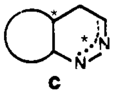
azabicyclo[3.1.0]hex-2-ene derivative nor a side reaction such as nitrogen extrusion was observed.

The above experimental evidence clearly indicates that aziridine formation, which has been proved by Huisgen[17] not to occur during *intermolecular* 1,3-dipolar cycloaddition reactions of diazomethanes and olefins, can take place *intramolecularly*. Since MO calculations[18] show that the contribution of a nitrene-like structure of the terminal nitrogen of diazomethane in its ground state is unimportant, a 1,1 cycloaddition through a nitrene form seems unfeasible. Plausible mechanistic alternatives, which are yet open without detailed stereochemical studies,[19] however, involve reactions of a linear diazomethane either via a stepwise pathway to form "a six-membered dipole C"[20] or via a concerted cheletropic pathway.[22] Nevertheless, the results described here provide a novel example of the intramolecular reactivity of 2-allyl-substituted diazomethanes and also provide a useful synthesis of 1,2-diazabicyclo[3.1.0]hex-2-enes. Details of stereochemical studies will be reported soon.



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(7) Melting points are not corrected. Satisfactory elemental analyses were obtained for all new compounds except for diazomethane.

(8) **3b**: *m/e* (rel intensity) 212 (M^+, 8), 184 (20), 141 (100); ν_{max}^{KBr} 2950, 1560, 1495, 1450, 750 cm^{-1}; λ_{max}^{EtOH} 254.5 nm (log ϵ 4.10); ^{1}H NMR (δ units in toluene-d_8) 7.5~7.8 (m, 2 H), 6.9~7.2 (m, 3 H), 2.91 (d, 1 H, J = 17.5 Hz), 2.57 (dd, 1 H, J = 17.5 and 1.8 Hz), 1.0~2.2 (m, 9 H).

(9) **3c:** *m/e* (rel intensity) 226 (M^+, 8), 198 (23), 155 (61), 141 (100); ν_{max}^{KBr} 2920, 1560, 1494, 1455, 750 cm^{-1}; λ_{max}^{EtOH} 254 nm (log ϵ 4.13); ^{1}H NMR (δ units in benzene-d_6) 7.6~7.8 (m, 2 H), 7.0~7.2 (m, 3 H), 2.99 (d, 1 H, J = 17.5 Hz), 2.53 (d, 1 H, J = 17.5 Hz), 1.0~2.1 (m, 11 H).

(10) **8:** ^{1}H NMR (δ units in CCl_4), 7.5~7.7 (m, 2 H), 7.1~7.4 (m, 3 H), 6.7~7.1 (m, 4 H), 3.81 (d, 1 H, J = 17.5 Hz), 3.30 (d, 1 H, J = 17.5 Hz), 2.96 (m, 1 H). **8** was found to be easily oxidized by air to 3-phenyl-9,10-dihydro-1,2-diazaphenanthrene (mp 111~113 °C) which was further dehydrogenated to 3-phenyl-1,2-diazaphenanthrene (mp 134 °C) by DDQ.

(11) **10**: $\nu_{max}^{CCl_4}$ 2040 cm^{-1}; ^{1}H NMR (δ units in CCl_4) 6.8~7.4 (m, 9 H), 6.29 (dd, 1 H, J = 1.5 Hz), 3.24 (d, 2 H, J = 0.7 Hz), 2.77 (m, 2 H), 2.22 (m, 2 H).

(12) **11**: *m/e* (rel intensity) 260 (M^+, 1), 232 (8), 143 (27), 142 (26), 141 (28), 128 (82), 115 (15), 105 (100); ν_{max}^{KBr} 2930, 1554, 1490, 1442, 935, 790, 744, 723 cm^{-1}; ^{1}H NMR (δ units in $CDCl_3$) 2.1~2.4 (m, 2 H), 2.60 (s, 1 H), 2.64 (m, 1 H), 3.10 (m, 1 H), 3.40 (d, 1 H, J = 17.2 Hz), 3.69 (d, 1 H, J = 17.2 Hz), 6.9~7.5 (m, 7 H), 7.7~7.9 (m, 2 H).

(13) Since among the five aziridines only **3c** is stable in refluxing carbon tetrachloride (76 °C), the control experiment to trap diazomethanes is valid only for **2c.** In fact decomposition of **1a** in the presence of dimethyl fumarate and the reaction of **3a** with dimethyl fumarate in refluxing carbon tetrachloride gave the same products, **4a** and **5**a. Similarly, both **1b** and **3b** gave **4b** and **5b.**

(14) **4c**: $\nu_{max}^{CCl_4}$ 3350, 1740, 1713, 1565, 1440, 1210, 692 cm^{-1}; ^{1}H NMR (δ units in CCl_4) 7.2~7.8 (m, 6 H), 5.7 (dd, 1 H, J = 6.5 Hz), 4.1 (s, 1 H), 3.8 (s, 3 H), 3.2 (s, 3 H), 2.7 (br s, 2 H), 0.8~2.3 (m, 10 H). **5c:** mp 126 °C; *m/e* (rel intensity) 370 (M^+), 261, 217; ν_{max}^{KBr} 3370, 1740, 1677, 1547, 1445, 1210 cm^{-1}; ^{1}H NMR (δ units in CCl_4) 7.2~7.6 (m, 5 H), 6.9 (s, 1 H), 5.6 (dd, 1 H, J = 6.0 Hz), 4.0 (s, 1 H), 3.8 (s, 3 H), 3.7 (s, 3 H), 2.6 (br s, 2 H), 0.7~2.2 (m, 10 H).

(15) **3c** was not subjected to temperature-dependent ^{1}H NMR analyses because **3c** was stable up to 130 °C, but decomposed releasing nitrogen over 130 °C.

(16) During heating in the probe toluene-d_8 soltuions turned wine-red. Analyses of diazomethanes **2**a and **2b** was carried out by integration of newly appeared signals assigned to side-chain methylene hydrogens at δ 2.90 (s) and olefinic hydrogen at 5.65 ppm (m) for **2**a and side-chain methylene hydrogens at δ 2.78 (s) and olefinic hydrogens at 5.47 ppm (m) for **2b.** Similar analyses were also carried out for 7 and **10.**

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(19) Our preliminary stereochemical studies show that (*E*)-1,4-diphenyl-4-diazobut-1-ene (**12**) afforded exclusively *exo*-3,6-diphenyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**13**).

(20) If "a six-membered dipole" C is an intermediate, one may conjecture the formation of 2,3-diazabicyclo[3.1.0]hex-2-enes together with B. However, the exclusive formation of B may be accounted for by the difference in the energy gained from forming the new bonds in B and in 2,3-diazabicyclo[3.1.0]hex-2-enes: 122 (N=C) + 73 kcal (C—N) for B; 93 (N=N) + 83 kcal (C—C) for 2,3-diazabicyclo[3.1.0]hex-2-enes. The estimated ring strain of the aziridine ring (27.7 kcal) is, on the other hand, almost same as that of the cyclopropane ring (27.6 kcal).[21]

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(22) In this case, the electron pair from the bonding antisymmetric σ orbital of the aziridine ring and the π oribtal of the N=C bond makes the 4π system of diazomethane and the lone pair at the nitrogen next to the pyramidal aziridine nitrogen enters the π orbital orthogonal to the 4π system, while the lone pair at the pyramidal aziridine nitrogen remains as that of the terminal nitrogen of diazomethane. Similar discussions have been made by Woodward and Hoffmann.[23]

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Comment on the Electronic Structure of HAlOH and $H_2O\cdot Al$

Sir:

The interaction of ground- and excited-state metal atoms with water molecules has attracted considerable experimental[1-5] and theoretical[6] interest. Matrix isolation studies by Grandsden and co-workers[1] indicate that aluminum interacts with water to yield the metal hydroxyhydride. Oblath and Gole[2] have suggested that emission from excited HAlOH may be responsible for the continuum resulting from the reaction of Al with H_2O in the gas phase. In this communication we present the results of theoretical calculations which suggest that insertion of Al into H_2O to yield HAlOH is exothermic by $\gtrsim$38 kcal/mol. Moreover, we find that there exist reaction paths leading to the HAlOH which are fully attractive, i.e., without a barrier.

To find the lowest energy structures of HAlOH and C_{2v} $H_2O\cdot Al$, we have employed the spin-unrestricted Hartree–Fock approximation, together with the effective core potential procedure[7] for aluminum. In this procedure only the valence (3s and 3p) electrons of the aluminum atom are treated explicitly, the inner core being modeled by an effective potential. This greatly reduces the cost of the calculations. The 3s/4p basis set of Topiol et al.[7] was employed for aluminum, while Dunning's[8] double ζ basis sets were employed for hydrogen and and oxygen. We have repeated the calculations at the optimized geometries for HAlOH and the C_{2v} $H_2O\cdot Al$ adduct, treating all the electrons explicitly and employing the aluminum basis set of Trenary et al.[6] The comparison of the all-electron and effective core potential results is especially important since core potentials are being increasingly applied to the study of complicated molecules.

The $^2B_2$ state of the C_{2v} $H_2O\cdot Al$ has been previously treated at the SCF level by Trenary et al. who found an equilibrium Al-O separation of 2.55 Å, corresponding to a dissociation energy (to Al + H_2O) of 4.4 kcal/mol. In the present study, the optimized C_{2v} geometry has an Al-O separation of 2.12

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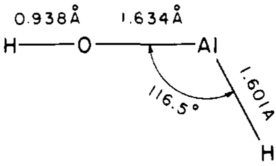
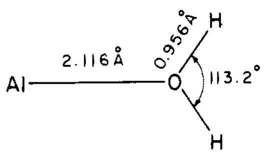
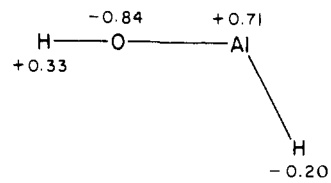
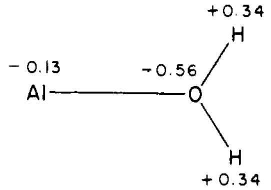
Å and a dissociation energy[9] of 12.3 kcal/mol using the model potential and 8.5 kcal/mol in the all-electron calculation. We also find that the $^2B_1$ state is bound by ~7.0 kcal/mol while the $^2A_1$ state is unbound.

For the HAlOH structure, we have carried out a complete optimization of all bond lengths and angles. The resulting HAlOH species is stable by 54.3 kcal/mol (38.1 kcal/mol in the all-electron calculation) with respect to H_2O + Al and has a HAlO bond angle nearly the same as the HAlH angle of AlH_2 and an Al–H bond distance close to that of Al–H_2.[10] Our minimum energy structures for the HAlOH and C_{2v} H_2O·Al species are shown. The charge densities obtained from a Mulliken population analysis reveal that the hydroxyhydride has appreciable ionic character, with the Al atom losing nearly one electron to the H and OH groups. On the other hand, the aluminum atom carries a small negative charge (0.1 e) in the C_{2v} adduct. ESR studies[3] on the H_2O·Li and H_2O·Na complexes have shown that the metal atom is negatively charged. This has also been found in the theoretical studies of Trenary et al.[6]









The differences between the geometry and energy of the C_{2v} species obtained in the present study and those of Trenary et al. arise primarily from two sourses: (1) the use of the effective core potential for Al and (2) differences in the basis sets employed, mainly the lack of d functions in our work. As noted earlier, all-electron C_{2v} calculations using a 6s4p Al basis reduce the dissociation energy to only 8.5 kcal/mol and give an optimal Al–O distance of 2.25 Å. For HAlOH, these calculations give an Al–O distance of 1.68 Å and an HAlO angle of 118.11°. From these results it seems that removal of the Al core potential does not have a significant effect on the structure of these compounds. At present we are exploring the effect of the basis set by adding d functions to both the O and Al and reoptimizing the HAlOH and H_2O·Al structures.

Gransden et al.[1] have found that the Al–H and O–H stretching frequencies of AlOH are 1743 and 818 cm^{-1}, respectively, indicating that the HAlOH complex is strongly bound. This is borne out by the results of the present study. The all-electron calculations, carried out at the geometry optimized using the effective potential, indicate that the HAlOH species is stable (with respect to Al + H_2O) by 38 kcal/mol. Reoptimization of the geometry in the all-electron SCF procedure should give rise to a slightly larger value.

While we have not yet mapped out the complete potential energy surface and have not established the minimum energy path for the Al + H_2O insertion, we have found that the approach of Al perpendicular to one of the O–H bonds inserts without encountering a barrier. Furthermore, we believe that the C_{2v} species may be a local minimum on the potential energy surface. However, the barrier for the $H_2O\text{·Al} \rightarrow \text{HAlOH}$ rearrangement may be small.

In addition to the more detailed studies employing d functions, examination of the effects of electron correlation are under was on the HAlOH species. We have also begun to examine the reaction of H_2O with other metals including Be, B, Mg, Sc, and Zn. Preliminary studies of B + H_2O indicate that HBOH is stable by 68 kcal/mol with respect to the reactants. We have found that, in agreement with Trenary et al.,[6] that the ground state of Li (^2S) + H_2O is the C_{2v} H_2O·Li adduct. There is the interesting possibility that the ^2P excited state of Li inserts into water to form the hydroxy hydride as do Al and B. The thermal Sc + H_2O reaction has been shown by Liu and Parson to yield ScO + H_2. The role of the unpaired d electron in this reaction is especially interesting. Hange, Kauffman, and Margrave[11] have observed spontaneous reactions of Sc, Ti, and V with water to form ScO, TiO, and VO, respectively, in rare gas matrices at 10 K.

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pH-Dependent Constraint Angle Effects on the Order Parameters of Bilayer Systems

Sir:

It has recently been reported that the absolute values of the quadrupole splittings for specifically deuterated cis unsaturated phospholipids in bilayer model membranes yield an unusual order parameter profile.[1] The degree of order of a C—D bond axis, S_{CD}, depends upon the angle θ between the C—D bond axis and the director. Because of the geometric constraint of the cis C=C bond, the degree of order undergoes a dramatic decrease in magnitude near the site of unsaturation and then rises once more to a value close to that of a fully saturated chain before falling off once more as the mobile chain terminus is approached. We have observed that the degree of order profile for bilayer lyotropic liquid crystalline systems depends upon several factors, one of which involves constraints placed upon the orientation of amphiphilic molecules in a bilayer model membrane.[1-11] It is reported here that, in certain cases, these constraints may be pH dependent.

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