 125.42 (C_6); 125.92 (C_7); 130.22 (C_{10}, $^1J_{(117,119Sn-13C)} = 4.4$ Hz); 130.82 (C_1, $^1J_{(117Sn-13C)} = 38.9$ Hz, $^1J_{(119Sn-13C)} = 40.2$ Hz); 132.65 (C_{12}, $^1J_{(117Sn-13C)} = 39.0$ Hz, $^1J_{(119Sn-13C)} = 40.7$ Hz); 139.24 (C_{11}, $^1J_{(117Sn-13C)} = 28.4$ Hz, $^1J_{(119Sn-13C)} = 27.3$ Hz); 143.46 (C_9, $^1J_{(117Sn-13C)} = 456.3$ Hz, $^1J_{(119Sn-13C)} = 477.4$ Hz).

RESULTS AND DISCUSSION

When **1** was irradiated with 365-nm light in aprotic solvents, the absorption band in the 300- to 400-nm range decreased gradually and a new band near 270 nm appeared (Fig. 1a), a behavior indicative of photodimerization [6]:



(**2**)

The NMR spectra of the reaction medium clearly showed that a head-to-tail photodimer (**2**) was formed. The ^1H NMR spectrum of the reaction medium exhibited a 3.6-ppm resonance signal ($^3J_{(117Sn-1H)} = 71.5$ Hz, $^3J_{(119Sn-1H)} = 73.0$ Hz), which belongs to the protons in the central cycle at $C_{10,\,10'}$.

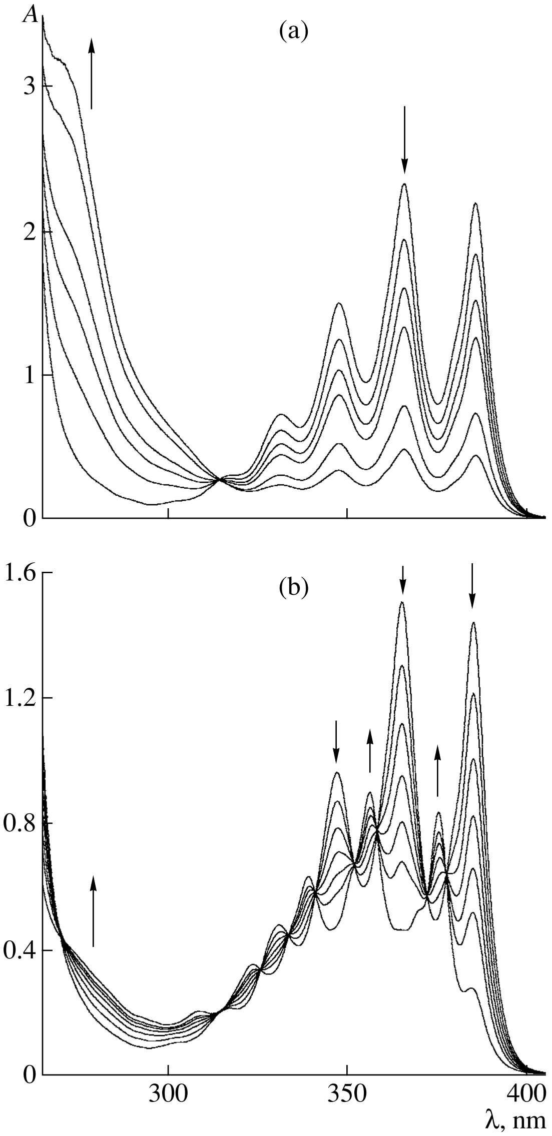
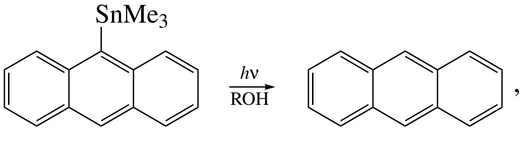


Fig. 1. Time evolution of the absorption spectrum of 9-trimethylstannylanthracene during its irradiation with the 365-nm mercury line in (a) acetonitrile and (b) methanol.

For irradiation **1** in alcohol, the main photoreaction is the cleavage of the C–Sn bond with the formation of anthracene:



This reaction is characterized by an 80–90% yield, with photodimerization becoming a process of minor importance. The quantum yields of photodimerization and anthracene formation in various solvents are listed in Table 1. To calculate the quantum yield of anthracene formation, we used a 375-nm extinction coefficient of

Table 1. Quantum yields of dimerization Φ_1 and anthracene formation Φ_2 during irradiation of 9-trimethylstannylanthracene with the 365-nm mercury line in various solvents at various p*K* values of the alcohols

No.	Solvent	$\Phi_1 \times 10^2$	$\Phi_2 \times 10^2$	p*K* [11]
1	Heptane	0.21	–	
2	Benzene	0.37	–	
3	Acetonitrile	3.35	–	
4	Methanol	0.6	4.8	15.22
5	Ethanol	0.4	2.6	15.84
6	Isopropanol	0.24	0.72	16.94
7	Trifluoroethanol	–	28	12.37

Note: The quantum yields are given for a 9-trimethylstannylanthracene concentration of 1×10^{-4} M.

Table 2. Lifetimes τ_0 and quantum yields φ_{fl} of 9-trimethylstannylanthracene fluorescence in various solvents

	Solvent	$\tau_0 \times 10^9$, s	φ_{fl}
1	Methanol	3.0	0.13
2	Heptane	3.2	0.15
3	Ethanol	3.5	0.17
4	*sec*-Butanol	3.5	0.18
5	Isopropanol	3.8	0.19
6	Acetonitrile	4.6	0.22
7	Benzene	5.6	0.3
8	Toluene	6.4	0.34

Note: The quantum yields and lifetimes were measured with an accuracy of 10%.

8500 $\text{M}^{-1}\,\text{cm}^{-1}$ [7]. When trifluoroethanol is used as the solvent, the formation of anthracene proceeds rapidly even without irradiation, at a rate constant of $2.7 \times 10^{-4}\ \text{s}^{-1}$. For this solvent, the quantum yield of anthracene formation under irradiation is higher than for the other alcohols by an order of magnitude (Table 1).

The formation of anthracene during photoexcitation of **1** in alcohols can proceed by one of the two mechanisms. The basicity of aromatic molecules in an excited state is higher by several orders of magnitude [8]; therefore, position 9 of **1** in an excited state can be protonated by an alcohol, as its ground state is protonated by strong acids. When a droplet of concentrated acetic acid was added to acetonitrile (5 ml), anthracene was formed without irradiation. In this case, the C–Sn bond is broken via the direct attack of the electrophile. Another possible mechanism involves the formation of a complex alcohol molecule with an excited molecule **1**, which then decays via the concerted cleavage of the Sn–C and RO–H bonds. These two mechanisms were discussed to interpret the photochemical cleavage of 9-trimethylsilylanthracene (a silicon analog of anthracene) by alcohols [9]. The authors found that the fluorescence lifetime and quantum yield of 9-trimethylsilylanthracene are half as large in methanol as in acetonitrile and methylcyclohexane and concluded that the photoprotonation of this compound with alcohols proceeds according to the second mechanism.

We measured quantum yields and lifetimes of **1** fluorescence in various solvents (Table 2). To determine the fluorescence quantum yields of **1**, we used anthracene as a reference with known fluorescence quantum yield (0.3 [10]). In contrast to the results obtained in [9] for 9-trimethylsilylanthracene, the fluorescence of **1** in alcohols exhibits neither an anomalous quantum yield nor an anomalous lifetime as compared with the other solvents. The quantum yields of anthracene formation during irradiation of **1** in alcohols (Table 1) correlate with the p*K* values for the alcohols. Based on the obtained experimental data, we cannot favor any of the mechanisms.

The quantum yield of dimerization of **1** and that of its cleavage with the formation of anthracene did not change after the solutions were blown with argon; therefore, we concluded that the reagents were in a singlet excited state. Thus, we can write down the following kinetic scheme of the dimerization of **1**:

$$\text{A} + h\nu \longrightarrow \text{A}^* \quad (w_0),$$

$$\text{A}^* \longrightarrow \text{A} \quad (k_0 = k_{\text{f}} + k_{\text{isc}}),$$

$$\text{A}^* + \text{A} \longrightarrow 2\text{A} \quad (k_{\text{d}}),$$

$$\text{A}^* + \text{A} \longrightarrow \text{A}_2 \quad (k_{\text{R}}),$$

where w_0 is the rate of light absorption by the sample; k_{f} and k_{isc} are, respectively, the fluorescence and intersystem-crossing rate constants; k_{d} is the rate constant of the deactivation of the excited molecule; and k_{R} is the photodimerization rate constant.

Thus, the quantum yield of photoreaction is

$$\Phi_{\text{R}} = \frac{(k_{\text{d}} + k_{\text{R}})\tau_0[\text{A}]}{1 + (k_{\text{d}} + k_{\text{R}})\tau_0[\text{A}]}\gamma, \tag{1}$$

where γ is the ultimate yield of photodimerization, a quantity defined as

$$\gamma = k_{\text{R}}/(k_{\text{d}} + k_{\text{R}}). \tag{2}$$

Since photodimerization was conducted at low concentrations of **1** ($<3 \times 10^{-4}$ M), the value $(k_{\text{d}} + k_{\text{R}})\tau_0[\text{A}]$ is negligibly small compared to unity, and, therefore, the quantum yield of the reaction is proportional to the concentration of **1**. The quantum yield of the photodimerization of **1** was plotted against its concentration (Fig. 2). This dependence is nearly linear, with a slope of $(k_{\text{d}} + k_{\text{R}})\tau_0\gamma$. Assuming that the sum of the rate constants of deactivation and dimerization is equal to the diffusion rate constant ($1 \times 10^{10}\ \text{M}^{-1}\,\text{s}^{-1}$ for benzene [12]), the slope of the plot in Fig. 2 (equal to 38.5 M^{-1}) yields an ultimate yield of photodimerization of ~0.7. This means that $k_{\text{R}} = 7 \times 10^9\ \text{M}^{-1}\,\text{s}^{-1}$ and $k_{\text{d}} = 3 \times 10^9\ \text{M}^{-1}\,\text{s}^{-1}$.

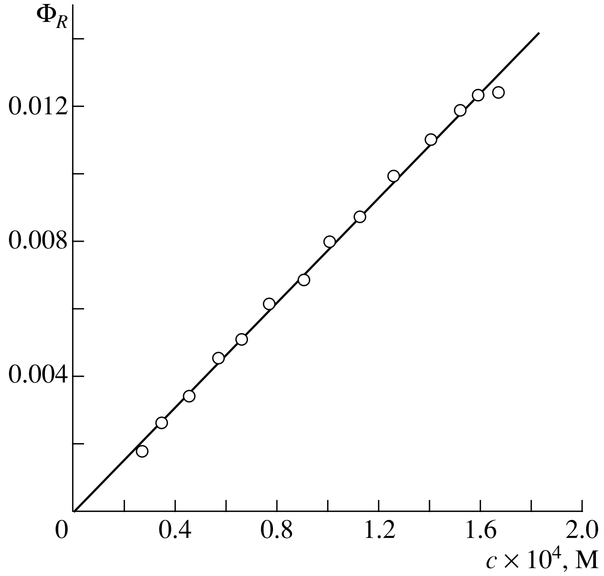


Fig. 2. Quantum yield of the dimerization of 9-trimethylstannylanthracene in benzene as a function of the concentration of the former.

Thus, we established that irradiation of 9-trimethylstannylanthracene (**1**) in aprotic solvents leads to its dimerization, while the cleavage of the C–Sn bond with the formation of anthracene is the main process in protic solvents, with dimerization playing only a minor role.

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