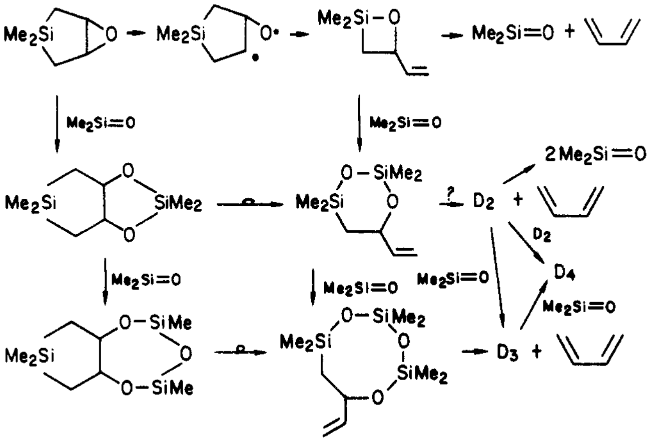
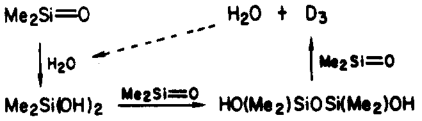
Scheme VI



Scheme VII



although formation of the alcohol IV was a very minor pathway, amounting to ca. 2% as opposed to 34% for the formation of the alcohol VII, rate constants for formation of IV were still greater than for formation of VII, but only by a factor of between 2 and 3. Accordingly, this process may also be concerted, but we cannot come to any definite conclusion in the absence of accurate Arrhenius parameters.

An interesting question in the pyrolysis of I, and in the pyrolysis of all other dimethylsilanone precursors, is the mechanism of formation of D_3 and D_4. Observation of these products is generally and reasonably taken to imply the intermediacy of dimethylsilanone, but it is not immediately obvious how they are formed. Silanones are more polar than silenes (indeed, they probably exist as ylids in solution[3]) and are likely to be at least as reactive and short-lived; consequently, the steady-state concentration of II in the pyrolysis of I will be small, not more than 10^{-4} times the concentration of I, which is ca. 10^{-5} mol dm^{-3} in our experiments. If D_3 is to be formed by self-combination of II, the first stage may be envisaged to be dimerization of II to form D_2 (D_2 has often been postulated as an intermediate product in silanone chemistry, but no convincing evidence has yet been found for its existence in the gas phase, although a cyclodisiloxane has recently been isolated in the solid state;[14] for the purposes of this calculation it is immaterial whether D_2 exists as a separate entity or not). The corresponding dimerization of dimethylsilene[15] has a rate constant of $10^{6.55}$ dm^3 mol^{-1} s^{-1}; even if we allow a higher value of, say, 10^8 dm^3 mol^{-1} s^{-1} for D_2 formation, the rate of dimerization of II would be $10^8 \times (10^{-4} \times 10^{-5})^2 = 10^{-10}$ mol dm^{-3} s^{-1}. At 460 °C the rate constant for pyrolysis of I $\simeq 0.1$ s^{-1}, giving a rate of pyrolysis of I of 0.1×10^{-5}, i.e., 10^{-6} mol dm^{-3} s^{-1}, 10^4 times faster than self-combination of II to form D_2, let alone D_3! The obvious conclusion is that we need to envisage a sequence of reactions of II with gaseous *molecular* species, or with the surface, to form D_3. In the pyrolysis of I we observed V, the insertion product of II into I, together with other unidentified gaseous compounds of higher molecular weight, which prompts us to suggest the mechanism in Scheme VI. The intermediacy of D_2 is possible but is not demanded. Formation of D_3 and D_4 is likely to be homogeneous, at least in part, because the insertion product V was observed and because formation of $[D_3 + D_4]$ had a higher activation energy than formation of butadiene. However, there may also be some formation of D_3 at the surface of the quartz reaction vessel, either by successive reactions of II with suitable adsorbed species, such as water, siloxanes, etc., or with the surface itself. A cycle involving water is illustrated in Scheme VII. We hope to investigate these questions further by comparative studies of the formation of D_3 and D_4 from different silanone precursors and by further studies of the effect of silanone traps and of surface modification.

Finally, it may be seen from the Arrhenius parameters in Table I that I is the most thermally labile precursor to dimethylsilanone yet discovered, enabling reactions of dimethylsilanone with substrates to be studied at lower temperatures than hitherto.[8]

Acknowledgment. I.M.T.D. and A.F. thank the Science and Engineering Research Council, Dow Corning (Europe), and the British Council for support.

Registry No. I, 65181-02-4.

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MNDO Study of 2,4,6-Trithia-1,3,5-tristannaadamantane

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MNDO calculations are reported for 2,4,6-trithia-1,3,5-tristannaadamantane and for the corresponding apical (C_8) radical and cation. Predictions are made concerning its reactivity toward free radical hydrogen abstraction.

We recently extended[2] the MNDO SCF MO model[3] to tin, and calculations[4] for a number of organotin compounds and their reactions have demonstrated the usefulness of MNDO in tin chemistry. Here we report its application

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Table I. Average Bond Lengths (Å) and Bond Angles (deg) Calculated for 2 and Observed for 1

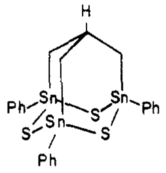
parameter	obsd[a]	calcd
Sn–S	2.408	2.280
Sn–C	2.153	2.100
C–C	1.529	1.544
S–Sn–S	108.7	108.5
Sn–Sn–C	108.8	108.1
Sn–C–C	119.3	118.4
C–C–C	114.1	113.8

[a] Values listed are averages of those reported for bonds of this type in 1.

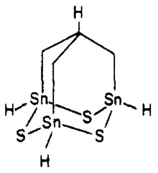
to an interesting polycyclic tin compound that has recently been reported,[5] i.e., 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane (1), and for some of its reactions.

Calculations of this kind are particularly rewarding when they lead to predictions that can be tested experimentally, as in the case here. While the crystal structure of 1 has recently been described[5] and while its central carbon–hydrogen bond is known[6] to be an active source of hydrogen in redox reactions, apparently by anionic or radical transfer of hydrogen, no other work on its chemistry has as yet been published. It has, however, been shown[7] that a model compound which allowed the carbon–tin bonds to be other than antiperiplanar to the reactive hydrogen was much less reactive than 1.

Our MNDO calculations were carried out for the parent compound 2,4,6-trithia-1,3,5-tristannaadamantane (2) because it seemed unlikely that the phenyl groups in 1 could seriously alter the reactivity of the central CH bond and because their inclusion would have greatly increased the amount of computing time required. Table I compares our calculated (MNDO) bond lengths and angles for 2 with average values reported[5] for 1. The agreement is quite reasonable, given the tendency of MNDO to underestimate lengths of Sn–X bonds.[2]



1



2

The bond angles at the apical carbon atom (C_8) in 2 are unusually large, due presumably to the distortion introduced by the large tin and sulfur atoms. Removal of the adjacent hydrogen atom should then lead to a radical (3) in which the central carbon atom can adopt a planar geometry without significant strain. Such loss of hydrogen should consequently occur much more easily from C_8 in 2 than from normal bridgehead methine groups, in particular from C_1H in adamantane itself. Indeed, since the bond to hydrogen in the case of 2 presumably involves a carbon AO with unusually high p character and is likely to be correspondingly weak, 2 is likely to be more reactive than even an acyclic trialkylmethane. The relative reactivity of 2 to hydride ion abstraction, to form the corresponding cation 4, should be even greater because 4 should be further stabilized by inductive and hyperconjugative effects involving the adjacent Sn–C bonds.

Table II. Average Bond Lengths (Å) and Angles (deg) for the Apical Cation 4

bond	length	angle	value
Sn–S	2.280	S–Sn–S	110.3
Sn–C	2.140	S–Sn–C	104.5
C–C	1.471	Sn–C–C	108.3
		C–C–C	119.8

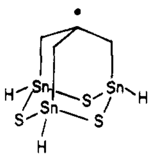
Table III. Average Bond Lengths (Å) and Angles (deg) for the Apical Radical 3

bond	length	angle	value
Sn–S	2.280	S–Sn–S	108.2
Sn–C	2.137	S–Sn–C	106.9
C–C	1.474	Sn–C–C	108.0
		C–C–C	119.7

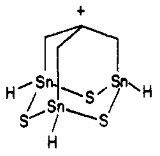
Table IV. Calculated Heats of Formation (ΔH_f)

compd	ΔH_f, kcal/mol	compd	ΔH_f, kcal/mol
2	16.0	5	23.2
3	25.5	7	17.0
4	212.2		

MNDO calculations for 3 and 4 confirmed these predictions. Their calculated geometries are shown in Tables II and III and their heats of formation (ΔH_f) in Table IV. As expected, the apical carbon atom is essentially planar in each of them.



3



4

The data in Table IV lead to an exceptionally low value (61 kcal/mol) for the corresponding CH bond strength. This is far less than for any position in any paraffin. Indeed, it is even less than the value (72 kcal/mol[9]) reported for the SnH bond strength in stannanes, accounting nicely for the similarity of 2 to a stannane in its reducing ability[7].

The inability of 1 to reduce chlorotrimethylstannane to trimethylstannane was cited as evidence that the apical CH bond in 1 is stronger than a tin–hydrogen bond.[6] Such a reduction would involve attack by the corresponding analogue of 3. However, since the bond strength of the tin–chlorine bond has been estimated to be 101 kcal/mol[8] and since the carbon–chlorine bond in 1 certainly should be much weaker than a normal carbon–chlorine bond, the energetics of such a reaction are not clear. The heat of formation of the cation suggests that the bridgehead position would also be very reactive in cation formation. The difference between the heats of formation of the cation and the parent compound is 196 kcal/mol. The corresponding (MNDO) differences between isobutane and *tert*-butyl cation, and between toluene and benzyl cation, are 214 and 204 kcal/mol, respectively. Thus the bridgehead hydrogen should be extremely easily converted to the cation by hydride abstraction, and the bromide 5 should likewise ionize very easily. Indeed, special precautions may need to be taken in isolating 5 from a reaction mixture. The ease with which 2 reduces triphenylmethyl cation is in any case easily understood.

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(1) On sabbatical leave from St. Michael's College, Winooski, VT 05404

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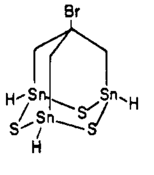
Koch and Gleicher[9] have determined the relative reactivities of bridgehead hydrogen atoms toward abstraction by trichloromethyl radical and have shown that there is a good linear relation between the heats of reaction and the rates of hydrogen abstraction. We have found that the heats of reaction given by MNDO show an equally good correlation with the experimental data ($r = 0.995$). Applying this relation to our data for **2** and **3** (Table IV), we conclude that **2**, and hence also **1**, should react with trichloromethyl radical about 6000 times faster than adamantane, a prediction which we hope will soon be tested by experiment.

Ducharme et al.[6] have stated that **1**, in presence of AIBN as a radical catalyst, reduces alkyl halides in a manner "similar to dehalogenations effected by tin hydrides". We accordingly calculated the energetics of the corresponding free radical chain reaction between **2** and ethyl bromide, using MNDO heats of formation; see eq 1 and 2. The

$$3 + C_2H_5Br \rightarrow 5 + C_2H_5\cdot \quad \Delta H = 27.9\ \text{kcal/mol} \quad (1)$$

$$C_2H_5\cdot + 2 \rightarrow 3 + C_2H_6 \quad \Delta H = -23.0\ \text{kcal/mol} \quad (2)$$

endothermicity of the first step seems too large for the reaction to occur with a reasonable chain length under other than drastic conditions. Ducharme et al. suggested that **3** may undergo intramolecular fragmentation to form the isomeric radical **6** which could then react as a normal stannyl radical with alkyl bromides, forming **7**. MNDO indeed predicts **7** to be lower in energy than **5** by 6.2 kcal/mol (Table III). We tried to check this idea by calculating **6**, but without success. All the structures studied reverted to **3** exothermically and without activation. While it is possible that rearrangement may accompany reaction with the alkyl bromide in a single concerted step, it seems likely that the activation energy for such a multibond process would be rather large. It should be noted that the only example of a reduction cited by Ducharme et al. referred to a compound (α-bromo-p-phenylacetophenone) where the corresponding radical must be strongly stabilized by the α-acyl group.



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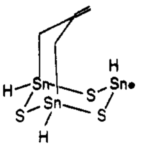
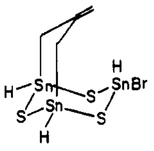


6



7

The remarkable stability of **3** can be interpreted nicely in terms of synergism between sigmaconjugation and hyperconjugation, of the kind recently invoked[10] to explain the anomeric effect and the preferred conformations of alkyl radicals. Synergism occurs in such cases when hyperconjugation involves a CX bond trans to the singly or doubly occupied AO and the stabilizing effect should be greater, the less electronegative is X. In **3**, all three C–Sn bonds are trans to the singly occupied AO. It should be noted in this connection that Hannon and Traylor[11] have shown that loss of hydride from a position β to tin in an organostannane occurs most readily when the hydrogen is antiperiplanar to the adjacent C–Sn bond, as the argument above predicts.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 49620 83 C 0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out with a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. 1, 87922-35-8; **2**, 88212-59-3; **3**, 96504-44-8; **4**, 96504-45-9; **5**, 96504-46-0; **6**, 96504-47-1; **7**, 96504-48-2; $CCl_3\cdot$, 3170-80-7; C_2H_5Br, 74-96-4; $C_2H_5\cdot$, 2025-56-1.

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Reaction of Tributyltin ω-Haloalkoxides with Isocyanates or Carbodiimides. A Possibility of the Addition of an Sn–O Bond across the C=O Group of Isocyanate

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In the reaction of tributyltin ω-haloalkoxides ($Bu_3SnO(CH_2)_nX$, X = Cl, Br, I) and isocyanates, the formation of iminodioxolane derivatives was observed. These products are not obtained in the direct addition of oxiranes and isocyanates, whereas $Bu_3SnO(CH_2)_2X$ is considered to be a synthon of ethylene oxide. The yield of iminodioxolanes was affected substantially by various factors such as solvent, temperature, the halogen (X), and the substituents on the isocyanates used. In particular, the iminodioxolane was obtained exclusively in the reaction with methyl isocyanate. A possibility of the formation of these compounds via the addition of the Sn—O bond across the C=O group of an isocyanate is discussed. In addition, the formation of various heterocyclic compounds from $Bu_3SnO(CH_2)_nX$ (n = 2, 3) and isocyanates or a carbodiimide under mild conditions is reported.

As the Sn–O bond is reactive, it is useful in organic synthesis.[1] A variety of unsaturated substrates such as RNCO, RNCS, CO_2, CS_2, and RCHO have been shown to undergo insertion into the Sn–O bond.[1] These reactions