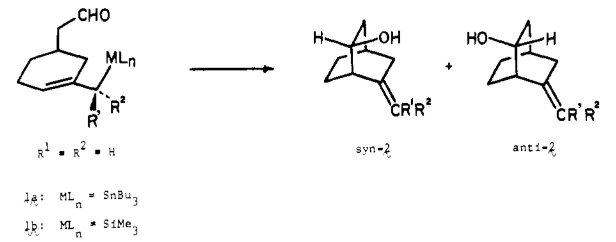
Scheme I



Scheme II

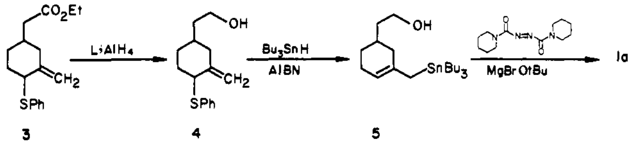
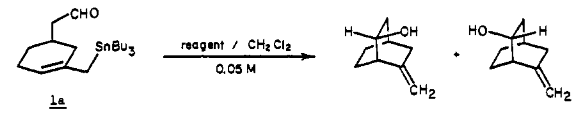


Table I.[a] Cyclization of **1a**



reagent[b]	time, min	temp, °C	% *syn*-**2**[c]	% *anti*-**2**[c]
$TiCl_4$	10	−85	82	18
$BF_3 \cdot OEt_2$	15	−70	87	13
$AlCl_3$	10	−70	89	11
Et_2AlCl	5	−70	90	10
$ZrCl_4$	10	−70	90	10
$SnCl_4$	5	−70	93	7
$FeCl_3$	20	−70	98	2
CF_3COOH	10	−70	99	1
Δ (C_6H_6)	480	90	97[d]	3

[a] The reactions were quenched at −70 °C ($NaOH/CH_3OH$) and analyzed by capillary GC. At least two runs with each reagent were performed to assure reproducibility, i.e., >85% conversion to **2** (vs. decane) and syn/anti ratios ±2%. [b] 1.05 equiv were used. [c] Ratios were calculated on the basis of independently determined response factors vs. decane. [d] Only *syn*-**2** was detected, in addition to 3% of a rearrangement product, thus 97% is the minimum selectivity.

group is oriented anti to the approaching aldehyde giving rise to the picture shown.

The origins of the strong preference for the synclinal geometry are as yet unclear. Inspection of Dreiding molecular models of the complexes of **1a** in which the Lewis acid is *E* complexed[16] is informative. In the analogous silanes we observed a significant steric contribution from the Lewis acid which favored the antiperiperiplanar orientation with increasing bulk.[5] The insensitivity to Lewis acid size in the case at hand indicates the lack of a steric component, which, in view of the facility of reaction, suggests an earlier transition state. The extremely selective cyclization induced by a proton (the sterically least demanding initiator) supports the contention that steric effects are not important contributors to the preference for synclinal geometry.

These results provide the first unambiguous picture of the double-bond orientation in reactions of allylstannanes and have important implications in the interpretation of intermolecular reaction pathways.

Work is in progress on a system that unambiguously defines the orientation of the metal atom in **1a** and **1b**. These results as well as investigations with other allyl metalloids will be the subject of future reports.

Acknowledgment. Financial support was provided by the National Science Foundation (CHE-8208565) to whom we are grateful. This work was supported in part by the University of Illinois Regional Instrumentation Facility (NSF-CHE 79-16100) and Mass Spectrometry Laboratory (NIH GM 27029).

Registry No. 1a, 92937-61-6; **1b**, 88354-72-7; *syn*-**2**, 87422-06-8; *anti*-**2**, 87422-07-9; **3**, 88354-75-0; **4**, 92937-62-7; **5**, 92937-63-8; AIBN, 78-67-1; $TiCl_4$, 7550-45-0; $BF_3 \cdot OEt_2$, 109-63-7; $AlCl_3$, 7446-70-0; Et_2AlCl, 96-10-6; $ZrCl_4$, 10026-11-6; $SnCl_4$, 7646-78-8; $FeCl_3$, 7705-08-0; CF_3CO_2H, 76-05-1; Bu_3SnH, 688-73-3; $LiAlH_4$, 16853-85-3; MgBrO-*t*-Bu, 19065-60-2; 1,1′-(azodicarbonyl)bispiperidine, 10465-81-3.

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(15) Sn: (a) Young, D.; Kitching, W.; Wickham, G. *Tetrahedron Lett.* **1983**, 5789, 5793. (b) Young, D.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 612. Si: (c) Fleming, I.; Terrett, N. K. *Tetrahedron Lett.* **1983**, 4153. (d) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (e) Wetter, H. J.; Scherer, P. *Helv. Chim. Acta* **1983**, *66*, 118.

(16) The precise structure of Lewis acid–aldehyde complexes has yet to be firmly established. Our assumption of an *E* configuration (Lewis acid cis to hydrogen) finds precedence in the BF_3 adducts of unsymmetrical ketones[17a] and enones[17b] wherein the preferred mode of complexation places the boron cis to the smaller group. Further support is found in the considerable body of structural information for protonated aldehydes[17c] in which the two hydrogens are nearly exclusively cis. Molecular orbital calculations for benzaldehyde–BF_3[17d] and acetaldehyde–H^+[11e] indicate a preferred *Z* configuration.

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Formation of the Long-Lived $H_2O^-\cdot$ Ion in the Gas Phase

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Recently the observation of long-lived H_3O^-[1] and NH_4^-[2] ions in our Fourier transform ion cyclotron resonance (FTICR) spectrometer[3,4] has been reported. The H_3O^- ions were generated by reaction of OH^- with formaldehyde through a successive proton and hydride transfer in the corresponding collision complex as summarized in eq 1. The NH_4^- ions could be formed by reaction

$$OH^- + CH_2O \rightleftarrows [OH^-\cdot CH_2O]^* \rightleftarrows [H_2O\cdot HCO^-]^* \rightarrow H^-\cdot H_2O + CO \qquad (1)$$

of NH_2^- with formaldehyde as well. In this case, however, the successive proton and hydride transfer do not occur in the same collision complex. This is due to the fact that the gas-phase acidity of formaldehyde lies in between that of water and ammonia,[5] so that NH_2^- can abstract a proton from formaldehyde in an exothermic reaction channel resulting in the formation of the product ion HCO^-. This then transfers a hydride to ammonia in a subsequent ion/molecule reaction. Equation 2 summarizes the

$$NH_2^- + CH_2O \rightarrow NH_3 + HCO^- \qquad (2a)$$

$$HCO^- + NH_3 \rightarrow H^-\cdot NH_3 + CO \qquad (2b)$$

formation of NH_4^-. Thus, the final step in the formation of both H_3O^- and NH_4^- is the transfer of a hydride to water and ammonia, respectively. This is consistent with the results of stable-isotopic

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(5) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 65–68.

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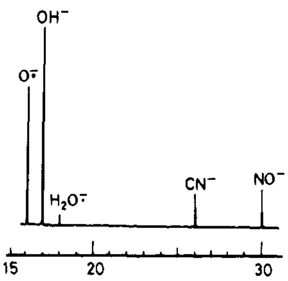


Figure 1. FTICR spectrum of the $O^-\cdot/N_2O/(CH_3)_2NH$ system. Experimental conditions: $p(N_2O) = 27\ \mu Pa$, $p(Me_2NH) = 14\ \mu Pa$, magnetic field strength 1.4 T, electron energy 1.1 eV, electron-beam pulse width 25 ms, emission current 600 nA. The spectrum is taken 400 ms after the electron-beam pulse started. 128 transients were accumulated.

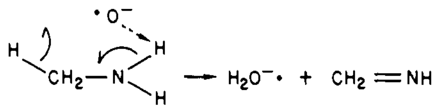
labeling experiments which have indicated that H_3O^-[1] and NH_4^-[2] can best be described as a hydride solvated by a water and an ammonia molecule, respectively, in agreement with recent ab initio molecular orbital calculations at the 4-31++G level.[6]

Another interesting ion which has received considerable attention both theoretically[7-10] and experimentally[7,11] is $H_2O^-\cdot$. Some theoretical calculations[7,9] have suggested that this ion might exist in a potential minimum and therefore might be stable, although to our knowledge it has never been observed experimentally.

We now wish to report that it has been possible to generate the $H_2O^-\cdot$ ion in our FTICR spectrometer[12,13] by reaction of $O^-\cdot$ with any of the aliphatic amines methylamine, ethylamine, or dimethylamine. As a typical example the FTICR spectrum of the $O^-\cdot/N_2O/(CH_3)_2NH$ system has been reproduced in Figure 1. This shows clearly the presence of the peak at m/z 18 having a relative intensity of 6%, which obviously is higher than expected on the basis of natural isotopic contributions. Although our instrument does not yet have the capability of performing high-resolution experiments, the mass of the ion m/z 18 can be measured with sufficient accuracy: 18.0104 ± 0.0021 daltons (exact mass of $H_2O^-\cdot$ is 18.0105 daltons). Support for the formation of $H_2O^-\cdot$ is derived from the observations that ions at m/z 19 are formed if CD_3NH_2 is used and at m/z 20 if $^{18}O^-\cdot$ is used. The masses of these ions are measured to be 19.0162 ± 0.0020 and 20.0146 ± 0.0021 daltons, respectively (the exact mass of $HDO^-\cdot$ is 19.0168 daltons and that of $H_2{}^{18}O^-\cdot$ 20.0148 daltons). Moreover, ion ejection[14] experiments have indicated that $O^-\cdot$ is the sole precursor of the ions at m/z 18. This clearly shows that $H_2O^-\cdot$ can be a stable species in the gas phase.

The question remains how this ion is formed. The generation of $HDO^-\cdot$ by reaction of $O^-\cdot$ with CD_3NH_2 (vide supra) at least proves that one of the hydrogen atoms in $H_2O^-\cdot$ originates from the amino group and the other from the methyl group. The presence of both types of hydrogen atoms in the substrate is essential to form $H_2O^-\cdot$ as neither ammonia nor a tertiary amine react with $O^-\cdot$ to give the ion of interest. These hydrogen atoms, however, could be transferred to the $O^-\cdot$ ion in the collision complex either in a stepwise or a concerted fashion. In the case of a stepwise mechanism the first step can in principle be either a proton or a hydrogen atom transfer to $O^-\cdot$. Proton transfer would involve the amine hydrogens being the most acidic ones but can be calculated to be 88, 73, and 59 kJ/mol endothermic for methylamine, ethylamine, and dimethylamine, respectively.[15] Of course, the solvation energy gained upon formation of the collision complex and which can be up to 80 kJ/mol could induce an endothermic proton transfer in the $O^-\cdot/(CH_3)_2NH$ system, but not in the $O^-\cdot/CH_3NH_2$ system. Furthermore, if the proton transfer occurs to give an $OH\cdot$/amide ion complex which cannot separate into its components, an electron transfer from the amide ion to the $OH\cdot$ radical can be expected to take place because of the large difference in electron affinities of the $OH\cdot$ (EA = 176 kJ/mol) and $RNH\cdot$ radicals (EA of $CH_3NH\cdot$ = 48 kJ/mol, EA of $C_2H_5NH\cdot$ = 64 kJ/mol, EA of $(CH_3)_2N\cdot$ = 55 kJ/mol).[16] It is difficult to distinguish this proton abstraction followed by electron transfer from a direct hydrogen atom transfer to the $O^-\cdot$ ion, which is calculated to be 44, 43, and 66 kJ/mol exothermic for methylamine, ethylamine, and dimethylamine, respectively.[17] Indeed, for all these amines OH^- is observed to be formed as the most abundant product ion.

Another possibility is that $O^-\cdot$ abstracts an α-hydrogen atom in the first step, which may be less exothermic than amino hydrogen abstraction although this is not supported by the reported thermochemical data on the $\cdot CH_2NH_2$[18] and CH_3NH radicals.[19] However, a C–H bond is generally ~25–40 kJ/mol stronger than an N–H bond.[20] Therefore we believe that α-hydrogen abstraction from methylamine by $O^-\cdot$ may even be only slightly exothermic. It should be noted that this is not inconsistent with the observation that OD^- and OH^- are formed in a ratio of ~1:19 by reaction of $O^-\cdot$ with CD_3NH_2, although here also an isotope effect is operative. The latter is clearly reflected in the much lower yield of $HDO^-\cdot$ from CD_3NH_2 than of $H_2O^-\cdot$ from CH_3NH_2 so much so that contrary to $H_2O^-\cdot$ (vide infra) unfortunately no ion/molecule reactions of $HDO^-\cdot$ could be studied. In any case, if the formed $OH^-/\cdot CH_2NH_2$ (c.q., $CH_3\dot{C}HNH_2$ or $(CH_3)\dot{C}H_2NH$) complex has a finite lifetime, then the OH^- ion might become hydrogen bonded via its oxygen atom to the amino hydrogen atom, so that by a subsequent homolytic cleavage of the N—H bond $H_2O^-\cdot$ and $CH_2{=}NH$ (c.q., $CH_3CH{=}NH$ or $CH_2{=}NCH_3$) can be formed. The reaction would thus involve the transfers of an α-alkyl and an amino hydrogen atom to $O^-\cdot$, which might also take place in a concerted fashion as summarized in eq 3 for methylamine.


(3)

The presently generated $H_2O^-\cdot$ species has been found to react fast with formaldehyde to give OH^- as the only observed product ion (eq 4). Reaction 4 seems to suggest that the $H_2O^-\cdot$ ion can

$$H_2O^-\cdot + CH_2O \rightarrow OH^- + \cdot CH_2OH \qquad (4)$$

best be described as a hydroxide ion to which a hydrogen atom is attached. From this reaction[21] and reaction 3[22] the heat of

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[15] (a) Heats of formation of neutral species have been taken from the following, unless stated otherwise. Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6* (1). (b) Heats of formation of anions with exception of $O^-\cdot$ and OH^- have been taken from the following: Bartmess, J. E.; McIver, R. T., Jr. in "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11, pp 87–121. (c) Heats of formation of $O^-\cdot$ and OH^- have been taken from the following: Franklin J. L.; Dillard, J. G; Rosenstock, H. M., Herron, J. T.; Draxl, K.; Field, F. H. NSRDS-NBS 26, National Bureau of Standards, Washington DC 1969.

[16] The electron affinity values have been taken from the literature given in ref 15b.

[17] The heats of formation of the $CH_3NH\cdot$, $C_2H_5NH\cdot$, and $(CH_3)_2N\cdot$ radicals have been obtained by adding their electron affinity values to the heats of formation of the corresponding amide ions, both taken from the literature given in ref 15b.

[18] $\Delta H_f°(\dot{C}H_2NH_2) = 155 \pm 8$ kJ/mol. Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 307–316.

[19] $\Delta H_f°(CH_3\dot{N}H) = 190 \pm 4$ kJ/mol. Golden, D. M.; Solly, R. K.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 363–369.

[20] Weast, R. C., Ed. "Handbook of Chemistry and Physics", 61st ed.; CRC Press: Boca Raton, FL, 1980.

[21] The heat of formation of $\dot{C}H_2OH$ has been taken from the following: O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 275.

formation of $H_2O^{-}\cdot$ can be bracketed between −50 and −18 kJ/mol. The present results do not provide information about bond lengths and bond angles in the $H_2O^{-}\cdot$ species. Apparently being trapped in a local energy minimum its geometry may differ substantially from that of ground-state water, which stabilizes the $H_2O^{-}\cdot$ ion with respect to electron detachment as indicated by theoretical calculations.[9,10]

Finally, it should be noted that at ambient temperature an optimum yield of $H_2O^{-}\cdot$ could be obtained. The production of $H_2O^{-}\cdot$ decreased as the cell was slightly heated up by the filament.

Neverthless, the generation of $H_2O^{-}\cdot$ could be reproduced over a period of 6 months, so that we are forced to assume that this ion can exist as a stable species in the gas phase.

Acknowledgment. We thank F. A. Pinkse for his expert technical assistance and the Netherlands Organization for Pure Research (SON/ZWO) for financial support.

Registry No. $H_2O^{-}\cdot$, 12259-30-2; $O^{-}\cdot$, 14337-01-0; CH_3NH_2, 74-89-5; $C_2H_5NH_2$, 75-04-7; $(CH_3)_2NH$, 124-40-3; CH_2O, 50-00-0; $CH_3NH\cdot$, 15622-51-2; $C_2H_5NH\cdot$, 41084-92-8; $(CH_3)_2N\cdot$, 15337-44-7.

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(22) $\Delta H_f^{\circ}(CH_2NH)$ = 94 kJ/mol, as calculated on the basis of group additivity rules: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

Rearrangements of Tolylmethylenes via Cycloheptatetraenes: Formation of Benzocyclobutene and Styrene[†]

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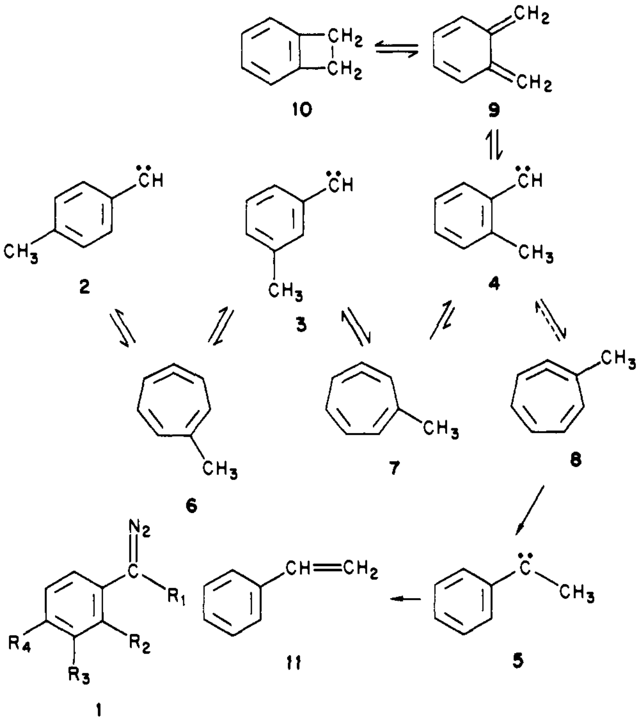
The thermolysis of *o*-, *m*-, and *p*-tolyldiazomethanes to styrene and benzocyclobutene poses a mechanism problem of substantial interest. Several intriguing solutions to this problem have been suggested,[1-4] and labeling studies,[1,3,4] have placed severe mechanistic constraints on possible solutions. Our studies on the phenylmethylene–cycloheptatetraene interconversion[5] prompted an investigation of the tolylmethylene rearrangement. We now wish to propose a mechanism for the rearrangement of the tolylmethylenes via cycloheptatetraenes and for the formation of benzocyclobutene and styrene in which all intermediates are observed.

Irradiation (>470 nm) of diazocompounds **1a–d** matrix isolated in argon at 10–15 K[6] provided the carbenes **2–5**. Each carbene was shown to be a triplet by electron spin resonance studies.[9] The UV/visible spectra of **2–5** showed the $\pi-\pi^*$ transitions characteristic of triplet arylcarbenes.[10] In addition, complete infrared spectra of **2**, **3**, and **5** were obtained.[11] The methylcycloheptatetraenes (**6–8**) were observed by infrared spectroscopy and each showed the bands at ~1810 cm^{-1} characteristic of the cycloheptatetraene–allene chromophore.[5] Complete infrared spectra of **6** and **7** were obtained.[11] 5-Methylcyclohepta-1,2,4,6-tetraene (**6**) was formed as the sole primary photoproduct (>416 nm) from **2**. Both 4- and 5-methylcyclohepta-1,2,4,6-tetraenes were formed from **3**. Irradiation (>261 nm) of 5-methylcyclohepta-1,2,4,6-tetraene gave 4-methylcyclohepta-1,2,4,6-tetraene, thus establishing the interconversion of **6** and **7**. Irradiation (>470 nm) of **1c** gave predominately *o*-xylylene (**9**)[12] via hydrogen atom transfer in carbene **4**.[13] A small amount of ring-expansion product, 1-methylcyclohepta-1,2,4,6-tetraene (**8**; 790, 710 cm^{-1}) was also

Scheme I



	R_1	R_2	R_3	R_4
a	H	H	H	CH_3
b	H	H	CH_3	H
c	H	CH_3	H	H
d	CH_3	H	H	H

[†] The title compound is correctly named 1,2-dihydrobenzocyclobutene. Benzocyclobutene is the systematic name for a compound with four double bonds.

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(5) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782.

(6) Apparatus for the observation of matrix-isolated species by electron spin resonance,[8] infrared,[7] and ultraviolet[7] spectroscopy has been described previously.

(7) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P.; Shou, H.-S., manuscript in preparation. Sheridan, R. S. Ph.D. Dissertation, UCLA, Los Angeles, CA, 1979.

(8) Kreil, C. L. Ph.D. Disseration, UCLA, Los Angeles, CA, 1983.

(9) **2**, D/hc = 0.516 cm^{-1}, E/hc = 0.0240 cm^{-1}; **3**, D/hc = 0.517 cm^{-1}, E/hc = 0.0246 cm^{-1}, rotomers indistinguishable; **4**, D/hc = 0.503 cm^{-1}, E/hc = 0.0253 cm^{-1}, rotomers indistinguishable; **5**, D/hc = 0.508 cm^{-1}, E/hc = 0.0278 cm^{-1}.

(10) Compound **2**, λ_{max} 444, 436, 429, 426, 422, 418, 415, 411, 408, 405, 402, 398, 395 nm; **3**, λ_{max} 448, 439, 433, 430, 426, 424, 420, 415, 410, 403, 399, 394 nm; **4**, λ_{max} 450, 440, 437, 435, 431, 427, 422, 419, 417, 413, 249, 244 nm; **5**, λ_{max} 449, 446, 432, 428, 417, 412, 405, 399, 392, 388, 381, 251, 244 nm. Our experimental technique does not permit the determination of extinction coefficients.

(11) A tabulation of the infrared absorptions of carbenes **2**, **3**, and **5** and methylcycloheptatetraenes **6** and **7** is available as supplementary material.

(12) Identified by comparison of the ultraviolet and infrared spectra with those of the authentic material matrix isolated in argon: Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840–4842.

(13) Carbene **4** does not absorb light beyond 450 nm (vide supra). Therefore, formation of *o*-xylylene (**9**) must occur by a thermal reaction, even at the cryogenic temperatures employed (15 K).

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