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SYNTHESIS AND PHOTOCHEMISTRY OF 2-TRIMETHYLSTANNYL-1,3-BUTADIENE

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Summary

2-Trimethylstannyl-1,3-butadiene has been synthesized by a Würtz-type coupling reaction and submitted to direct excitation by light of 253.7 or 228.8 nm wavelength in cyclohexane solution. The photolysis produced, with equally low quantum yields, polymers and three valence isomers identified as 1-trimethylstannylcyclobutene, 1-methylene-2-trimethylstannylcyclopropane and 3-trimethylstannyl-1,2-butadiene; the latter is not a primary product and is believed to arise from the thermal rearrangement of 3-methyl-3-trimethylstannylcyclopropene. No homolytic splitting of the excited molecule could be detected. The disappearance quantum yield of 2-trimethylstannyl-1,3-butadiene exhibits a strong concentration dependence from which a lowest lifetime limit of 3×10^{-7} s is deduced for the excited state. The complex-forming ability and the long lifetime which are associated with the presence of the tin atom suggest that an important interaction occurs between the π^* system and the empty 5*d* orbitals of the metal.

Introduction

Little work has been done on the photochemistry of organotin compounds, and in most cases the major processes which are reported correspond to the cleavage of a carbon—tin bond followed by thermal free radical reactions [1]. The light-induced transformations might provide a useful means of synthesizing relatively complex structures which may be accessible only with difficulty via thermal routes because of the weakness and high reactivity of the metal—carbon bond; conversely the empty 5*d* orbitals of tin, whose importance has been well established for the ground state reactions [2], might well induce new or enhance known photochemical transformations of organic substrates. We describe below a study of the response of 2-trimethylstannyl-1,3-butadiene (TMSB) to direct excitation by light of 253.7 or 228.8 nm wavelength in cyclohexane solution.

The results provide direct information on the extent to which the tin atom is capable of interfering with the well documented properties of the diene chromophore [3].

Experimental

Synthesis of TMSB

In order to avoid the formation of a mixture of dienes [4] substituted in positions 1 and 2, which would prove difficult to separate, we used a modified version of the Würtz-type coupling reaction described by Juenge [5].
A solution of sodium naphthalene was prepared by treatment of 1.8 g of sodium wire with 2 g of sublimed naphthalene in 30 ml of DME* freshly distilled over H_4AlLi; Me_3SnNa was then prepared by dropwise addition, with vigorous stirring of 7.5 g of Me_3SnBr dissolved in 30 ml of DME, the addition being carried out at 0° at a rate such that an excess of sodium naphthalene was present throughout, as indicated by the persistence of the green color. (This is essential to prevent the production of hexamethylditin.) Chloroprene was then freshly distilled under helium from a stabilized solution in toluene, and 2.4 g were immediately transferred under vacuum and trapped at 77 K in a funnel containing 8 ml of DME; this solution was added at room temperature to Me_3SnNa over a period of not less than 60 min and the reaction was then completed by heating at 60° for 15 min. Since unchanged chloroprene would readily polymerize and also copolymerize with TMSB, it is essential both to avoid any excess of it and to maintain its concentration as low as possible during the addition; the coupling is not rapid, in line with the chemical inertness of chlorine in chloroprene**. It is essential that all the steps described above are carried out in the absence of air and moisture; the apparatus was thus fitted to a vacuum line allowing transfer of reactants from bulb to bulb and reaction under either their own vapor pressure or an atmosphere of helium***. At this stage the mixture was worked up according to a usual procedure: following hydrolysis with ice, TMSB was extracted with ether, the solution dried over $MgSO_4$ and the ether distilled off. The residue was chromatographed on silica using cyclohexane as the eluant, and the fractions which decolorized a dilute solution of bromine in CCl_4 were collected. Removal of the solvent gave 3.5 g (60% yield) of TMSB which was pure to VPC except for a trace of cyclohexane. For photolysis experiments the product was further purified by preparative GLC.

Analysis and spectrometric characterization of TMSB

The product gave a satisfactory analysis, (found: C, 38.65; H, 6.47. $C_7H_{14}Sn$ calcd.: C, 38.77; H, 6.51%). It reacted with HCl to give Me_3SnCl and 1,3-butadiene as the only products. When pure and stored under helium it was found to be fairly stable at room temperature, and did not polymerize

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[*] Dimethoxyethane: the nature of the solvent is very important; with THF a fast and complete polymerization predominates, when chloroprene is added.

[**] Chloroprene reacts neither with Ag^+ nor with Corey's reagent R_2LiCu [16].

[***] Helium N45 from "L'Air Liquide".

to any appreciable extent during several weeks at −20°. The structure was confirmed by spectroscopic analysis. The UV spectrum recorded in cyclohexane on a Cary 14 instrument resembled closely that of isoprene in respect of the $\pi \rightarrow \pi^*$ transitions, with poorly resolved maxima at 217.5 (ϵ 14300 cm^2 mol^{-1}), 222 (ϵ 14800 cm^2 mol^{-1}) and 230 nm (sh) (ϵ 11000 cm^2 mol^{-1}), but exhibited an unusually large tailing towards long wavelengths (ϵ_{254} 600 cm^2 mol^{-1}), which may be associated with a soft transition into an anti-bonding orbital involving the 5*d* orbitals of tin. The O—O band can thus not be assigned. The IR spectrum was recorded in CCl_4 on a Perkin—Elmer 357 instrument and showed the expected strong absorptions at 3090-3055, 2990-2890, 1615 (C=C), 1390 (CH_3), 1195 and 710 (Me_3Sn), 998 and 920 ($HC{=}CH_2$) and 905 cm^{-1} ($C{=}CH_2$). The mass spectrum recorded with a Hitachi—Perkin—Elmer RMU-6D instrument at 70 eV showed the following pattern of *m/e* ratios (based on ^{120}Sn) and intensities: 218 ($C_7H_{14}Sn^{+\cdot}$) 2.3, 203 ($C_6H_{11}Sn^+$) 39.2, 173 ($C_4H_5Sn^+$) 2.4, 165 ($C_3H_9Sn^+$) 100, 151 ($C_2H_7Sn^+$) 13.5, 150 ($C_2H_6Sn^{+\cdot}$) 6.3, 135 (CH_3Sn^+) 34.3, 121 (HSn^+) 7, 120 ($Sn^{+\cdot}$) 7, 53 ($C_4H_5^+$) 1.3. It is noteworthy that, in contrast to the behavior of vinylmethyltins [6], the preferred cleavage takes place at the C(sp^2)—Sn bond, which is not what would be expected from the non-allylic character of C2 in 1,3-butadienes. This might reflect assistance to the σ bond breaking by $\pi \rightarrow d$ back donation. The general rule favoring the production of fragments in the Sn^{II} and Sn^{IV} states is seen to hold. The PMR spectrum obtained in CCl_4 from a Varian T60 spectrometer bears close analogy with that of 1,3-butadienylmagnesium chloride [7], and confirms unambiguously the structure of TMSB: δ 6.5 (1H, dd, J 17 and 10 Hz), 5.8 (1H, d, J 2.5 Hz), 5.3 (1H, d, J 2.5 Hz), 5.0 (1H, d, J 10 Hz), 4.9 (1H, d, J 17 Hz) and 0.2 ppm (9H, s, $J(^{117}Sn{-}CH_3)$ 53.5 Hz).

Photolyses

All photolyses were performed on degassed cyclohexane solutions of TMSB contained in sealed quartz cells. Preparative runs were carried out in an annular vessel coaxial with an RPR Rayonet low pressure mercury lamp ($I_a = 4.4 \times 10^{15}$ quanta s^{-1} cm^{-3} at 253.7 nm)*. For the trapping and identification of the products the conversion of a 10^{-2} mol l^{-1} solution was allowed to proceed to 50%, most of the cyclohexane was then removed under reduced pressure and the residue analyzed by VPC with an F&M model 500 fractometer fitted with a 4 m, Apiezon L 20% column heated at 85°. All the products were trapped at 77 K.

The self-quenching of TMSB was studied at lower conversions (< 20%) in the range from 1.5×10^{-4} mol l^{-1} (followed by UV at 240 nm) up to 10^{-2} mol l^{-1} (checked by VPC with n-pentane as internal reference), using optical cells (1 cm path length) and the 228.8 nm output of a Philips No. 93107 cadmium lamp ($I_a = 1.5 \times 10^{14}$ quanta s^{-1} cm^{-3}) in order to ensure a constant absorption of light even at the lowest concentrations.

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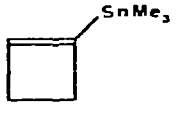
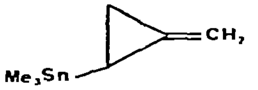
* Calibrated by conventional ferrioxalate actinometry, the figure including a correction for the output at higher wavelengths.

Results and discussion

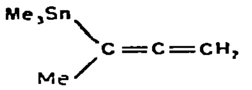
Direct photolysis of TMSB yielded in significant amounts three products isomeric with the starting material (mol. wt. by mass spectrometry 218 based on ^{120}Sn) along with an equivalent quantity of polymers. When not more than 20% of TMSB was converted, these isomers accumulated according to a linear function of time with a zero intercept, thus indicating that they are primary products. The first isomer had infrared absorptions at 705 and 1190 (Me_3Sn), 880 ($C{=}CH_2$), 1723 ($C{=}C$) and 1120 cm^{-1} (small ring). Its PMR spectrum consisted of absorptions at δ 5.24 (2H, m), 0.8 (3H, broad) and 0.07 ppm (9H, s $J(^{117}Sn{-}CH_3)$ 53.5 Hz). The structure 1-methylene-2-trimethylstannylcyclopropane (II) would fit all these data, including the high $C{=}C$ stretching frequency [8]. The second isomer had a much less characteristic infrared pattern, with absorptions at 705 and 1190 (Me_3Sn), 1614 ($C{=}C$) and 870 cm^{-1} ($C{=}CH$); its NMR spectrum showed absorptions at δ 5.13 (1H, broad), 2.82 (2H, t, J 3 Hz), 2.59 (2H, t, J 3 Hz) and 0.10 ppm (9H, s, $J(^{117}Sn{-}CH_3)$54.4 Hz). The presence of only one olefinic proton for the formula $Me_3Sn{-}C_4H_5$ suggested a cyclic structure, 1-trimethylstannylcyclobutene(I), and this was confirmed by the fact that the product readily reverted thermally to the initial TMSB. The third isomer proved unstable to the conditions of the TCD system of our fractometer: after being trapped as a recorded single peak and reinjected in VPC it produced two peaks, none of which had the initial retention time; these two products were trapped and analyzed. One of them was identical to TMSB and the other had characteristic IR absorptions at 848 ($C{=}CH_2$), 1948 ($C{=}C{=}C$), 1438 and 1345 (CH_3 adjacent to a double bond), 708 and 1190 cm^{-1} (Me_3Sn), and NMR signals at δ 4.98 (2H, broad), 1.56 (3H, broad) and 0.23 ppm (9H, s, $J(^{117}Sn{-}CH_3)$52.5 Hz). The compound 3-trimethylstannyl-1,2-butadiene (III) unambiguously fits the data. By analogy with the known thermal rearrangement of cyclopropenes [9], and given the predominance of allenes over acetylenes when the system is bound to tin [10], it is evident that the primary unisolated photoproduct was 3-methyl-3-trimethylstannylcyclopropene (IV).



(I)

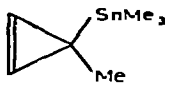


(II)



$$Me_3Sn(Me)C{=}C{=}CH_2$$

(III)



(IV)

Thus from a qualitative standpoint TMSB responds to electronic excitation essentially like regular 1,3-dienes, for which photoinduced 1,3 and 1,4 electrocyclizations are well known [3]. It is remarkable that in the present system no observable carbon—tin bond cleavage occurred *, and this adds to the similarity with homoconjugated dienes, since Seyferth had already reported that the presence of Me_3Sn groups does not inhibit the (2+2) intramolecular cycloaddition of perchloronorbornadiene [11]. When examined quantitatively, however, the photochemical behavior of TMSB is very different from that of normal dienes, in that the quantum yields exhibit an unusually strong concentration dependence.

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* The homolytic cleavage of tetraorganotin compounds ultimately gives a highly colored polymeric Sn^{II} species [1].

Thus under the typical preparative conditions described above (10^{-2} mol l^{-1} solutions), the quantum yields are: Φ(TMSB) (disappearance) $\approx 8 \times 10^{-3}$; Φ(II) $\approx 10^{-3}$; Φ(IV) $\approx 2 \times 10^{-3}$. The overall quantum efficiency for photochemical transformations therefore, does not exceed 1%, and TMSB can be considered as basically inert to optical excitation in the concentration range which could be of interest for synthetic purposes. This contrasts with the data obtained at lower concentrations since Φ(TMSB) (disappearance) increased to 12% when a 1.5×10^{-4} mol l^{-1} solution was irradiated.

Obviously a specific self-quenching operates to induce the decay of TMSB from its electronically excited state to its ground state. The concentration dependence of Φ(TMSB) (disappearance) was thus investigated further between 1.5×10^{-4} and 2.5×10^{-3} mol l^{-1} (polymerization was negligible under these conditions) and was found to obey a linear Stern-Volmer relationship, which is best rationalized by the kinetic Scheme 1, from which eqn. 1 may be derived. The ordinate intercept gave $k_1/k_2 \sim 5$ and the slope k_q/k_2

$$1/\Phi(\text{TMSB})\ (\text{disappearance}) = 1 + k_1/k_2 + (k_q/k_2)\ [\text{TMSB}] \qquad (1)$$

SCHEME 1

$$\text{TMSB} \xrightarrow{I_a} \text{TMSB}^*$$

$$\text{TMSB}^* \xrightarrow{k_1} \text{TMSB (spontaneous decay)}$$

$$\xrightarrow{k_2} \text{Products}$$

$$\text{TMSB}^* + \text{TMSB} \xrightarrow{k_q} 2\ \text{TMSB}$$

was equal to 10^4 l mol^{-1}. Hence if we assume that quenching takes place at a diffusion controlled rate* ($k_q = 6 \times 10^9$ s^{-1} l mol^{-1} in cyclohexane at 20°), it follows that $k_2 = 6 \times 10^5$ s^{-1} and $k_1 \approx 3 \times 10^6$ s^{-1}, which yields a lowest natural lifetime limit of $\tau = 1/(k_1 + k_2) \approx 3 \times 10^{-7}$ s, and this is a surprisingly high value for a singlet excited state. It is not possible at the present stage to rule out a tin-catalyzed cross-over of the excited TMSB to the triplet manifold even though it gave its cyclobutene tautomer (a product specific of the singlet state [12]) and failed to sensitize the *cis* → *trans* isomerization of 1,3-pentadiene, whose polymerization was instead efficiently initiated. (This is not the case when the pentadienes are sensitized with e.g. triplet benzophenone). A more attractive explanation can be proposed on the basis of the threefold observations that TMSB (*i*) quenches itself strongly, (*ii*) is fairly unreactive towards its own photopolymerization, and (*iii*) yields an unusually long-lived excited state; all these facts can be explained by assuming that the vibrationally relaxed (twisted [13]) S_1 state is further stabilized into a low-lying energy well by an intramolecular d—π^* interaction involving the empty orbitals of the metal [14]. Indeed this would induce a radical character** in the excited

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* This assumption is allowable because it can only underestimate the lifetime deduced.

** We favor a radical rather than a zwitterion structure, since a cationic hydrocarbon moiety would neither interact suitably with the 5*d* orbitals of the ground state quencher nor account for the self-inhibited polymerization of TMSB.

TMSB, and therefore account for the non-polymerizing self-quenching (via the electrophilic 5*d* orbitals of tin in the ground state partner [15]) as well as for the polymerization-catalyst properties towards a regular 1.3-diene.

More definite conclusions must await further investigations, but in view of the photochemical inertness and the high extinction coefficients of TMSB at relatively long wavelengths we wish to emphasize its potential usefulness as a light-protecting agent for saturated polymers.

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