the solution stirred overnight. After filtration and concentration the solution was analyzed by GLC and showed a 7% yield of dimers 3 and a 12% yield of bis(cyclopentadienyl)dimethylsilane, 11, which was identified by comparison of retention time and GC–MS with an authentic sample.[14]

Reaction of 2 with Methylenetriphenylphosphorane in the Presence of Me_3SiOMe. A three-neck 100-mL round-bottom flask equipped with a stirring bar, gas inlet, and 100-mL addition funnel fitted with a septum was charged with 20 mL of Et_2O, 0.41 g (2.6 mmol) of 2, and 400 μL (2.9 mmol) of Me_3SiOMe. The addition funnel was charged with 0.68 g (2.5 mmol) of $Ph_3P{=}CH_2$ and 10 mL of Et_2O. The round-bottom flask was cooled with a dry ice–acetone bath, and the phosphorane/ether mixture was added dropwise. After the addition was complete, the reaction was stirred an additional 1.5 h and the cooling bath removed. The reaction mixture was allowed to come to room temperature and to stir overnight. The salts were removed by centrifugation, the solution was concentrated under reduced pressure, and internal standard was added. Analysis of the mixture by GLC showed a 7% yield of 3 and an 18% yield of 11. No 9 was observed.

Vacuum Flow Pyrolyses. The vacuum flow thermolyses were carried out in a horizontal, unpacked, 30-cm quartz tube, 10-mm i.d. at 0.10 torr. The temperature was measured by using a chromel–alumel thermocouple. During the thermolysis the pyrolysate was condensed in a spiral trap, cooled to −196 °C with liquid nitrogen and located following the hot zone. Percent yields and decomposition were determined by GLC analysis after addition of internal standard and are based on the percentage decomposition. In these experiments most of the dimer 3 formed was deposited in essentially pure form on the room temperature portion of the trap: white crystals; mp 107.5–109 °C (lit.[1] 107–109 °C).

FVP of 10. A 0.0958-g sample of 10 was placed in a graduated vial attached to the thermolysis apparatus and allowed to evaporate into the hot zone held at 600 °C. Methylene chloride was used to rinse the dimer into the trap, and the analysis of the pyrolysate by GLC showed 82% of 3 and 60% of dimethyldimethoxysilane based on 95% decomposition of 10.

FVP of 10 and Me_3SiOMe. A solution consisting of 0.0463 g (0.191 mmol) of 10 and 0.53 g (5.1 mmol) of Me_3SiOMe was prepared. Aliquots of ca. 75 μL of this solution were injected directly into the hot zone at 600 °C using a gas-tight syringe until all of the solution had been pyrolyzed. Analysis of the pyrolysate showed 46% decomposition of 10 and dimethoxydimethylsilane and 3 in 52 and 28% yields, respectively.

Vacuum-Sealed-Tube Thermolyses (VSTT). These thermolyses were carried out in a sealed tube, 6.3 mm (o.d.) × 120 mm Pyrex (thick wall, 1.2 mm). The reactants (and cyclohexane solvent in the experiment using benzophenone as trapping agent) and hexadecane were placed in the tube and degassed under a vacuum (0.05 torr). The thermolysis tube was then sealed under a vacuum and placed in a vertical pyrolysis furnace and heated to the temperature indicated, which required 10–15 min. During thermolysis the temperature was controlled to within ±2 °C and was measured with a calibrated thermometer. Analysis of the reaction mixture was accomplished by GLC, and yields were calculated by an internal standard method.

VSTT of 10. A sample of 0.0210 g of 10 and 0.0514 g of hexadecane were thermolyzed at 240 °C of 0.5 h. GLC analysis of the thermolysate showed, in addition to polymeric material, a 78% yield of dimethyldimethoxysilane based on 83% decomposition.

VSTT of 10 and Me_3SiOMe. A mixture of 0.0191 g (0.079 mmol) of 10, 0.1533 g of hexadecane, and 104 μL (0.79 mmol) of Me_3SiOMe was thermolyzed for 1 h at 240 °C. On the basis of 96% decomposition of 10, the products $Me_2Si(OMe)_2$ (83%) and 9 (59%) were identified by GLC retention times and mass spectral patterns identical with those of authentic samples.

VSTT of 10 and Benzophenone. A mixture of 0.0204 g (0.0844 mmol) of 10, 0.0175 g (0.0961 mmol) of benzophenone, 50 μL of cyclohexane, and 0.0206 g of hexadecane was thermolyzed at 248 °C for 15 min. The products obtained from 93% decomposition of 10 were $Me_2Si(OMe)_2$ (60%), **D3** (12%), **D4** (3%), and diphenylfulvene (19%) and were identified by comparison of GLC retention times and mass spectral fragmentation patterns with those of authentic samples.

Acknowledgment. The support of the Robert A. Welch Foundation and the North Texas State Faculty Research Fund is gratefully acknowledged.

Registry No. 2, 13688-59-0; **3a**, 78921-94-5; **3b**, 79317-67-2; 4, 96502-48-6; 6, 96502-51-1; 7, 96502-49-7; 8, 3559-74-8; 9, 78133-11-6; 10, 96502-50-0; 11, 18053-74-2; Me_2SiCl_2, 75-78-5; Me_3SiOMe, 1825-61-2; $Me_2Si(OMe)_2$, 1112-39-6; hexamethylcyclotrisiloxane, 541-05-9; octamethylcyclotetrasiloxane, 556-67-2; diphenylfulvene, 2175-90-8; methylenetriphenylphosphorane, 3487-44-3.

Kinetics and Mechanism of the Pyrolysis of 6-Oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane, a Dimethylsilanone Precursor

Iain M. T. Davidson* and Andrew Fenton

Department of Chemistry, The University, Leicester LE1 7RH, Great Britain

Georges Manuel and Guy Bertrand

Laboratoire des Organométalliques, Université Paul Sabatier, 31062 Toulouse Cedex, France

Received December 11, 1984

The kinetics and mechanism of pyrolysis of the title compound in the gas phase have been investigated. The kinetic results are consistent with the formation of dimethylsilanone by a radical process, followed by silanone insertion reactions. Some general conclusions are drawn about the mechanism of cyclization of dimethylsilanone and about the kinetics of pyrolysis of bicyclo epoxides.

Introduction

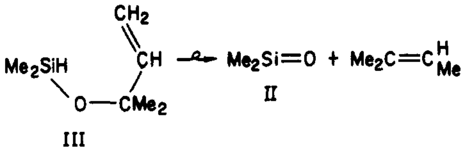
A convenient synthetic route to 6-oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane (I) has been reported,[1] and this compound has been shown[2] to undergo pyrolysis at 460 °C to give cyclosiloxanes and butadiene as the main products, thus implying the formation of dimethylsilanone, $Me_2Si{=}O$ (II).

---

[1] Manuel, G.; Bertrand, G.; El Anba, F. *Organometallics* **1983**, *2*, 391.

[2] Manuel, G.; Bertrand, G.; Weber, W. P.; Kazoura, S. A. *Organometallics* **1984**, *3*, 1340.

Scheme I



Silenes, $R_2Si{=}CH_2$, the silicon-carbon π-bonded intermediates, are now well established in silicon chemistry but much less is known about silanones. Barton and his co-workers have pointed out that many reactions in the condensed phase which appear to involve the intermediacy of silanones have alternative mechanistic explanations.[3] In the gas phase, however, good evidence for the existence of dimethylsilanone (II) came from kinetic studies of the pyrolysis of octamethylcyclotetrasiloxane, D_4; products were observed consistent with extrusion of II from D_4, with insertion of II into the silicon-oxygen bond of D_4 and into the silicon-chlorine bond of added trimethylchlorosilane.[4] Evidence for the intermediacy of II also came from gas-phase experiments in which silenes were generated in the presence of carbonyl compounds,[5] but neither of these methods is a very convenient way of generating silanones or studying their chemistry, the former because D_4 requires high temperatures for its pyrolysis and the latter because of its complexity.

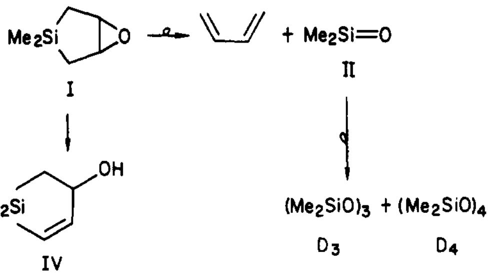
Lane and Frye[6] prepared (vinyldimethylcarbinoxy)dimethylsilane (III) and suggested that it had good potential as a source of dimethylsilanone; this suggestion has been confirmed in gas kinetic studies,[7] which showed that III decomposed to II, as shown in Scheme I, at considerably lower temperatures than those required for the pyrolysis of D_4. III has therefore been found to be more useful than D_4 as a silanone source in kinetic studies of the reactions of II with various substrates.[8] Clearly, it is important at this stage of knowledge to evaluate quantitatively new silanone sources such as I.[2] We now report a gas kinetic study of the pyrolysis of I which sheds some further light on the pyrolysis mechanism and on the usefulness of I as a silanone precursor. Some general conclusions about the mechanism of pyrolysis of bicyclo epoxides may also be drawn from a comparison of our kinetic results with those for a carbon analogue.

Experimental Section

The gas kinetic techniques used in this work were low-pressure pyrolysis (LPP), in which the decay of reactant and formation of products in a static system at ca. 0.05 torr were monitored directly by quadrupole mass spectrometry, medium-pressure pyrolysis (MPP), a similar technique in which the addition of a separator between the reaction vessel and the mass spectrometer allowed the pressure range to be extended upward to ca. 10 torr, and pyrolysis in a stirred-flow reactor (SFR), in which batch samples of reactant at a partial pressure of ca. 0.3 torr were pyrolyzed in a dry nitrogen carrier gas stream at ca. 2.5 atm, with analysis by gas chromatography.[9] This technique could also be complemented by GC/mass spectrometry.

Compounds I and IV were prepared as previously described;[1] the cyclic siloxanes D_3–D_6 were gifts from Dow Corning (Europe), while butadiene was obtained commercially.

Scheme II



Scheme III

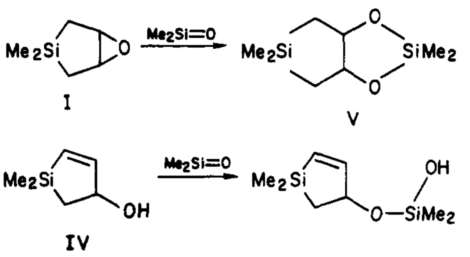
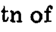


Table I

reaction	ref	log *A*	*E*/kJ mol^{-1}	k_{800K}/s^{-1}
decompn of D_4	4	14.9	301	1.76×10^{-5}
decompn of III	7	12.6	208	0.104
formatn of  from I	this work	15.2	227	2.39

Results

The main products of pyrolysis of I had previously[2] been found to be hexamethylcyclotrisiloxane (D_3), D_4, and butadiene, with some of the 3-silacyclopent-4-en-1-ol (IV) isomeric with I, as shown in Scheme II. Experiments by LPP and MPP covering a pressure range of 0.05–3.0 torr between 420 and 469 °C confirmed the presence of all of these products, together with higher mass peaks of low intensity at *m/e* 202^+ and 187^+, implying the formation of small amounts of 1:1 adducts or insertion products of dimethylsilanone with I and/or IV. Butadiene was by far the major product. Over this 60-fold range of initial pressure, rate constants for the decomposition of I only increased by a factor of ca. 1.3, implying an order of reaction close to unity. In a separate series of experiments between 0.2 and 5.0 torr, the orders of reaction for the formation of butadiene and D_3 were found to be ca. 1.10 and ca. 1.14, respectively. However, because of contributions to the mass spectrum of I from IV and from other products of higher molecular weight, the LPP and MPP techniques were not as suitable as the SFR technique for the measurement of accurate Arrhenius parameters for the pyrolysis of I. Accordingly, I was pyrolysed in the SFR between 408 and 492 °C, with initial pressures of I of 0.30 ± 0.05 torr. A feature of this method is that better kinetic data may be obtained for formation of products than for decomposition of reactant; first-order rate constants were measured for formation of butadiene, giving $\log A = 15.2 \pm 0.2$ and $E/\text{kJ mol}^{-1} = 227 \pm 3$, and for formation of $[D_3 + D_4]$, giving $\log A = 16.4 \pm 0.5$ and $E/\text{kJ mol}^{-1} = 256 \pm 8$. These values correspond to a silicon balance of 30–40% when the number of silicon atoms in D_3 andd D_4 is taken into account. The ratio of D_3 to D_4 varied from 4.5 at 420 °C to 3.7 at 469 °C. It is evident from Table I (vide infra) that D_4 does not decompose to D_3 between 420 and 469 °C. The alcohol IV amounted to 1.4% of the butadiene

---

[3] Barton, T. J.; Hoekman, S. K.; Burns, S. A. *Organometallics* **1982**, *1*, 721. Goure, W. F.; Barton, T. J. *J. Organomet. Chem.* **1980**, *199*, 33.

[4] Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc. D* **1971**, 251. Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2260.

[5] Golino, C. M.; Bush, R. D.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1974**, *66*, 29.

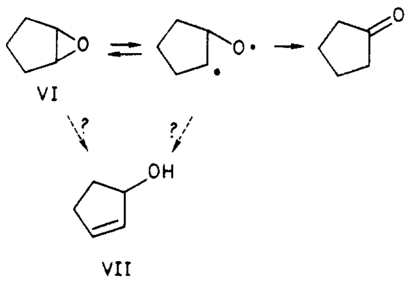
[6] Lane, T. H.; Frye, C. L. *J. Organomet. Chem.* **1979**, *172*, 213.

[7] Wood, I. T. Ph.D. Thesis, University of Leicester, 1983.

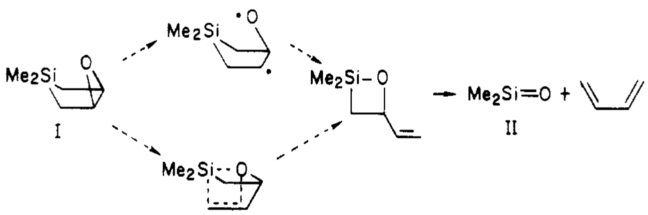
[8] Davidson, I. M. T.; Fenton, A.; Wood, I. T., unpublished work.

[9] Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972.

Scheme IV



Scheme V



formed at 420 °C, rising to 2.6% at 469 °C; it was not feasible to measure accurate Arrhenius parameters for the formation of such a minor product.

Minor products of the pyrolysis of I detected in the SFR experiments were the alcohol IV, D_5, D_6 (all identified by comparison with authentic samples), the product with mass spectral peaks at m/e 202^+ and 187^+ (V), and small quantities of higher molecular weight products. The product V could be formed by insertion of dimethylsilanone into the carbon–oxygen bond in the epoxide ring of I or into the oxygen–hydrogen bond in the alcohol IV, as illustrated in Scheme III. The first of these possibilities was tested by pyrolyzing I at 423 °C in the presence of 2-methyloxirane (propylene oxide) in the LPP apparatus; new mass spectral peaks at m/e 132^+ and 117^+ were observed, corresponding to the expected product. Likewise, pyrolysis of I in the presence of the alcohol IV gave enhanced intensities of the m/e 202^+ and 187^+ peaks. However, in view of the small yield of IV in the pyrolysis of I, the product V probably resulted from insertion of II into I.

The effect of silanone traps on the kinetics of decomposition of I was also studied in the LPP apparatus. We have found previously[8] that methanol, methoxytrimethylsilane, and trimethylchlorosilane all react rapidly with dimethylsilanone, the reactivity sequence being MeOH > Me_3SiOMe > Me_3SiCl. The effectiveness of each of these substrates in reducing the rate of decomposition of I followed the same sequence, but the effect was small. These traps also inhibited the formation of D_3 and D_4.

The Arrhenius parameters and rate constants for formation of butadiene from I are compared with those for the decomposition of D_4 and III in Table I.

Discussion

Attention has already been drawn[2] to the interesting parallel between the pyrolysis of I and its carbon analogue, 6-oxabicyclo[3.1.0]hexane, VI. Flowers and Penny[10] studied the kinetics of pyrolysis of VI between 400 and 470 °C. Two isomers of VI, cyclopentanone (66%) and cyclopent-2-en-1-ol, VII (34%), accounted for 97% of the primary reaction products; the most likely route to cyclopentanone was via the biradical formed by homolysis of a carbon–oxygen bond in the epoxide ring, while VII may have resulted from isomerization of the same biradical or from a concerted process. These reactions are summarized in Scheme IV. Pyrolysis of VI followed first-order kinetics; Arrhenius parameters for the main reaction forming cyclopentanone were $\log A = 14.16 \pm 0.11$ and $E/\text{kJ mol}^{-1} = 240.4 \pm 1.5$.

The primary reactions in the pyrolyses of both I and VI are first order and unimolecular. The transannular interaction between silicon and oxygen in I is obviously the cause of the striking differences between Schemes I and II; it seems very likely that the result of that interaction is the transient formation of a silaoxetane,[2] which then decomposes to give the observed products, but the formation of that silaoxetane could be either concerted or via biradical formation, as shown in Scheme V. Our observed A factor for the formation of butadiene seems to be considerably too high for the concerted process in Scheme V, in which there would be substantial restrictions in the transition state. On the other hand, if we favor the radical route we have to account for the different Arrhenius parameters observed for the formation of butadiene from I and for the formation of cyclopentanone from VI. We suggest that these differences can indeed be explained as follows.

Silicon is known to undergo S_H2 reactions[11] and to form a strong bond to oxygen. If the biradical is formed, the oxygen atom would therefore be expected to undergo a rapid irreversible displacement reaction at silicon. As subsequent reactions would be relatively rapid, formation of butadiene would then be rate-determined by the rupture of the carbon–oxygen bond in the epoxide ring. An unstrained alkyl–oxygen bond has[12] a dissociation energy of ca. 343 kJ mol^{-1}, while the ring strain in oxirane is[12] 113 kJ mol^{-1}; the ring strain in I may be greater because of distortions caused by the silicon–oxygen interaction. Consequently, the expected activation energy for carbon–oxygen bond-breaking in I simply equals the enthalpy change, $(343 - \geq 113)$, i.e., ≤ 230 kJ mol^{-1}, in excellent agreement with our experimental value. Likewise, the experimental A factor is a reasonable size for a ring-opening homolysis.[12] In the pyrolysis of VI, on the other hand, the ring-opening carbon–oxygen homolysis is reversible;[10] the observed overall A factor would therefore be reduced, while the activation energy would be greater than ΔH by a small amount equal to the energy barrier for cyclization of the radical. In oxirane, this barrier has been estimated[13] to be ≤ 20 kJ mol^{-1}. [As noted above, a further minor factor is that the epoxide ring strain in VI may be slightly less than in I.] These features account for the observed differences in Arrhenius parameters for the pyrolyses of I and VI. We conclude that our kinetic measurements confirm the earlier suggestion[2] that the main primary reaction in the pyrolysis of I is homolysis of a carbon–oxygen bond to form a biradical. Because ring-opening is irreversible in the pyrolysis of I, our kinetic data for the formation of butadiene may be interpreted as the first to relate directly to simple carbon-oxygen bond homolysis in a bicyclo epoxide ring.

On balance, Flowers and Penny[10] favored a concerted reaction for the formation of the alcohol VII from VI. Because the homolysis of the carbon–oxygen bond is reversible in VI but not in I, the rate constant for the overall pyrolysis of I was ca. 100 times greater than for VI. Hence,

---

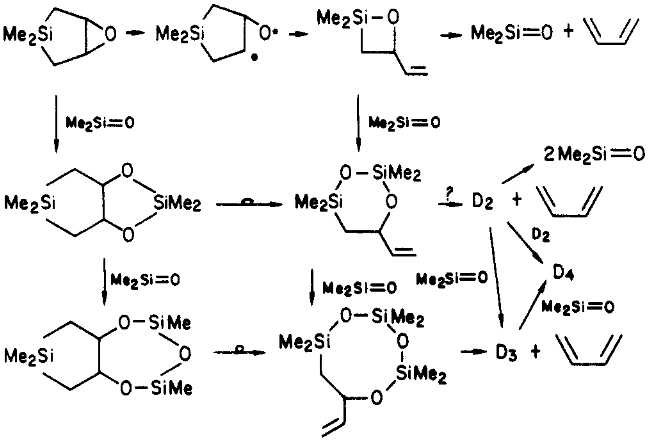
[10] Flowers, M. C.; Penny, D. E. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 355.

[11] Band, S. J.; Davidson, I. M. T. *Trans. Faraday Soc.* **1970**, *66*, 406.

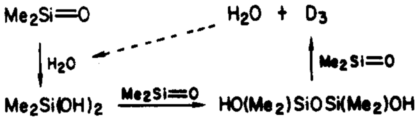
[12] Benson, S. W. "Thermochemical Kinetics", 2nd. ed.; Wiley: New York, 1976.

[13] Benson, S. W. *J. Chem. Phys.* **1964**, *40*, 105.

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.

---

(14) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* 1984, *106*, 822.

(15) Gusel'nikov, L. E.; Komoboeyevsky, K. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Adak. Nauk SSSR* 1977, *235*, 1086.

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

Michael J. S. Dewar* and Gilbert L. Grady[1]

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received November 9, 1984

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

0276-7333/85/2304-1327$01.50/0