Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.68; H, 10.48. Found: C, 78.68; H, 10.62.

Oxidation of 8 with Chromium Trioxide/3,5-Dimethylpyrazole. To 15 mmol of chromium trioxide/3,5-dimethylpyrazole complex in 25 mL of methylene chloride formed as above at −20 °C was added 0.33 g (0.000 75 mol) of **8** in 3 mL of methylene chloride. The reaction mixture was stirred at −20 °C for 2 h before addition of 50 mL of 5 N sodium hydroxide solution. After being stirred for 30 min, the layers were separated and worked up as above to give 0.29 g of dark oil. Thin-layer chromatography on POLYGRAM Sil G/uv plates (Macherey-Nagel and Co.) with 25% ethyl acetate/toluene as the eluant showed two new major components more polar than the starting material, neither of which corresponded to **4**. Low-pressure chromatography over Woelm silica with 5% ethyl acetate/toluene as the eluant gave 34 mg of the less polar component which was not characterized further. The more polar major component (54 mg) proved to be the 7,15-diketone **10**: mp 139–141 °C; UV (MeOH) 259 nm (ϵ 10 400); mass spectrum, m/e 456 (M^+).

Anal. Calcd for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found: C, 76.41; H, 9.72.

Registry No. **2**, 34495-42-6; **3**, 6562-21-6; **4**, 16780-48-6; **5** (R = H), 434-16-2; **8**, 21152-11-4; **10**, 71369-91-0.

Transannular Carbene Insertion Reactions in the Bicyclo[4.2.1]nonane System

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The study of the conformations of medium ring compounds has raised much interest in the field of NMR spectroscopy[1,2] and chemical reactivity.[1,3] From the conformational point of view, the seven- and eight-membered rings are complex substrates, because of the multiplicity of the conformations which can be involved.[1,4a] The introduction of linkages between two nonvicinal carbons in such rings gives rise to bicyclic derivatives in which the medium ring freedom degree is decreased. The purpose of this paper is to show the particular interest of such substrates in the study of: the proximity of transannular carbons in bridged molecules such as bicyclo[4.2.1]nonanes or bicyclo[3.2.1]octanes; and the structural features of carbene insertion reactions, which has been the subject of current interest and which appears as being a reaction particularly well adapted to the study of transannular reactions. These reactions have been extensively studied in medium ring compounds,[5] but much less in bridged substrates involving seven- or eight-membered rings.[6]

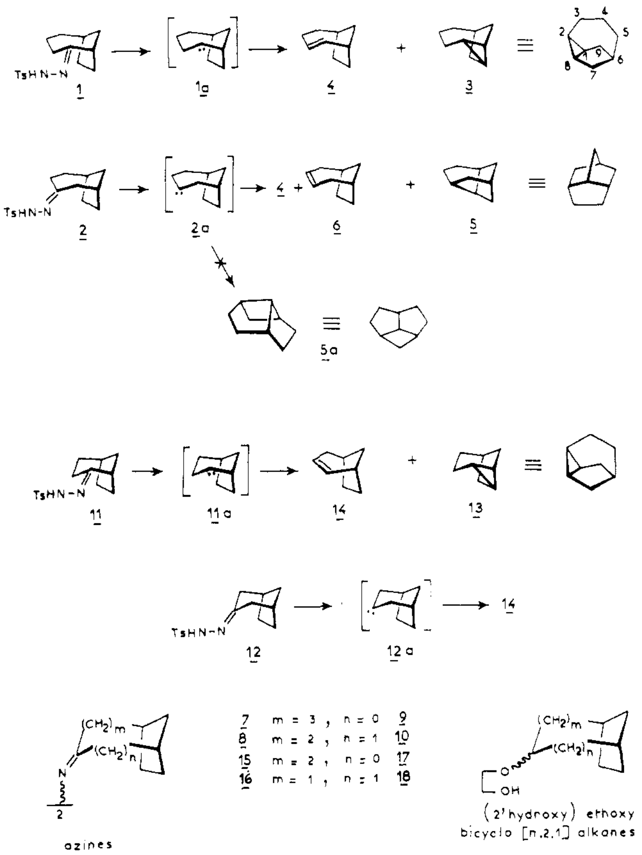

Figure 1.

Tosylhydrazones were used as starting materials, since it is possible, by submitting them to different experimental conditions, to induce carbanionic, carbenic, or cationic reactions.[7c,d] Tosylhydrazones **1**, **2**, **11**, and **12** have been prepared from bicyclo[4.2.1]nonan-2- and -3-ones and bicyclo[3.2.1]octan-2- and -3-ones by standard procedures. They were reacted under conditions recorded in Tables I and II, which also report the yield of the different products obtained.

When carbanionic conditions are used (alkyllithium in aprotic solvents)[7cd,9] olefins are the exclusive reaction products as expected.

It has been shown previously, that in the presence of excess sodium methoxide in aprotic solvent (diglyme) tosylhydrazones lead to free carbenes.[7,8] The carbene **1a** yielded a mixture of tricyclo[4.2.1.0^{2,8}]nonane (**3**) and bicyclo[4.2.1]non-2-ene (**4**) in the ratio 1:0.85, while **2a** gave

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Table I. Decomposition of Tosylhydrazones 1 and 2

			% yield from 1				% yield from 2			
solvent	equiv of base	temp. °C	3 + 4	3/4	7	9	4 + 5 + 6	5/4 + 6	8	10
ether	3 MeLi	room temp	80	0/100			71	0/100		
diglyme	10 MeONa	160	70	54/46	14		43	20/80	37	
ethylene glycol	10 MeONa	160	24	79/21		43	27	0/100		52

Table II. Decomposition of Tosylhydrazones 11 and 12

			% yield from 11				% yield from 12		
solvent	equiv of base	temp, °C	13 + 14	13/14	15	17	14	16	18
ether	3 MeLi	room temp	75	0/100			70		
diglyme	10 MeONa	160	25	44/56	39		28	56	
ethylene glycol	10 MeONa	160	24	81/19		65	35		44

a mixture of tricyclo[4.2.1.0^{3,7}]nonane (**5**) (brendane) and two bicyclo[4.2.1]nonenes (**4** and **6**) in the ratio 1:4 (Figure 1). In the bicyclo[3.2.1]octane series, the carbene **11a** gives rise to tricyclo[3.2.1.0^{2,7}]octane (**13**) and bicyclo[3.2.1]oct-2-ene (**14**) in the ratio 1:1.3, while the latter olefin was the only hydrocarbon obtained from **12a**. In all cases, an intermolecular reaction leading to variable amounts of the corresponding azines **7**, **8**, **15**, and **16**, respectively, parallels the intramolecular reaction.[5c,7]

When the decompositions were carried out in a protic solvent like ethylene glycol (cationic conditions),[8] we have observed that the cyclopropanic products **3** and **13** were produced along with the olefins **4** and **14** from **1** and **11**, respectively. In contrast no traces of brendane **5** was formed from **2**. In these decompositions, in all cases, the major compound was the corresponding (2′-hydroxy)ethoxybicycloalkane **9**, **10**, **17**, and **18**, respectively, produced by intermolecular nucleophilic substitution of the intermediate carbocation.[7]

^{13}C NMR has been particularly useful for the identification of these tricyclic molecules. In the case of **3**, the ^{13}C NMR spectrum exhibits seven peaks. Two of them (corresponding respectively to equivalent carbons 1 and 8 and 7 and 9) have an intensity of twice the others. These data are consistent only with structure **3**. The proton decoupled ^{13}C NMR spectrum of **5** shows six signals, three of them having an intensity of twice the three others. This would be consistent with both structures **5** and **5a**. The latter could result from the cyclization of **2a** in a conformation where the seven-membered ring is a boat form and the eight-membered ring a chair form. However, the ^{1}H NMR spectrum shows particularly significant signals at 0.7 and 0.87 ppm.[10] Furthermore, **5** was identified by comparison with an authentic sample prepared independently from brendan-2-one.[11] The proton-decoupled ^{13}C NMR spectrum of **13** shows only five signals but it obviously appears from the relative intensities of the signals and the single-frequency off-resonance decoupling spectrum[12] that these data are consistent with the proposed structure.

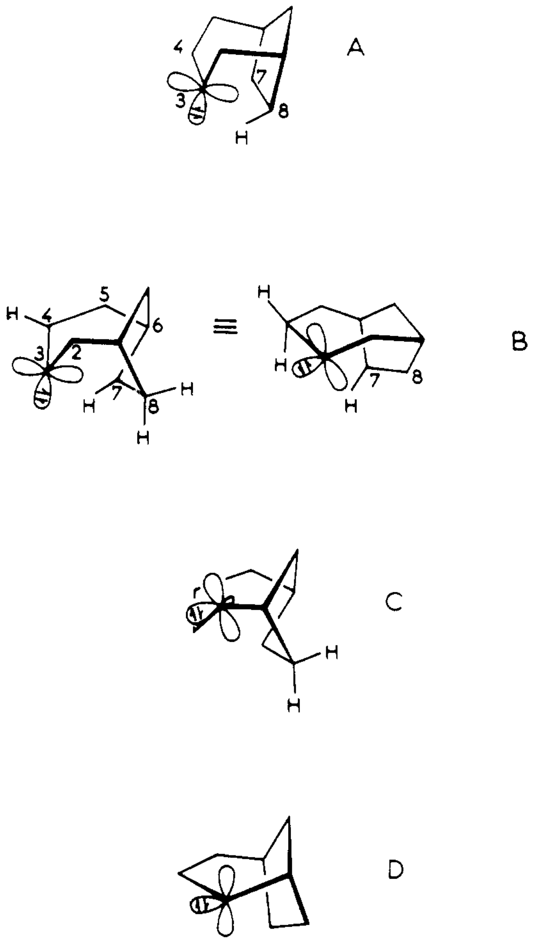

Figure 2.

Discussion

The formation of brendane (**5**) from the bicyclo[4.2.1]non-3-ylidene is particularly informative about the hindered flexibility of the eight-membered ring. These experiments also allow a better insight into the conformation of the relative sites as well as the electronic structures of the carbenic intermediates leading to the insertion reaction. If the cyclooctane ring adopts the boat form (Figure 2A), the carbene orbitals and the C_8–H bond would be coplanar and sufficiently close to one another to give rise to an insertion reaction. However, this reaction does not occur probably because of too strong steric interactions (for instance, the endo hydrogens at C_4 and C_7) operative in this conformation. Furthermore, such a reaction would lead to a tricyclic compound containing a four-membered ring which is unexpected in this type of reaction.[7a,b] If the eight-membered ring is twisted in such a manner that the carbenic carbon 3 gets close to the C_7–H bond, one obtains a slightly deformed boat–chair conformation. The latter is known to have the lowest energy for cyclooctane itself.[4] In this conformation, the carbon skeleton does not allow a strictly linear approach of the carbon empty p orbital toward the hydrogen at C_8 as calculated by Dobson, Hayes, and Hoffman.[13] However,

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nearly all the orbitals involved lie in one plane; this geometry is thought to be the most favorable for the insertion process as it allows a maximum overlap.[14] It is also interesting to note that in this conformation the carbene's empty p orbital (see Figure 2B) is also parallel to one of the C_4–H bonds, whereas it bisects the H–C_2–H angle. This very nicely explains the 1:2 ratio observed in the formation of olefins **4** and **6**. It is known that 1,2-H shifts in alkylcarbene leading to olefin formation occur preferentially when the C–H bond is parallel to the empty p orbital of the carbene.[15] This explanation looks particularly reasonable in rigid bicyclic carbenes such as the ones presently studied.[15] However, as pointed out by a referee, experimental results and semiempirical calculations have suggested that other factors might also affect the formation of olefin from a carbene center, especially in cyclohexanic substrates.[25]

Similar arguments can reasonably be applied for the behavior of carbenes **1a** and **11a**. During the formation of a cyclopropane ring by an intramolecular insertion reaction, it seems difficult to have all the appropriate orbitals lying in the same plane[14,16] (see Figure 2C). However, the intramolecular carbene insertion occurs despite this geometrically less favored conformation, since proximity effects are obviously decisive. Here again the appropriate geometry for cyclopropanic cyclization corresponds to a slightly deformed boat–chair conformation of the eight-membered ring in the bicyclo[4.2.1]nonane system.

The same arrangement of C_7–H bond and carbene orbitals in the bicyclo[3.2.1]octane system (**11a**) leads to a flattened boat conformation for the six-membered ring and a flattened chair for the seven-membered ring (see Figure 2D).

Conclusion

In this paper we have shown that the limited flexibility of the medium ring involved in bridged bicyclic systems allows a better understanding of the insertion processes of carbenes in C–H bonds. Incidently this can be used for synthetic purposes as shown in the case of the brendane skeleton, which can be prepared in a straightforward manner from a bicyclo[4.2.1]nonane system. Finally, it appears that in bridged bicyclic molecules it is the largest ring involved in the molecule, which imposes its preferred conformation for carbene insertion reactions (slightly twisted boat–chair conformation of the eight-membered ring in bicyclo[4.2.1]nonane or flattened chair form of the seven-membered ring in bicyclo[3.2.1]octane).

Experimental Section

General. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer (4000–625 cm^{-1}, in chloroform unless stated otherwise). Proton and carbon-13 nuclear magnetic resonance spectra were recorded respectively on Varian XL 100 and Varian CFT 20 instruments, in deuteriochloroform, with tetramethylsilane as internal standard. All chemical shifts are expressed in δ (ppm) and s, d, t, m refer to singlet, doublet, triplet, and multiplet, respectively. For carbon spectra, numbers in parentheses refer to relative signal intensities. Mass spectra were recorded on an AEI MS 50 instrument. Gas chromatographic analyses (GLC) were performed on an Intersmat 120 ML. Preparative GLC was done on an Aerograph 90 P4. Silica gel 60 (0.063–0.200 mm) from Merck (Darmstadt) was used for column chromatography.

Bicyclo[4.2.1]nonan-2-one, Bicyclo[4.2.1]nonan-3-one, Bicyclo[3.2.1]octan-2-one, and Bicyclo[3.2.1]octan-3-one. These ketones were prepared according to known procedures.[17-19]

Tosylhydrazones 1, 2, 11, and 12. An equimolecular amount of ketone and tosylhydrazine was refluxed for 1 h in ethanol. After cooling, the crystalline product was filtered and washed off three times with ethanol.

Tosylhydrazone 1: 85%; mp 149–150 °C; IR ($CHCl_3$) 3300, 3220, 3030, 3010, 1600, 1380, and 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86 (d, 2 H, J = 8 Hz), 7.32 (d, 2 H, J = 8 Hz), 2.7–3.1 (m, 1 H), 2.42 (s, 3 H), 2.24–2.6 (m, 3 H), 1.2–2.2 (m, 11 H); mass spectrum 306 (P, 6%), 151 (P – tosyl, 100), 122 (P – NNH – tosyl, 18).

Tosylhydrazone 2: 82%; mp 137–138 °C; IR ($CHCl_3$) 3300, 3230, 3030, 1600, 1380, and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86 (d, 2 H, J = 8 Hz), 7.32 (d, 2 H, J = 8 Hz), 2.42 (s, 3 H), 2.1–2.4 (m, 7 H), 1.1–2.0 (m, 8 H); mass spectrum 306 (P, 9), 151 (P – tosyl 100).

Tosylhydrazone 11: 85%; mp 189–190 °C; IR ($CDCl_3$) 3300, 3220, 3020, 1600, 1380, and 1160 cm^{-1}; ^1H NMR δ 7.84 (d, 2 H, J = 8 Hz), 7.30 (d, 2 H, J = 8 Hz), 2.4 (s, 3 H), 1.3–3.3 (m, 13 H); ^{13}C NMR see ref 20; mass spectrum 292 (P, 6), 137 (P – tosyl 100).

Tosylhydrazone 12: 82%; mp 177–178 °C; IR ($CDCl_3$) 3300, 3230, 1600, 1380, and 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (d, 2 H, J = 8 Hz), 7.30 (d, 2 H, J = 8 Hz), 2.42 (s, 3 H), 1.1–2.7 (m, 13 H); ^{13}C NMR see ref 20; mass spectrum 292 (P, 6), 137 (P – tosyl 100).

Decomposition of Tosylhydrazones 1, 2, 11, and 12 by Methyllithium in Ether. MeLi in ether (3 mmol, 1.5 mL of 2 N solution) was slowly added with a syringe at room temperature to a magnetically stirred solution of 1 mmol of tosylhydrazone in 10 mL of dry ether. After stirring for 1 h, the reaction mixture was hydrolyzed and extracted with pentane; the organic solution was dried over $MgSO_4$ and the solvent was distilled off. The crude material was purified on a short silica gel column to yield the decomposition olefins (see Tables I and II). The tosylhydrazone **2** yielded a mixture of olefins **4** and **6** in a ratio 22:78 (analyzed by ^1H NMR).

Bicyclo[4.2.1]non-2-ene (4):[21] IR ($CHCl_3$) 3000, 1645, 900, and 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.9–6.2 (m, 1 H), 5.46–5.76 (m, 1 H), 2.4–2.8 (m, 2 H), 2.06–2.3 (m, 2 H), 1.4–2.0 (m, 8 H).

Bicyclo[4.2.1]non-3-ene (6):[22] IR ($CHCl_3$) 3010, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (m, 2 H), 1.2–2.6 (m, 12 H).

Bicyclo[3.2.1]oct-2-ene (14):[23] IR ($CHCl_3$) 3030, 1640, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (m, 1 H), 5.2 (m, 1 H), 2.3 (br s, 2 H), 1.0–2.3 (m, 8 H).

Decompositions of Tosylhydrazones 1, 2, 11, and 12 by Sodium Methoxide in Diglyme. The tosylhydrazone (10 mmol) in 40–60 mL of dry diglyme (distilled over $LiAlH_4$) was added to a preheated (150–160 °C), magnetically stirred solution of sodium methoxide (100 mmol) in 40 mL of diglyme. Stirring and heating were maintained until no more nitrogen was evolved. After cooling, water was added and the solution was then extracted with pentane. The extracts were washed with water and dried over $MgSO_4$. The solvent was distilled off. The reaction compounds were separated on a silica gel chromatography column. The hydrocarbons were eluted with pentane. The azines partially decompose during the chromatography and lead to the corresponding ketone.[5c] The mixtures of azine and ketone were eluted

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with ether/pentane (10–50% ether). They are transformed to the corresponding ketones by stirring with a small amount of *p*-toluenesulfonic acid. The hydrocarbons were separated by GLC (SE 30, 15%, 3 m), the cyclopropanic compounds **3** and **13** being eluted after the olefins **4** and **14**, respectively, while the brendane **5** was eluted before the mixture of **4** and **6** (not separated).

Tricyclo[4.2.1.0^{2,8}]nonane (3): IR ($CHCl_3$) 3020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (m, 13 H), 0.64–0.94 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.9 (t, 20), 33.3 (d, 18), 32.6 (t, 50), 24.4 (t, 22), 22.5 (t, 24), 21.5 (d, 32), 17.0 (d, 10); mass spectrum 122 (P, 17), 80 (100).

Tricyclo[4.2.1.0^{3,7}]nonane (brendane) (5):[10] IR ($CDCl_3$) 1453, 1311, 1288, and 1149 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15–1.9 (m, 12 H), 0.87 (s, 1 H), 0.70 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 48.2 (d, 38, C-7), 41.0 (t, 99, C-2, C-9), 40.0 (t, 51, C-8), 39.1 (d, 66, C-3, C-6), 35.8 (d, 43, C-1), 32.3 (t, 100, C-4, C-5); mass spectrum 122 (P, 17), 80 (100).

Tricyclo[3.2.1.0^{2,7}]octane (13):[24] IR ($CHCl_3$) 3020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15–1.95 (m, 11 H), 0.5–0.75 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.3 (t, 73), 30.4 (d, 25), 28.1 (t, 39), 16.8 (t + d, 100), 12.9 (d, 27); mass spectrum 108 (P, 25), 79 (100).

Decompositions of Tosylhydrazones 1, 2, 11, and 12 by Sodium Methoxide in Ethylene Glycol. The tosylhydrazones were treated as above in ethylene glycol (distilled over sodium). The compounds were separated by chromatography on silica gel and eluted on the following order: hydrocarbons (pentane), ketones (4–5% yield, ether/pentane 10:90), ether alcohols (ether/pentane 50:50).

(2′-Hydroxy)-2-ethoxybicyclo[4.2.1]nonane (9): IR ($CHCl_3$) 3620, 3460, 1100, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.2–3.8 (m, 5 H), 2.2–2.8 (m, 2 H), 1.2–2.2 (m, 13 H); mass spectrum 184 (P, 7), 123 (P – OCH_2CH_2OH, 29), 122 (P – $HOCH_2CH_2OH$, 100).

(2′-Hydroxy)-3-ethoxybicyclo[4.2.1]nonane (10): IR ($CHCl_3$) 3580, 3430, 1100, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.2–3.8 (m, 5 H), 1.1–2.6 (m, 15 H); mass spectrum 184 (P, 10), 122 (P – $HOCH_2CH_2OH$, 100).

(2′-Hydroxy)-2-ethoxybicyclo[3.2.1]octane (17): IR ($CHCl_3$) 3670, 3590, 3450, 1105, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.2–3.8 (m, 5 H), 2.5 (s, 1 H), 2.3 (br s, 1 H), 2.1 (br s, 1 H), 1.1–1.9 (m, 10 H); mass spectrum 170 (P, 17), 109 (P – OCH_2CH_2OH, 100), 108 (P – $HOCH_2CH_2OH$, 96).

(2′-Hydroxy)-3-ethoxybicyclo[3.2.1]octane (18): IR ($CHCl_3$) 3670, 3600, 3450, 1110, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.3–3.8 (m, 5 H), 2.62 (s, 1 H), 2.26 (br s, 2 H), 1.7–2.1 (m, 2 H), 1.1–1.7 (m, 8 H); mass spectrum 170 (P, 19), 109 (P – OCH_2CH_2OH, 93), 108 (P – $HOCH_2CH_2OH$, 100).

Registry No. **1**, 70941-65-0; **2**, 70941-66-1; **3**, 27197-55-3; **4**, 5307-64-2; **5**, 1521-75-1; **6**, 16456-33-0; **9**, 70941-67-2; **10**, 70941-68-3; **11**, 70941-69-4; **12**, 64850-60-8; **13**, 285-43-8; **14**, 823-02-9; **17**, 70941-70-7; **18**, 70941-71-8; bicyclo[4.2.1]nonan-2-one, 3850-55-3; bicyclo-[4.2.1]nonan-3-one, 3850-54-2; bicyclo[3.2.1]octan-2-one, 5019-82-9; bicyclo[3.2.1]octan-3-one, 14252-05-2; tosylhydrazine, 1576-35-8.

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Organometals as Electron Donors. Effects of Alkyl Groups on the Ionization Potentials of Tetraalkyltin Compounds in the Correlation with Taft σ* Values

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Organometals, particularly those with alkyl groups as ligands, are excellent electron donors. As electron-rich species, they are subject to cleavage by various organic electrophiles including acids, alkyl halides, carbonyl and nitro compounds, as well as metal complexes.[2] Since alkylmetals have rather low ionization potentials, electron-transfer mechanisms are also possible in which the rate is limited by the ability of the organometal to transfer an electron to an electrophile acting as an electron acceptor. In order to delineate the energetics of such processes, it would be desirable to evaluate quantitatively the effects of alkyl ligands on the ionization potentials IP of organometals such as tetraalkyltin compounds, i.e.,

$$R_4Sn \xrightarrow{IP} R_4Sn^{+\cdot} + \epsilon \tag{1}$$

where R represents the same or different saturated alkyl groups.

Table I. Photoelectron Spectra of Tetraalkyltin Compounds

	SnR_4	$-\Sigma\sigma^*$	IP_1, eV	$\overline{IP}$, eV
1	Me	0	9.7	9.7
2	Et	0.40	8.93	8.93
3	*n*-Pr	0.46	8.82	8.82
4	*i*-Pr	0.76	8.46	8.46
5	*n*-Bu	0.52	8.76	8.76
6	*i*-Bu	0.50	8.68	8.68
7	*s*-Bu	0.84	8.45	8.45
8	neopentyl	0.66	8.67	8.67

	Me_2SnR_2	$-\Sigma\sigma^*$	IP_1, eV	IP_2, eV	IP_3, eV	$\overline{IP}$, eV
9	Et	0.20	9.01	9.28	9.64	9.31
10	*n*-Pr	0.23	8.8	9.2	9.5	9.17
11	*i*-Pr	0.38	8.56	8.99	9.55	9.03
12	*n*-Bu	0.26	8.8	9.2	9.5	9.17
13	*t*-Bu	0.6	8.22	8.74	9.47	8.81

	Me_3SnR	$-\Sigma\sigma^*$	IP_1, eV	IP_2, eV	$\overline{IP}$, eV
14	Et	0.10	9.1	9.5[b]	9.37
15	*n*-Pr[a]	0.115	9.1		
16	*i*-Pr	0.19	8.9	9.45 9.76	9.37
17	*n*-Bu	0.13	9.0	9.49[b]	9.33
18	*i*-Bu	0.125	9.05	9.50[b]	9.35
19	*t*-Bu	0.30	8.50	9.62[b]	9.24
20	Et_3MeSn	0.30	8.95	9.3	9.07

[a] Taken from ref 8. [b] Not completely resolved.

The UV photoelectron spectrum (PES) of the parent member of the series, tetramethyltin, shows two well-defined, but broad, bands, A and B, centered at 9.65 and 13.4 eV, respectively, with a shoulder at 14.8 eV.[3] The lowest-energy band A, which is of principal concern to us, is associated with ionization from the Sn–C σ-bonding orbital.[3-5] Semiempirical calculations for tetramethyltin with tetrahedral (T_d) symmetry are in agreement with a highest occupied molecular orbital (HOMO) which is triply degenerate ($3t_2$).[3,6,7]

The lowest vertical ionization potentials of three series of homologous tetraalkyltin compounds, viz., R_4Sn,

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