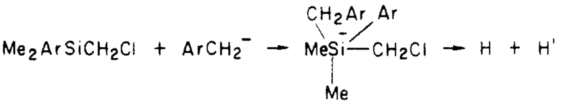
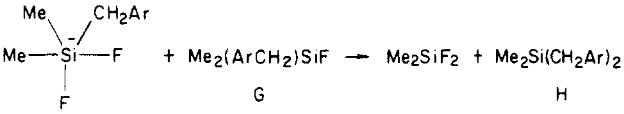
cisely detail the steps leading to secondary reaction. We have two measures of the effect of substituents on secondary product formation: both ρ values are larger than those obtained in the earlier stages of the reaction and suggest that a greater charge develops in the transition state of the secondary reaction ("$ArCH_2^-$" like). It could be argued that secondary products form by two other mechanistic schemes (eq 6 and 7). In the first of these,



$$\mathrm{Me_2ArSiCH_2Cl + ArCH_2^- \rightarrow \underset{Me}{\overset{CH_2Ar\ \ Ar}{MeSi}}{-}CH_2Cl \rightarrow H + H'} \quad (6)$$



$$\mathrm{\underset{F}{\overset{Me\ \ CH_2Ar}{Me{-}Si{-}F}} + \underset{G}{Me_2(ArCH_2)SiF} \rightarrow Me_2SiF_2 + \underset{H}{Me_2Si(CH_2Ar)_2}} \quad (7)$$

$ArCH_2^-$ (or a "$ArCH_2^-$" species) reacts with starting chlorosilane forming a pentacoordinate intermediate from which either Ar or Me migrate giving H and H′, respectively. The other reaction scheme is similar to ones we have proposed for gas-phase reactions[8] where groups are "soft transferred" from pentacoordinate intermediates to neutral silanes. On this point we have obtained direct evidence that $Me_2(ArCH_2)SiF$, where Ar = phenyl, reacts with F^- to give $Me_2Si(CH_2Ar)_2$ under conditions similar to those of our other reactions. Thus, we feel certain that eq 5 is operating although we cannot exclude the possibility that either or both eq 6 and 7 are occurring simultaneously. It is difficult to know how free the $ArCH_2^-$ anion is. Although the ρ values are quite a bit larger when the secondary reaction is probed, the complexity of this part of these reactions makes it impossible to say with certainty to what extent the carbanion is free. Furthermore, it is difficult to be sure the extent to which water has been excluded from our reactions although we have demonstrated that reactivity is not altered under carefully controlled inert-gas conditions. The nagging doubt remains that water cannot be completely excluded, a doubt fueled by the knowledge that KF is so readily hygroscopic. We believe, however, that in totality the evidence suggests a reasonable amount of carbanionic character in these reactions.

Thus, we feel that the mechanistic scheme set forth in eq 5 adequately describes the series of reactions we have studied. Further mechanistic details as well as studies expanding the scope of such reactions are in progress.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (Grant CHE-8313826) and Research Corp. We also wish to thank the University of Colorado Health Sciences Center Clinical Mass Spectrometry Resource for extensive use of their GC–MS facility. We also thank Robert Meglen, Center for Environmental Studies, for help with the statistical analysis.

Registry No. **1**, 2344-80-1; **2**, 3121-77-5; **3**, 54690-67-4; **4**, 22429-26-1; **5**, 3121-75-3; **6**, 3944-19-2; **7**, 18306-73-5; **8**, 17201-83-1; **9**, 2917-46-6; **10**, 2344-83-4; **11**, 5926-38-5; **12**, 7787-87-3; **13**, 16709-86-7; **14**, 1833-51-8; **15**, 1833-32-5; **16**, 770-90-1; **17**, 770-89-8; **18**, 779-69-1; $MeEt_2SiF$, 681-07-2; MeEt(C-Pr)SiF, 97878-78-9; MeEt(*i*-Pr)SiF, 97878-79-0; MeEt(n-Bu)SiF, 97878-80-3; $Me_2(EtCH_2)SiF$, 27977-39-5; Me_2(c-$PrCH_2$)SiF, 97878-81-4; Me_2(*i*-$PrCH_2$)SiF, 97878-82-5; Me_2(n-$BuCH_2$)SiF, 96164-67-9; $Me_2(CH_2Ar)SiF$ (Ar = phenyl), 1842-25-7; MeArEtSiF (Ar = *p*-chlorophenyl), 14132-22-0; $Me_2Si(CH_2Ar)_2$ (Ar = *p*-chlorophenyl), 97878-83-6; $MeArEtSiCH_2Ar$ (Ar = *p*-chlorophenyl), 97878-84-7; CsF, 13400-13-0; KF, 7789-23-3; 18-crown-6, 17455-13-9.

Stannylenes: An MNDO Investigation[1]

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Calculations are reported for insertion and cycloaddition reactions of compounds containing divalent tin.

Introduction

While the chemistry of carbon(II) compounds (carbenes) has been extensively studied, references to the organic chemistry of tin(II) compounds (stannylenes) remain sparse.[3] While the stable tin(II) halides have been well characterized and MNDO studies of them reported,[4] organotin(II) compounds have remained elusive and most of the early claims for their preparation have been refuted.[3] In recent years, however, mostly through the efforts of Neumann and his co-workers,[5-10] clear evidence for the preparation and reactions of stannylenes has emerged. The reactions so far reported include insertion into car-

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(1) Part 72 of a series reporting studies of chemical problems, using quantum mechanical molecular models. For part 71, see: Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R. *Organometallics* **1985**, 4, 1041.

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Table I. Calculated Heats of Formation (ΔH_f), Dipole Moments (μ), and Ionization Energies (IP)

molecule	ΔH_f, kcal/mol	μ, D	IP, eV
$SnMe_2$ (**1**)	0.25	2.94	9.63
Cl_2SnMe_2 (**2**)	−68.44	5.50	11.39
$ClSnMe_3$ (**3**)	−44.10	4.22	11.08
$Me_2ClSnSnClMe_2$ (**6**)	−73.28	0.157	10.30
$Me_2SnCl\cdot$ (**7**)	−24.10	4.03	9.38
[TS] (**9**)	−58.06	4.54	9.37
$Me_3SnSnClMe_2$ (**10**)	−47.73	5.22	10.02
[TS] (**11**)	−29.65	7.83	9.00
$SnMe_3\cdot$	8.03	0.72	8.73

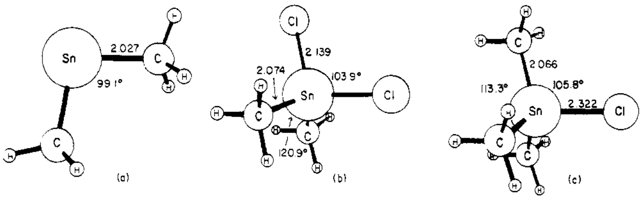

Figure 1. ORTEP plots with calculated bond lengths (Å) and angles for (a) dimethylstannylene (**1**), (b) dimethyldichlorostannane (**2**), and (c) trimethylchlorostannane (**3**).

bon–halogen or tin–halogen bonds, polymerization, and cheletropic cycloadditions.[10,11]

As in the case of divalent carbon, the reactions may take place either via "free" stannylenes or through "stannylenoid" intermediates.[10] We have now examined several such processes, using the MNDO SCF MO model.[12] MNDO parameters for tin have recently become available,[4] and extensive studies of tin compounds[13,14] have led to satisfactory results.

Procedure

The calculations were carried out by using the standard MNDO procedure[12] and parameters,[4,12] as implemented in the MOPAC[15] package of computer programs. Open-shell systems were studied by using the "half electron",[16] CI, or UHF[17] versions of MNDO. Geometries were calculated by a derivative optimization procedure and transition states located either by the reaction coordinate method,[18] followed by minimizing the norm of the energy,[19] or by a new procedure (SADDLE) recently developed here.[20] Stationary points were characterized by calculating force constants.[19] All these procedures are included in MOPAC.

Results and Discussion

Dimethylstannylene (**1**) has been found[9] to insert into the tin–chlorine bond of dichlorodimethylstannane (**2**) but to polymerize in the presence of chlorotrimethylstannane (**3**). In addition, some insertion products, and the polymer, reversibly regenerate **1**.[9,10] Neumann et al.[9] attributed the difference to kinetic factors, **1**, being nucleophilic, reacting faster with **2** than with **3** because the tin atom in the former is more positive. Neumann et al.[7] have also reported that **1** inserts quantitatively into the C–I bond of methyl iodide. We began by studying these reactions, using MNDO.

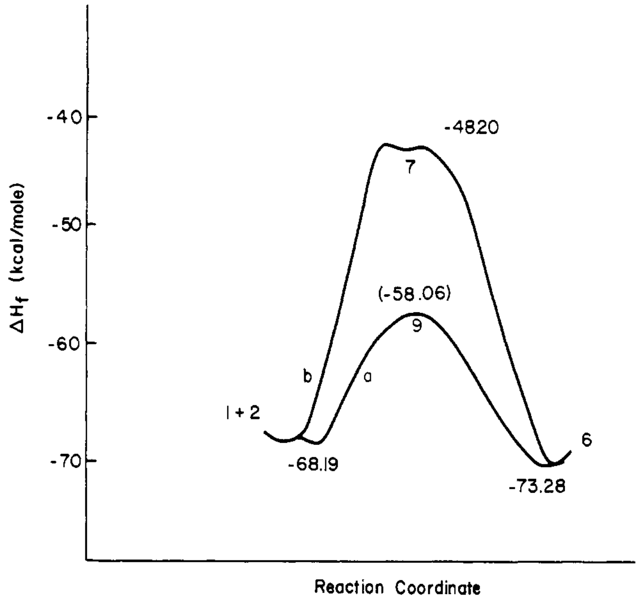

Figure 2. Minimum energy reaction paths (MERPs) for insertion of **1** into a CCl bond of **2**: (a) one-step reactions; (b) two-step reaction.

Table I shows the heats of formation, dipole moments, and ionization potentials calculated for **1**–**3** by MNDO while Figure 1 shows the corresponding geometries.

Dimethylstannylene (**1**) is predicted to have a singlet ground state with a heat of formation of 0.3 kcal/mol, SnC bond lengths of 2.03 Å, and C–Sn–C bond angle of 99.1°. While no structural information, other than an infrared spectrum,[21] is available for comparison, MNDO has been shown to give reasonable results for the tin(II) halides.[4] The structure of a derivative[22–24] (**4**) of **1** has been reported,[24] the C–Sn bond lengths being 2.24 Å and the C–Sn–C bond angle 96°. The Sn–C bond length is longer than normal, suggesting stretching of the bonds by the bulky groups attached to tin. MNDO, on the other hand, consistently underestimates the lengths of bonds to tin.[4,5]

$$\underset{\textbf{4}}{[(SiMe_3)_2CH]_2Sn:} \qquad \underset{\textbf{5}}{H_2Sn:}$$

Few theoretical calculations have been reported for the geometries of organotin compounds. An ab initio calculation[25] for stannylene (**5**) predicted it to have a singlet ground state with a H–Sn–H bond angle of 92.7°, bond lengths of 1.756 Å, and a heat of formation of 89.0 kcal/mol. By way of comparison MNDO also predicts **5** to have a singlet ground state with a bond angle of 92.6°, bond lengths of 1.57 Å, and a heat of formation of 22.3 kcal/mol. The "normal" SnH bond length, e.g., in stannane (SnH_4), is 1.701 Å.[26] The agreement is good except for the heat of formation, for which no experimental value is available. Assuming the H–Sn bond energy to be 72.2 kcal/mol[27] and using the known[28] heats of atomization for tin and hy-

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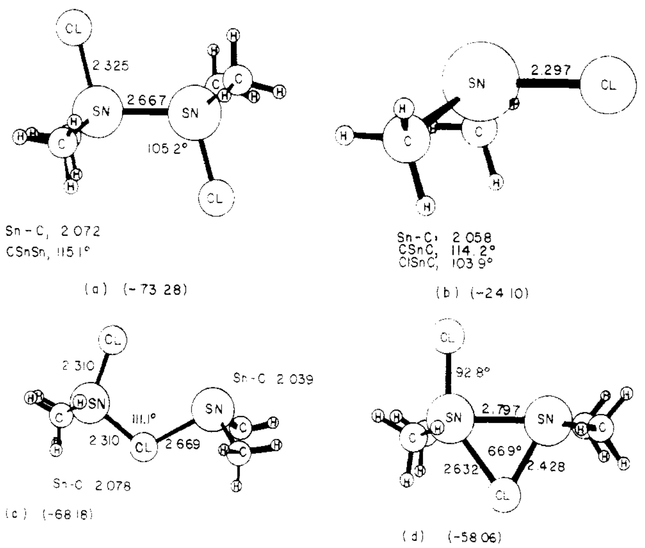
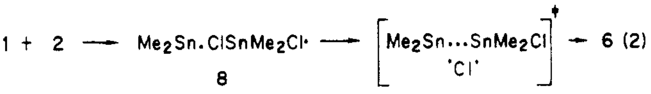


Figure 3. ORTEP plots with bond lengths (Å), bond angles (deg), and, in parentheses, heats of formation (kcal/mol) calculated for (a) 1,2-dichloro-1,1,2,2-tetramethyldistannane (**6**), (b) dimethylchlorostannyl radical (**7**), (c) molecular complex from **1** and **2**, and (d) transition state **9** for the one-step insertion of **1** into a SnCl bond of **2**.

drogen, one finds the heat of formation of (gaseous) **5** to be of 2.8 kcal/mol. While this estimate is open to obvious uncertainties, it seems clear that the MNDO estimate must be much closer to the truth than the ab initio one.

Next we studied the insertion of **1** into the Sn–Cl bond of **2** to form 1,2-dichloro-1,1,2,2-tetramethyldistannane (**6**). As the calculated heat of formation of **6** (Table I) shows, the overall reaction is predicted to be exothermic, by 4 kcal/mol. Two alternative routes from (**1** + **2**) were found: a two-step process (eq 1) involving two chlorodimethylstannyl radicals (**7**) as intermediates and a direct concerted insertion of **1** into a C–Cl bond of **2** (eq 2). The latter reaction was predicted to take place via an initial adduct (**8**) formed by association of **1** with a chlorine atom in **2**. Figure 2 shows the corresponding minimum energy reaction path (MERP).

$$\underset{\mathbf{1}}{\mathrm{Me_2Sn:}} + \underset{\mathbf{2}}{\mathrm{Cl_2SnMe_2}} \rightarrow \underset{\mathbf{7}}{\mathrm{2Me_2SnCl\cdot}} \rightarrow \underset{\mathbf{6}}{\mathrm{Me_2ClSnSnMe_2Cl}} \qquad (1)$$



$$1 + 2 \longrightarrow \underset{8}{\mathrm{Me_2Sn.ClSnMe_2Cl\cdot}} \longrightarrow \underset{9}{\left[\begin{matrix}\mathrm{Me_2Sn...SnMe_2Cl}\\ \mathrm{\cdot Cl\cdot}\end{matrix}\right]^{\ddagger}} \longrightarrow 6 \qquad (2)$$

The heats of formation and geometries calculated for **6**, **7**, **8**, and the transition state (TS; **9**) for the concerted insertion are shown in Figure 3. The activation energy (20.0 kcal/mol) calculated for the two-step route was greater by 10 kcal/mol than that (10.1 kcal/mol) for the concerted one. Since MNDO tends to give energies for radicals that are too negative, the difference between the two is likely to be even greater, so there seems little doubt that the concerted mechanism is preferred. This conclusion is supported by failure[8] to observe CIDNP during the reaction.

Similar results were obtained for the reaction of **1** with **3** to form chloropentamethyldistannane (**10**). Here again the activation energy calculated for the two-step route (28.4 kcal/mol; eq 3) was much greater than that (14.2 kcal/mol) for the concerted one (eq 4). The heats of formation and geometries calculated for **10** and for the TS (**11**) for its formation from **1** and **3** by the concerted route are shown in Figure 4.

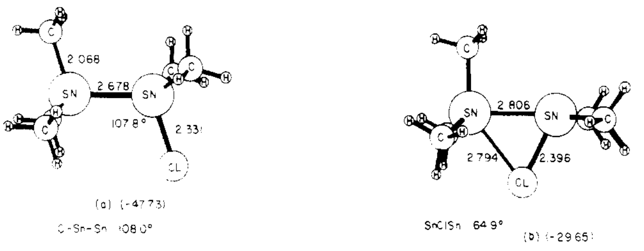


Figure 4. ORTEP plots with bond lengths (Å), bond angles (deg), and, in parentheses, heats of formation (kcal/mol) calculated for (a) pentamethylchlorodistannane (**10**) and (b) the transition state **11** for formation of **10** from **1** and **3**.

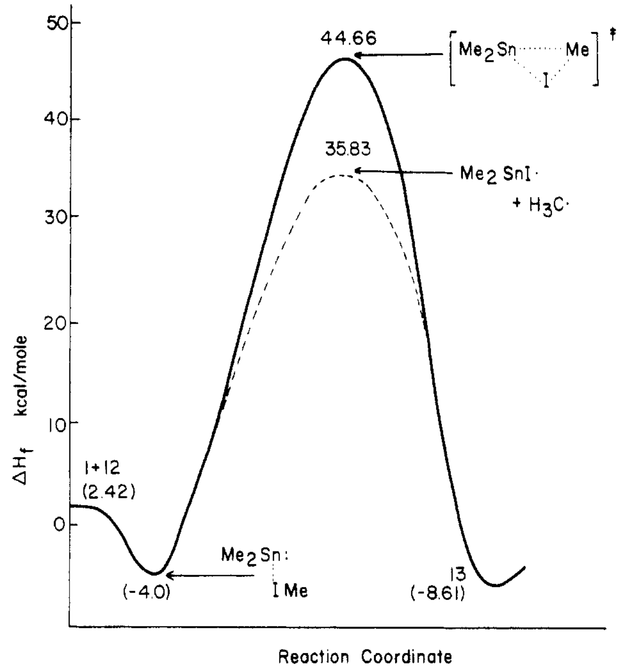
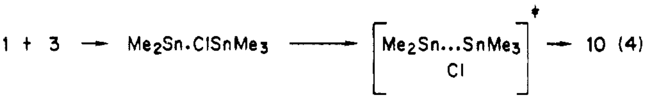


Figure 5. MERPs for one-step (—) and two-step (- - -) insertion of **1** into the CI bond of methyl iodide (**12**).

$$\underset{\mathbf{1}}{\mathrm{Me_2Sn:}} + \underset{\mathbf{3}}{\mathrm{ClSnMe_3}} \rightarrow \mathbf{7} + \mathrm{Me_3Sn\cdot} \rightarrow \underset{\mathbf{10}}{\mathrm{Me_3SnSnMe}} \qquad (3)$$



$$1 + 3 \longrightarrow \mathrm{Me_2Sn.ClSnMe_3} \longrightarrow \underset{11}{\left[\begin{matrix}\mathrm{Me_2Sn...SnMe_3}\\ \mathrm{Cl}\end{matrix}\right]^{\ddagger}} \longrightarrow 10 \qquad (4)$$

While **1** undergoes insertion into **2** to form **6**, it polymerizes in preference to inserting into **3**.[9] Neumann et al.[9] assumed the difference to be kinetic in origin, insertion being faster than polymerization in the case of **2** but slower in the case of **3**. Our calculations indeed predict this to be the case, the activation energy for the latter reaction being predicted to be greater by 4.1 kcal/mol (see Table I).

Neumann et al.[7] have also studied the reaction of **1** with methyl iodide (**12**). They found that **1** inserts quantitatively into the C–I bond to form trimethyliodostannane (**13**); i.e.

$$\underset{\mathbf{1}}{\mathrm{Me_2Sn:}} + \underset{\mathbf{12}}{\mathrm{MeI}} \rightarrow \underset{\mathbf{13}}{\mathrm{Me_3SnI}} \qquad (5)$$

Our MNDO calculations for the concerted insertion of stannylene (**1**) into the C–I bond of **12** are summarized in Figure 5. The situation here differs, however, from that

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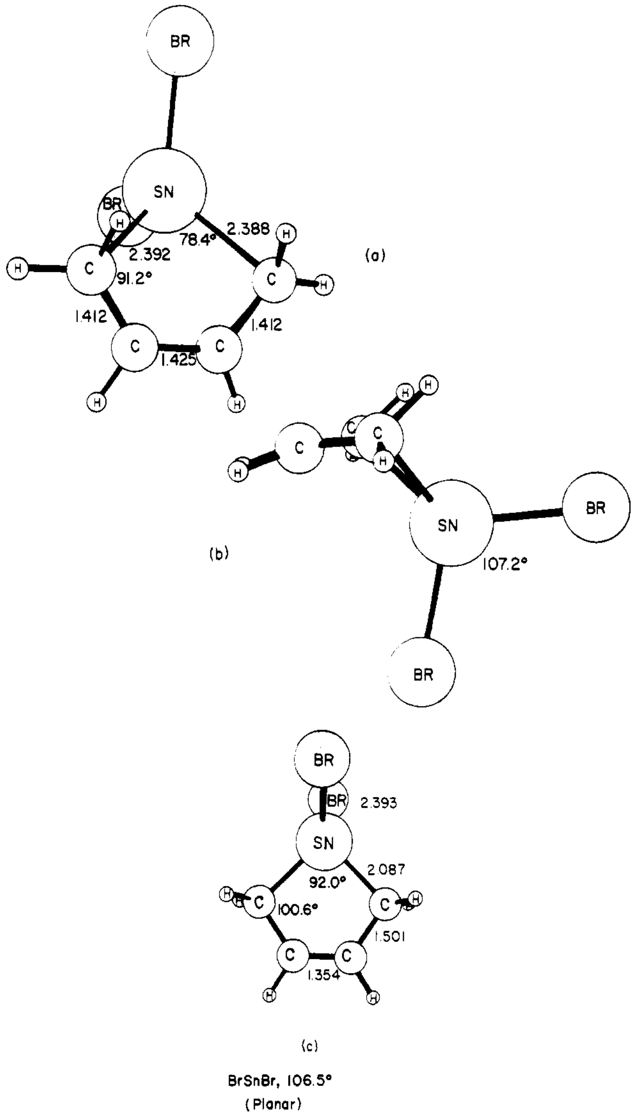

Figure 6. ORTEP plots with bond lengths (Å) and angles (deg): (a) and (b) for the TS for addition of $SnBr_2$ to butadiene and (c) for the adduct.

in the case of 2 or 3 in that MNDO predicts the reaction of 1 with 12 to take place more easily by the two-step route, via methyl ($H_3C\cdot$) and dimethyliodostannyl ($Me_2SnI\cdot$) radicals, the activation barrier for the latter (33.0 kcal/mol) being less than that (42.3 kcal/mol) for the concerted insertion. The latter is again predicted to take place via an intermediate adduct, $Me_2Sn{\cdot}ICH_3$, this being formed exothermically by 6.4 kcal/mol.

While our calculations agree qualitatively with experiment, the calculated activation barrier is clearly too large, given that the reaction takes place rapidly at room temperature. This error is not, however, surprising because MNDO underestimates[4] the strengths of SnI bonds. Since the error should be greater for the two-step reaction, our prediction that this is the preferred route for insertion still stands. A CIDNP study of the reaction would be of interest (cf. ref 8).

Another reaction of stannylenes that has been studied recently is the cheletropic addition of dihalostannylenes to dienes,[11] which has been reported to be a concerted disrotatory process. We have examined the addition of tin(II) bromide (**14**) to butadiene (**15**) by MNDO.

MNDO predicts the addition of **14** to **15** to take place syn and in a synchronous[29] manner, via a symmetrical TS (**16**). The calculated activation energy (19.5 kcal/mol) accounts nicely for the observation that the reaction takes place at room temperature. The geometries calculated for **16** and the product **17** are shown in Figure 6 while the calculated heats of formation are 10.7 kcal/mol and −1.0 kcal/mol, respectively.

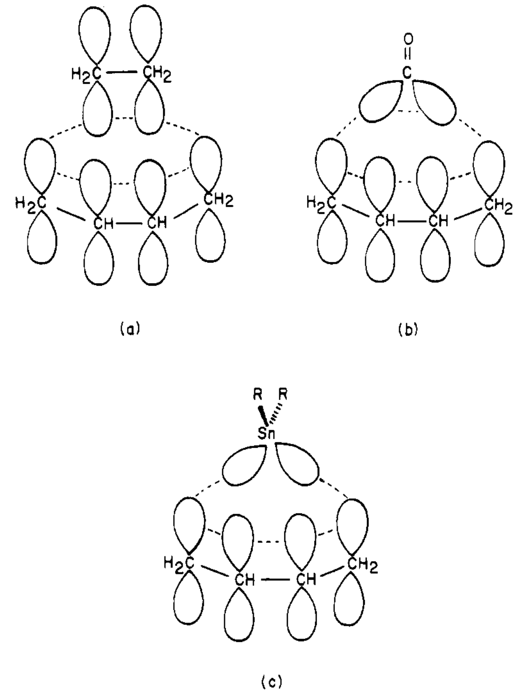

Figure 7. Orbital interactions in a symmetrical TS for cycloadditions of 1,3-butadiene to (a) ethylene, (b) carbon monoxide, and (c) tin(II) compounds (**16**, R = Br).

The prediction of a symmetrical TS is interesting in view of a recent discussion[30] of the mechanisms of multibond reactions in general and cycloaddition reactions in particular. As noted there, while reactions involving the breaking and/or forming of more than one bond tend not to take place in a synchronous manner, exceptions can occur when some special circumstance favors a synchronous mechanism. One such factor is the stabilization of aromatic TSs in the case of pericyclic reactions, of which the reaction between **14** and **15** is a typical example. In the Diels–Alder reaction, steric problems arise in forming a symmetrical TS because the distances between the pairs of carbon atoms involved (1.33 and 2.81 Å) are very different. Because carbon–carbon bonds are short, a symmetrical TS is necessarily quite severely strained, given that the interacting AOs are, at least initially, of p type; see Figure 7a. Similar remarks apply to cheletropic reactions[31] of small dienophiles such as CO or N_2 (Figure 7b). In the case of **14**, however, the relevant atom (Sn) is very large. Formation of a symmetrical TS (Figure 7c) should then involve relatively little strain.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. F49620-83-C-0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out with a DEC VAX 11-780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. 1, 23120-99-2; 2, 753-73-1; 3, 1066-45-1; 5, 63366-64-3; 6, 58529-40-1; 7, 41079-92-9; 10, 80048-66-4; 12, 74-88-4; 13, 811-73-4; 14, 10031-24-0; 15, 106-99-0; 17, 97752-10-8.

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