Photochemistry of Ketoalkyltrimethylstannanes in Alkanes and in Carbon Tetrachloride[1]

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Abstract: The photochemistry in hydrocarbon solvents and in carbon tetrachloride of a series of ketoorganostannanes $MeCO(CH_2)_nSnMe_3$ with $n = 2$-4 has been examined. When $n = 2$, the major primary chemical process in hydrocarbon solvents appeared to be formation of the trimethylstannyl radical which could fragment to form methyl radicals and dimethyltin. When $n = 3$ or 4, competition with the Norrish type II process was observed. In the first compound, no quenching by piperylenes was observed; in the other two,. quenching was extremely inefficient. In carbon tetrachloride, the major product which was identified was trimethyltin chloride, and quantum yields were higher than in the hydrocarbon solvents; each of the three substrates showed fairly inefficient quenching by piperylenes. 2-Trimethylstannylnorbornan-5-one and 2-trimethylstannylnorbornan-6-one gave large amounts of type I product. However, each also showed some carbon–tin bond cleavage as shown by the formation of norbornan-2-one with the latter showing this to a much higher degree.

The photochemistry of ketones with a wide variety of structural modifications has been the subject of extensive and intensive study especially during the last decade. New synthetic methods and new compounds have been discovered; and a deeper understanding of the behavior of electronically excited states has resulted. The literature reveals that the chemistry of ketones with main group organometallic functions has received relatively little attention. We have been interested in this matter from the standpoint of the question "under what circumstances will the energy absorbed by a chromophore in a molecule be mainfested as chemistry at a nonabsorbing (relatively weak) carbon metal bond within the same molecule?"

Our initial efforts dealt with ketoorganosilanes.[1,2] We observed that benzoyltrimethylsilane underwent inefficient photolysis in methylcyclohexane; but both this compound and acetonyltrimethylsilane underwent photocatalyzed hydrolysis in wet ether. In carbon tetrachloride, acylsilanes generally give type I cleavage to silyl and acyl radicals as primary photochemical processes in carbon tetrachloride.[3,4] Brook and his co-workers have shown that the primary process with acylsilanes in hydroxylic solvents is formation of a siloxycarbene by rearrangement,[5] which can then react with solvent to form solvolysis products. When the silyl function is separated from the carbonyl group by two to four methylene groups, only "normal" ketone photochemistry is observed; the carbon–silicon bonds appear undisturbed in the reaction products observed.[2] We, therefore, turned to an examination of ketoorganotins as alternative substrates because the carbon–tin bond (ca. 65 kcal/mol) is considerably weaker than the carbon–silicon bond (ca. 80 kcal/mol).[6] In this paper we report on the photochemical behavior of ketoalkyltrimethylstannanes of the structure $MeCO(CH_2)_nSnMe_3$ with $n = 2$, 3, and 4 in hydrocarbon solvents and in carbon tetrachloride.

Results and Discussion

Synthesis. The preparations of 3-oxobutyltrimethylstannane and of 4-oxopentyltrimethylstannane were effected by methods previously described.[7] 5-Oxohexyltrimethyltin was prepared by photochemically induced hydrostannation of 5-hexen-2-ol, with trimethyltin hydride, followed by Jones oxidation of the adduct to the ketone (eq 1).

$$Me_3SnH + CH{=}CH(CH_2)_2CHOHCH_3 \longrightarrow$$

$$Me_3Sn(CH_2)_4CHOHCH_3 \xrightarrow[Me_2CO]{CrO_3} Me_3Sn(CH_2)_4C({=}O)CH_3 \quad (1)$$

Although the carbon–tin bond is cleaved by chromic acid in acetic acid,[8] the method which we used gave excellent yields of ketostannanes, indicating strong preferential oxidation of the hydroxyl function, at least in acetone.

The infrared spectra, the proton and ^{13}C magnetic resonance spectra, and the Mössbauer spectra revealed no characteristics other than those expected from simple additivity of those of the carbonyl and trimethylstannyl functions.[7] The electronic spectra in the carbonyl region were examined closely with the results gathered in Table I. The results in cyclohexane revealed a red shift of 4 to 6 nm in λ_{max} and a slight increase in the extinction coefficients in the ketoorganostannanes. That these effects are intramolecular is shown by their absence in a neat mixture of 2-butanone and n-butyltrimethylstannane. The shifts range from 8 to 13 nm in carbon tetrachloride. These changes are small enough that it may be assumed that the excited states of the carbonyl groups should differ little from those of simple alkanones.

Trimethylstannylnorbornanones were prepared by hydrostannation of an isomeric mixture norborn-2-en-5-ols with trimethylstannane, followed by oxidation with chromic acid. The usual probes (see Experimental Section) showed that the product was a mixture of *exo*-2-trimethylstannylnorbornan-5-one and *exo*-2-trimethylstannylnorbornan-6-ones. Although both could be characterized, only the former was obtained in a pure state.

Photolysis in Hydrocarbon Solvents. Irradiations were usually conducted using the 313-nm region in Pyrex vessels. Tetraalkyltins become transparent at wavelengths shorter than the carbonyl region and are stable to irradiation in Pyrex. Tetramethylstannane was irradiated in cyclohexane solutions containing 2-butanone, benzaldehyde, acetophenone, and benzophenone, respectively; and 3-cyanopropyltrimethyltin was irradiated with 2-butanone, all for periods exceeding those used in the photolysis experiments described below by factors of at least 2. In no case was there any significant consumption of organotin, thus eliminating intermolecular sensitization as a cause of the observed reactions.

When 20–30% solutions of 3-oxobutyltrimethylstannane in cyclohexane were irradiated exhaustively (60–95% conversion), a gas was evolved. This was shown by its infrared spectrum to consist mainly of methane (up to ca. 0.7 mol), along with small amounts of ethane and carbon monoxide. Exposure of the photosylate solution to air led to appearance of a precipitate (ca. 0.5 mol) whose formation could be

Table I. Ultraviolet Spectra Data[a]

Compd	λ_{max} (ϵ)		
	Cyclohexane	Carbon tetrachloride	
n-BuSnMe$_3$		242 (155)	
MeC(=O)CH$_2$Me	278 (17)		275 (22)
n-BuSnMe$_3$/MeC(=O)CH$_2$Me (1:1)	278 (17)[b]	242 (159)	280 (21)[c]
MeC(=O)CH$_2$CH$_2$SnMe$_3$	282 (33)	242 (173)	288 (46)
MeC(=O)(CH$_2$)$_3$SnMe$_3$	284 (24)	242 (140)	285 (32)
MeC(=O)(CH$_2$)$_4$SnMe$_3$	282 (21)	242 (141)	283 (27)

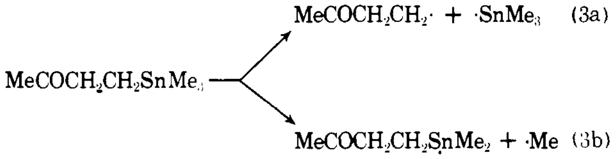
[a] In range 200–320 nm. [b] No solvent. [c] Both reagents 0.1 M.

hastened by addition of hydrogen peroxide. This was shown to be dimethyltin oxide by conversion to the dichloride upon treatment with hydrogen chloride, and then to the salicylate complex, also shown to be identical with authentic material.[9] Immediate treatment of the photolysate with iodine resulted in formation of dimethyltin diiodide, and treatment with sulfur resulted in formation of dimethyltin sulfide. These observations indicate that dimethyltin is formed during the photolysis. No volatile products derived from the 3-oxobutyl group could be isolated.

Because methane and dimethyltin were presumed not to be primary products, further photolyses were conducted using Pyrex vessels with dodecane as solvent (for analytical convenience) in more dilute solutions (2.1 M) to about 10% conversion. In addition to the gaseous products cited above, small amounts of tetramethylstannane, characterized by its mass spectrum, and of hexamethyldistannane, characterized by GLC retention times on two columns, and reaction with iodine were detected. Of the several products which might result from initial type I cleavage (eq 2)

$$\mathrm{MeC({=}O)CH_2CH_2SnMe_3} \longrightarrow \mathrm{MeC({=}O)\cdot} + \mathrm{\cdot CH_2CH_2SnMe_3} \quad (2)$$

it was shown that acetaldehyde, biacetyl, and vinyltrimethylstannane were definitely absent by coinjection of each with the reaction product mixture into the gas chromatograph. These results suggest that the primary chemical process in the photolysis involves cleavage of a carbon–tin bond as in eq 3a or 3b.



$$\mathrm{MeCOCH_2CH_2SnMe_3} \longrightarrow \mathrm{MeCOCH_2CH_2\cdot} + \mathrm{\cdot SnMe_3} \quad (3a)$$

$$\mathrm{MeCOCH_2CH_2SnMe_3} \longrightarrow \mathrm{MeCOCH_2CH_2\dot{S}nMe_2} + \mathrm{\cdot Me} \quad (3b)$$

On the basis of other evidence,[6] the former is probably the predominant or exclusive process. Coupling of trimethylstannyl radicals with each other leads to hexamethyldistannane, and with methyl radicals to tetramethylstannane (eq 4 and 5).

$$\mathrm{2Me_3Sn\cdot} \longrightarrow \mathrm{Me_3Sn{-}SnMe_3} \quad (4)$$

$$\mathrm{Me_3Sn\cdot} + \mathrm{\cdot Me} \longrightarrow \mathrm{Me_3Sn{-}Me} \quad (5)$$

Methane is formed by hydrogen abstraction by methyl radicals from solvent. Dimethyltin results from fragmentation of trimethylstannyl radicals (eq 6).

$$\mathrm{Me_3Sn\cdot} \longrightarrow \mathrm{(Me_2Sn)} + \mathrm{\cdot Me} \quad (6)$$

Such fragmentation has been observed in photochemically generated tri-n-butylstannyl[10] and triphenylstannyl[10,11] radicals and was confirmed by independent irradiation of hexamethyldistannane in this investigation.

Photolysis of 4-oxopentyltrimethyltin in quartz yielded results similar to those described for 3-oxobutyltrimethyltin; at 35% comsumption of ketone in cyclohexane, 0.3 mol of dimethyltin and 0.7 mol of methane containing small amounts of ethane and carbon monoxide were isolated per mole of ketone consumed. When 2.1 M dodecane solutions in Pyrex were photolyzed to 10% consumption of ketone, additional volatile products were detected. These included the gaseous products along with tetramethylstannane, hexamethyldistannane, acetone, trimethylvinylstannane and 2-pentanone, all characterized by mass spectrometry. In addition, the white precipitate of dimethyltin oxide appeared upon exposure of the photolysate to air.

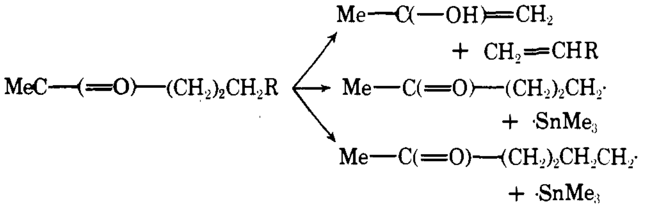
Table II. Quantum Yields for Reactions of Oxalkyltrimethylstannanes[a]

Compd	Φ_{disapp}	$\Phi_{Type\ II}$	$\Phi_{Sn-C(max)}$
MeCO(CH$_2$)$_2$SnMe$_3$	0.34		
MeCO(CH$_2$)$_2$CH$_2$SnMe$_3$	0.29	0.07[b]	0.22[d]
MeCO(CH$_2$)$_2$CH$_2$CH$_2$SnMe$_3$	0.18	0.085[c]	0.10[d]

[a] In cyclohexane at 30°. [b] Based on acetone formed. [c] Based on acetone (0.08) and allytrimethylstannane (0.09) formed. [d] Maximum value for tin–carbon cleavage assuming that the only other process occurring is the type II reaction.

The photolysis of 5-oxohexyltrimethylstannane in dodecane through Pyrex as above yielded the usual gaseous products, along with tetramethylstannane, hexamethyldistannane, acetone, allyltrimethylstannane and 5-hexen-2-one. No 2-hexanone was detected. Although absolute yields were not determined, the amounts of acetone and its type II co-product formed were similar to each other from each of these two oxostannanes. No products which might correspond to cyclobutanols were detected.

The results obtained with these oxopentyl- and hexyltrimethylstannanes demonstrate that the type II reaction and carbon-tin cleavage occur in competition as the primary chemical processes (R = SnMe$_3$, CH$_2$SnMe$_3$).



$$\mathrm{MeC{-}({=}O){-}(CH_2)_2CH_2R} \longrightarrow \mathrm{Me{-}C({-}OH){=}CH_2} + \mathrm{CH_2{=}CHR}$$

$$\mathrm{MeC{-}({=}O){-}(CH_2)_2CH_2R} \longrightarrow \mathrm{Me{-}C({=}O){-}(CH_2)_2CH_2\cdot} + \mathrm{\cdot SnMe_3}$$

$$\mathrm{MeC{-}({=}O){-}(CH_2)_2CH_2R} \longrightarrow \mathrm{Me{-}C({=}O){-}(CH_2)_2CH_2CH_2\cdot} + \mathrm{\cdot SnMe_3}$$

Other products are then derived by well-known reactions of the initially formed radicals.

Quantum Yields and Quenching. Quantum yields for the disappearance of the three oxoalkyltrimethylstannanes in cyclohexane were determined using 313-nm radiation at 30° with an n-butyrophenone actinometer. Yields of acetone and of allyltrimethylstannane were also determined. Results are gathered in Table II. Data were not obtained to permit assignment of quantum yields for carbon-tin bond cleavage, although this is probably the major other primary reaction; maximum possible values are given in the table. The quantum yields for the 4-oxopentyl and 5-oxohexyl derivatives can be compared with those for disappearance of

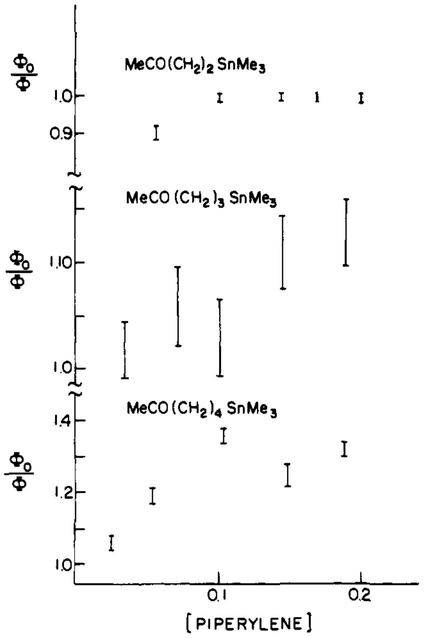


Figure 1. Stern-Volmer plots for ketoorganostannanes in dodecane.

2-pentanone and 2-hexanone which have been reported to be 0.27 and 0.33, respectively.[12] The yields of type II products were 68 and 88% making the type II quantum yields 0.18 and 0.29, respectively.[13] Thus, the presence of the trimethyl- stannyl group has relatively little effect on the overall quantum yield of photodecomposition of an alkanone but decreases that for the type II reaction substantially in favor of carbon-tin cleavage.

Quenching studies using piperylene were carried out in order to glean information concerning the identity of the excited species undergoing chemical reaction. Results for the three ketones are displayed in Figure 1. The presence of piperylene up to 0.2 *M* has no effect on the quantum yield for disappearance of 3-oxobutyltrimethyltin. The normal conclusion is that the reaction proceeds only by way of the singlet. An alternative is an "unquenchable" triplet or a combination of the two pathways. If the first case obtains, one is led to say that a tin atom separated from the carbonyl group by two carbons does not enhance intersystem crossing by its heavy atom effect via spin-orbit coupling to a degree sufficient to compete with cleavage of the carbon-tin bond, which must be accompanied or preceded by internal conversion with localization of most of the excitation energy in the tin-carbon bond vibrations. El-Sayed[14] has predicted on theoretical grounds that spin-orbit coupling in the carbonyl group is great enough that intramolecular heavy-atom effects due to halogen atoms would not be detected, and Wagner has shown experimentally that this is true for intermolecular halogen heavy-atom effects.[15] Our results now show this to be true also for intramolecular tin.

The results obtained with 4-ketopentyl- and 5-ketohexyltrimethyltins show very small amounts of triplet quenching with the latter showing a slightly greater effect.[16]

Photolyses in Carbon Tetrachloride. In order to test the postulate that trimethyltin radicals are formed in a primary chemical process in the photolysis of the ketoorganostannanes, we sought to trap these by reaction with a suitable substrate. It was observed that irradiation of solutions of tetramethylstannane or *n*-butyltrimethylstannane in carbon tetrachloride through Pyrex showed no reaction under conditions which consumed 3-oxobutyltrimethylstannane. When the initial concentration of the latter was 0.01 *M*, a total of 0.78 mol of trimethylchlorostannane was found for each mole of ketone consumed. When 0.005 *M* solutions were irradiated to 98% consumption of 4-oxobutyltrimethylstannane, 0.46 mol of trimethylchlorostannane was found. Small amounts of chloroform and hexachloroethane were also detected. No evidence of methane, tetramethylstannane, or dimethyltin was obtained.

Table III.

Compd	Φ_{disapp}	Φ_{Me_3SnCl}
MeCO(CH$_2$)$_2$SnMe$_3$	0.99	0.97
MeCO(CH$_2$)$_3$SnMe$_3$	0.43	0.24
MeCO(CH$_2$)$_4$SnMe$_3$	0.28	0.17

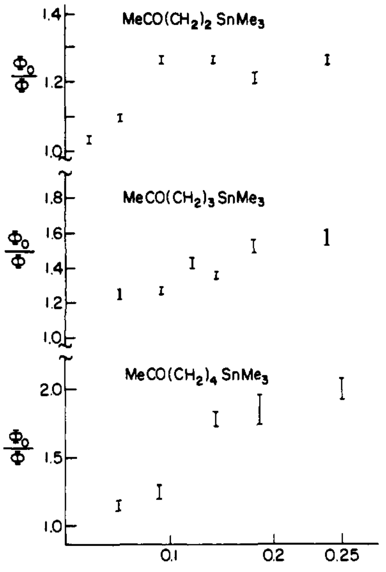


Figure 2. Stern-Volmer plots for ketoorganostannanes in carbon tetrachloride.

Quantum yields for the disappearance of reactant and for formation of trimethylchlorostannane in carbon tetrachloride were determined for 3-oxobutyltrimethylstannane, 4-oxopentyltrimethylstannane, and 5-oxohexyltrimethylstannane with the results displayed in Table III. The most obvious result is that the values are 2.9, 1.5, and 1.6 times larger for photolysis in carbon tetrachloride than in cyclohexane for the three ketostannanes, respectively. The high proportions of trimethyltin chloride are consistent with the formation of trimethyltin radicals in the primary chemical reaction in these photolyses.

The effects of piperylene on the quenching of the photoreactions of these ketones are shown in Figure 2. It is clear that the quenching is relatively inefficient. The results also lead to the conclusion, clouded by the scatter, that the quenching may level off at higher quencher concentrations, suggesting both singlet and triplet mechanisms for the disappearance of ketostannanes.

The photochemistry of simple alkanones in carbon tetrachloride is significantly different from that observed in hydrocarbon solvents. For example, Guillet[17] et al. have observed that normal alkanone photoreactions are substantially by-passed in carbon tetrachloride, and fluorescence is quenched by carbon tetrachloride in cyclohexane. For example, whereas 8-pentadecanone irradiation in hydrocarbon solvent has a type II quantum yield of 0.07, a decrease to 0.034 is observed in carbon tetrachloride; a quantum yield of 0.95 is observed for the formation of hydrogen chloride; and substantial amounts of hexachloroethane are formed. Exciplex formation followed by internal conversion and dissociation of a C–Cl bond or a single-step process were suggested as possibilities for the primary chemical step (eq 7).

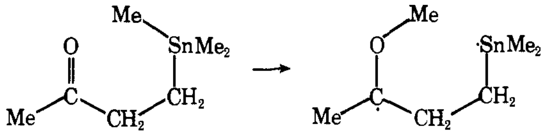
$$K^* + CCl_4 \longrightarrow [K\cdot CCl_4]^* \longrightarrow K_0 + Cl\cdot + \cdot CCl_3 \qquad (7)$$

Subsequent reactions then follow from the chlorine and trichloromethyl radicals. If this primary reaction occurs with our ketoorganostannanes, it is easy to account for the high yields of trimethyltin chloride, for the chlorine atoms formed in reaction could react with the stannyl function by an SH2 process (eq 8).

$$Cl\cdot + Me_3SnR \longrightarrow Me_3SnCl + R\cdot \qquad (8)$$

Thus the question of whether we are trapping discrete trimethyltin radicals in the carbon tetrachloride photolyses remains unresolved at this juncture. As noted in Table I, a weak absorption band is observed at 242 nm in the ketoorganostannanes, and in *n*-butyltrimethylstannane, but not in 2-butanone. Thus it is due to the organostannane function. This band shifts to 230 nm (ϵ 62) in chloroform, and to 223 nm (ϵ 56) in methylene chloride, and is not observed in methanol, nitromethane, or cyclohexane. Thus it appears to be a charge-transfer band involving the halogen atoms and indicates complexation between the organostannane and carbon tetrachloride, which lends credibility to the postulate of an exciplex intermediate.

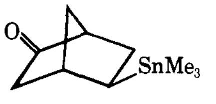
An analog of the type II reaction as shown in eq 9 might have been anticipated in the case of 3-oxobutyltrimethylstannane. The normal type II reaction is approximately thermoneutral,[18] whereas eq 9



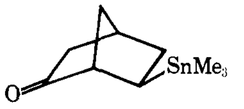
(9)

would be exothermic by about 12 kcal/mol.[19] Apparently other factors, most obviously conformational and steric, mitigate against the occurrence of this reaction which could lead to interesting products.

Trimethylstannylnorbornanones. In the examples discussed above, it is possible that direct contact between the carbonyl group and the organotin function is involved in the energy-transfer process which leads to tin–carbon bond cleavage. In order to ascertain whether such direct contact is essential, we sought to examine the photochemistry of the exo isomers of 2-trimethylstannylnorbornan-5-one (**1**), and 2-trimethylstannylnorbornan-6-one (**2**). We were unable to find a method for complete separation of the two isomers, but did obtain **1** in the pure state for characterization and study, and then were able to draw inferences about **2** from studies on mixtures of **1** and **2**.



1



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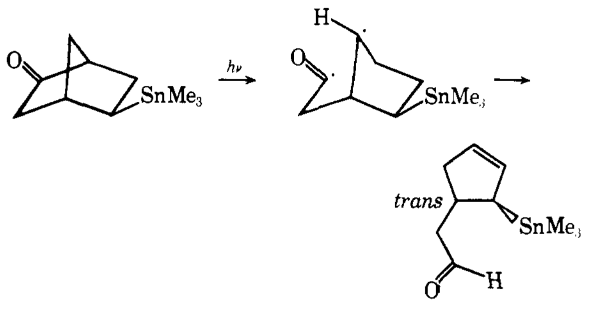
Photolysis of **1** in cyclohexane led to the formation of small amounts (<5%) of norbornanone, characterized by its spectral properties. The major volatile product (~95%) was shown to be an aldehyde by a positive Tollen's test, and to contain tin from its mass spectrum: $(M - CH_3)^+$ at *m/e* 259 (^{120}Sn); and Me_3Sn^+ at *m/e* 165, among other peaks characteristic of organotins. A 100-MHz Fourier transform ^1H NMR spectrum on the small sample which could be collected by GLC revealed an aldehyde triplet at δ 9.78, a vinyl multiplet at δ 5.82, an allylic multiplet at δ 2.65, and the trimethyltin proton singlet at δ 0.07. The most probable structure is **3**, resulting from α-cleavage of the C_4–C_5 bond and abstraction of the endo 7-hydrogen by the acyl radical (eq 10). This has been shown to be the pathway by which norbornanone reacts photochemically.[20] The proton on the carbon bearing the trimethylstannyl group in the product was apparently lost under the dodecane signals present as an internal standard. The quantum yield for disappearance of **1** in cyclohexane was 0.40 in cyclohexane, which may be compared with the value of 0.28 observed for norbornanone in benzene.[21] The product contained no hexamethyldistannane but did develop a small amount of precipitate characteristic of dimethyltin upon exposure to air. These observations clearly suggest that, although some carbon–tin bond cleavage does occur in the photolysis of **1**, the major reaction pathway is the normal type I reaction.



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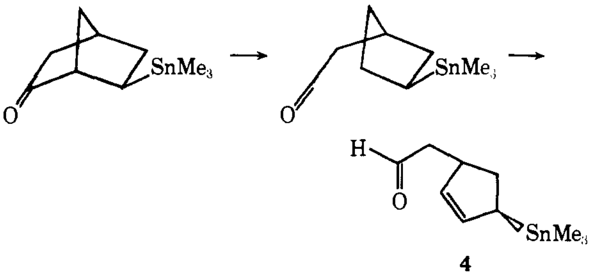
3

When the solvent used in the photolysis was carbon tetrachloride, less than 5% of trimethyltin chloride was formed. Other volatile photolysis products were formed in such small amounts that they were not characterized. The quantum yield for disappearance was 0.56. The presence of 0.2 *M* piperylene in either cyclohexane or carbon tetrachloride had no effect on the quantum yield. This is consonant with the observation that norbornanone undergoes decomposition exclusively from the singlet and is unaffected by the presence of the tin atom.

When a mixture of **1** and **2** was photolyzed in cyclohexane, GLC analysis revealed that the relative area of the peak due to norbornanone was increased, but no quantitative estimate of the proportion resulting from photodecomposition of **2** was made. A new peak with a retention time slightly longer than that of **3** was observed. In addition to the peaks at *m/e* 259 $(M - CH_3)^+$ and 165 $(Me_3Sn)^+$, a peak absent from the spectrum of **3** was observed at *m/e* 109 corresponding to $(M - Me_3Sn)^+$. This is unusual because most of the charge in the mass spectra of organotins is usually carried by tin-containing fragments rather than hydrocarbon ions.[22] The ^1H NMR spectrum was different from that of **3** in detail, although similar signals were observed: δ 9.75 (J = 2 Hz) for the aldehydic proton; a broad vinyl multiplet centered at δ 5.78; allylic proton multiplet centered at δ 2.52; and the trimethyltin protons as a singlet at δ 0.09. By analogy with the previous example, the course of the photolysis is assumed to lead to *trans*-**4** via eq 11.



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Determination of relative quantum yields of a mixture of **1** and **2** at 13% decomposition showed that piperylene concentrations up to 0.19 *M* had no effect, thus indicating a singlet reaction for both isomers.

Photolyses in carbon tetrachloride of mixtures of **1** and **2** revealed a large increase in the amount of trimethyltin chloride formed and an overall increase in quantum yield to about 1.1 at 7% reaction. On the basis of the initial concentrations of **1** and **2**, one estimates a quantum yield for disappearance of the latter of about 2. Here again the presence of piperylene up to 0.25 *M* did not affect the quantum yield for disappearance of the ketones.

The results discussed above may be summarized as follows with reference to the question presented at the outset: the energy introduced by the absorption of a photon by the carbonyl group in a molecule can bring about reaction at a carbon-tin bond with an efficiency which decreases with distance of separation; this can compete effectively with the Norrish type II process; it appears to be most efficient when rotational freedom can permit close contact between the carbonyl and trimethyltin functions; however, even in the rigid systems, **1** and **2**, where direct contact is more difficult, some energy transfer from the carbonyl to trimethyltin can occur as manifested by tin-carbon bond cleavage. When carbon tetrachloride is used as solvent in place of a hydrocarbon, the chemistry is markedly altered and may be the result of primary chemical reactions initiated by energy transfer from the carbonyl group to carbon tetrachloride.

Experimental Section

General. Melting and boiling points are uncorrected. Infrared spectra were obtained with Beckman IR-8 and IR-10 instruments. Ultraviolet spectra were recorded with a Cary-14 spectrophotometer. Mass spectral data were obtained with an AE1-MS-902 instrument using either direct injection when ample material was available, or by introduction of the effluent from a gas-liquid chromatograph interfaced with the spectrometer through a heated inlet system.

Elemental analyses were performed by Instranal, Rensselaer, N.Y., or by Galbraith Microanalytical Laboratory, Knoxville, Tenn.

Gas-liquid partition chromatography required the use of the following columns, depending on the specific compound(s) to be cleanly separated: 20% Apiezon L on Chromosorb W (A); 5% silicon oil 210 on Haloport F (S); 20% SE 30 on Chromosorb W (SE); 10% UCW 98 on Chromosorb W (U); 10% Carbowax 20M on Chromosorb W (C); 10% polyphenyl ether on Chromosorb W (P). Each column was 6 ft × 0.25 in. Column U was used for separating hexachloroethane; C for tetramethyltin; S for hexamethylditin, chloroform, and acetone; P for trimethylchlorostannane.

The preparations of *3-oxobutyltrimethylstannane* and *4-oxopentyltrimethylstannane* have been described previously.[7]

5-Hydroxyhexyltrimethylstannane. A solution of 50 g (0.50 mol) of 5-hexen-2-ol and 67 g (0.40 mol) of trimethylstannane was irradiated in a Rayonet photochemical reactor with 300-nm lamps under argon in a Pyrex vessel. After 23.5 hr, work-up yielded 94.3 g (88.9%) of 5-hydroxyhexyltrimethylstannane, bp 78-80° (1 Torr).

The 60-MHz ^{1}H NMR spectrum of the compound showed: a multiplet at δ 3.40 (CHOH); a multiplet at δ 1.40 (-CHOHCH_2-CH_2CH_2-); a doublet at δ 1.12 (J = 6 Hz; CH_3CHOH-, 6 position protons); a triplet at δ 0.82 (J = 11 Hz (SnCH$_2$-); and a singlet at δ 0.03 (J (^{119}SnH) = 54 Hz, the trimethylstannyl methyl protons); relative areas, 2:6:3:2:9. The infrared spectrum of the compound showed bands at 3350 (s), 2970 (s), 2930 (s), 2830 (m), 1380 (m), 1110 (m), 760 (s)cm^{-1}. At 70 eV the parent peak of the compound was not evident in the mass spectrum; a peak corresponding to the fragment resulting from the loss of a methyl group appeared at *m/e* 251.

Anal. Calcd for $C_9H_{22}SnO$: C, 40.80; H, 8.37. Found: C, 40.64; H, 8.53.

5-Oxohexyltrimethylstannane. To a solution of 35 g (0.35 mol) of chromium trioxide (Fisher, technical grade) in 250 ml of water was slowly added 30.5 ml of 16 *M* sulfuric acid (Fisher, reagent grade).[23] The resulting solution was cooled to room temperature and added dropwise to a 1-l. erylenmeyer flask containing 90 g (0.34 mol) of 5-hydroxyhexyltrimethylstannane dissolved in 200 ml of acetone (Fisher, ACS grade). The contents of the flask was cooled in an ice-water bath, and the chromium trioxide solution (210 ml; 0.26 mol) was added with stirring until the solution turned orange and remained orange for an hour. The reaction mixture was washed with 250 ml of water, resulting in a lower yellow organic layer and an upper green aqueous layer. The water layer was extracted three times with 250-ml portions of dichloromethane. The organic layer and the dichloromethane washings were combined and the solvents removed with a rotary evaporator. The resulting impure product was washed with three 75-ml portions of water and dried over anhydrous sodium sulfate. The yield of 5-oxohexyltrimethylstannane was 65.9 g (74.0%), despite some accidental loss, bp 72-75° (1.25 Torr).

The 60-MHz ^{1}H NMR spectrum of the compound showed: a triplet at 2.35 (J = 11 Hz, C-4 protons); a singlet at 2.03 (C-6 protons); a multiplet at 1.52 (C-2 and C-5 protons); a triplet at 0.8 (J = 12 Hz, C-1 protons); and a singlet at 0.03 (J(^{119}SnH) = 54 Hz, the trimethylstannyl methyl protons); relative areas, 2:3:4:2:9. The infrared spectrum of the compound showed bands at 2970 (m), 2930 (s), 2850 (m), 1715 (s), 1360 (m), 1175 (m), and 770 (s) cm^{-1}.

Anal. Calcd for $C_9H_{20}SnO$: C, 41.11; H, 7.67. Found: C, 41.07; H, 7.67.

Isomeric Mixture of 2-Trimethylstannylnorbornan-5-ol and 2-Trimethylstannylnorbornan-6-ol. A solution of 25 g (0.23 mol) of a mixture of *exo-* and *endo-*2-norbornen-5-ol (Aldrich Chemical Co.) and 47 g (0.28 mol) of trimethylstannane was reacted under conditions similar to those described for the preparation of 3-hydroxybutyltrimethylstannane. A similar work-up yielded 57.6 (92.0%) of an isomeric mixture of 2-trimethylstannylnorbornan-5-ol and 2-trimethylstannylnorbornan-6-ol, bp 86-89° (0.1 Torr). The product was oxidized as described later to the corresponding ketones, without further purification.

Trimethylstannylnorbornanones. A mixture containing 119.5 g (0.435 mol) of isomeric trimethylstannylnorbornanols was dissolved in 1.2 l. of pyridine and added to 84 g (0.84 mol) of chromium trioxide in 1 l. of pyridine. After standing overnight, it was worked up, and the product was distilled, bp 72-78° (0.75 Torr).

Separation of Isomeric Trimethylstannylnorbornanones. The following conditions were found suitable for the separation of pure *exo-*2-trimethylstannylnorbornan-5-one. The other isomer could not be obtained pure by this procedure, because of tailing of *exo-*2-trimethylstannylnorbornan-5-one, which contaminated it. While attempts to separate the two isomers by GLC were partially successful on a 0.25-in. diameter 6-ft column of 10% LAC-728 on 60-80 mesh Chromosorb W, attempts to scale the process up to 0.75-in. preparative column size were unsuccessful, due to much lower resolution.

A 25.5-in. glass column of 1.25-in. inside diameter was packed 20 in. high with Fisher Neutral Alumina (activity I). Approximately 1.5 g of the mixture of isomeric trimethylstannylnorbornanones was introduced and eluted with a solution of 20% benzene and 80% petroleum ether (Fisher, bp 37-45°). After elution of approximately 2.5 l. of the solvent, a small amount of pure *exo-*2-trimethylstannylnorbornan-5-one (**1**) was obtained. Loss of material was estimated to be as high as 80%.

The infrared spectrum of *exo-*2-trimethylstannylnorbornan-5-one showed bands at 2960 (s), 2920 (s), 2880 (s), 1755 (s), 1720 (m), 1413 (m), 1180 (m), 1093 (m), 765 (s), and 510 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_{18}SnO$: C, 44.01; H, 6.54. Found: C, 44.83; H, 6.7.

The ^{13}C Fourier transform spectra of the pure **1** and of the mixture were obtained so that the paramaters of **2** could be obtained by difference. Given are chemical shift for ^{13}C parts per million and J(^{119}Sn-^{13}C) in hertz for 2-trimethylstannylnorborn-5-one (**1**): C_1, 39.7, 7; C_2, 24.1, 390; C_3, 28.1, 29; C_4, 49.6, 14; C_5, 213.7, 5; C_6, 48.2, 80; C_7, 37, —; CH_3, −10.9, not determined. For 2-trimethylstannylnorbornan-6-one: C_1, 50.5, 10; C_2, 18.9, 364; C_3, 35.0, 20; C_4, 31.1, 19; C_5, 43.3, —; C_5, 211.3, 62; C_7, 36.4, —; CH_3, −11.3, not determined. The assignments were based on the additivity principle using published data for norbornane,[24] *exo-*2-trimethylstannylnorbornane,[25] *endo-*2-trimethylstannylnorbornane,[26] and norbornan-2-one.[23]

Photolysis Procedures. The light source most frequently used was a 400-W, medium-pressure, mercury, General Electric lamp H400 A-33-1. However, removal of the outer glass shell from this street lamp and slight bending of the electrical connections make it suitable as an inexpensive source of ultraviolet radiation. Light in the vicinity of 313 nm was isolated by placing the mercury lamp in a water-cooled quartz well filled with an aqueous solution, 0.0025 *M* in K_2CrO_4 and 1% in K_2CO_3.[27] The jacket surrounded the lamp with a 7-nm thickness of filter solution.

The solutions to be photolyzed were placed in 75-mm long, cylindrical, 20 mm o.d. Pyrex tubes. The tops of the tubes were fitted with 14/20 ST outer joints. The tubes could be sealed with a 14/20 ST inner joint to which was attached a Pyrex ST stopcock.

The contents of the tubes were first frozen with either liquid nitrogen or a dry ice-acetone slurry. The stopcock to the tube was then opened, and the tube was evacuated to 0.005 Torr. The stopcock was closed and the contents of the tube was allowed to thaw. The cycle was repeated four times.

To ensure that the samples received equal amounts of incident light during the quantum yield determinations, the tubes to be photolyzed were rotated about the light source at 5 revolutions/min with a Southern New England Ultraviolet Company Model MGR 500 "merry-go-round".

The samples to be irradiated for quantum yield determinations were maintained at 30 ± 0.4° throughout the photolysis by immersing the samples, "merry-go-round", and light source into a constant-temperature bath.

For product studies, samples were photolyzed in degassed Pyrex tubes, suspended in a Rayonet photochemical reactor, equipped with 300-nm bulbs. The light from the bulbs was filtered by suspending the solutions in the same dichromate carbonate solution used as a filter in quantum yield determinations and quencher studies.

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Photoelectron Spectra and Molecular Properties. L.[1-3] On the Blue Color of Bis(trimethylsilyl)diimine

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Abstract: Photoelectron (PE) and uv spectra of group 4 azo compounds $R_3X—N{=}N—YR_3$ (X, Y = C, Si) and $H_5C_6—N{=}N—XR_3$ (X = C, Si, Ge) are reported. A comparative discussion, based on CNDO calculations, attributes the low ionization potentials of the trimethylsilyl derivatives to substantial electron donation from the R_3Si substituents. The unique electronic spectrum of the title compound can be rationalized considering in addition electron-electron interaction as well as Rydberg excitations.

It is the blue color of bis(trimethylsilyl)diimine which has stimulated investigation of its molecular properties[3,4] as well as those of related compounds.[2,3,5] In spectroscopic terms, its long wavelength $n_N{}^+ \rightarrow \pi^*$ transition[6-9] is bathochromically shifted by more than 14000 cm^{-1} (!) relative to that of the isoelectronic *tert*-butyl derivative.[3,6,7] As pointed out for the corresponding ketones,[5] analogous substituent dependent shifts of the long wavelength absorption are also observed for other chromophoric systems. For bis(trimethylsilyl)diimine and its challenging spectroscopic prop-

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