

structured the heated inlet assembly, and to Professors P. Kebarle and R. W. Taft for helpful discussions and providing the gas-phase basicities, respectively.

References and Notes

- (1) (a) P. Beak, *Acc. Chem. Res.*, **10**, 186 (1977), and references therein; (b) P. Beak, F. S. Fry, J. Lee, and F. Steele, *J. Am. Chem. Soc.*, **98**, 171 (1976); (c) P. Beak, J. B. Covington, and S. G. Smith, *ibid.*, **98**, 8284 (1976); (d) D. H. Aue, L. D. Betowski, W. R. Davidson, M. T. Bowers, P. Beak, and J. Lee, *ibid.*, **101**, 1361 (1979); (e) P. Beak and F. S. Fry, *ibid.*, **95**, 1700 (1973).
- (2) (a) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956); (b) S. F. Mason, *ibid.*, 674 (1958).
- (3) From ref 1b, $\Delta G^\circ (1a \rightleftharpoons 2a) = 0.8$ kcal/mol at 132 °C.
- (4) (a) R. S. Brown, *J. Am. Chem. Soc.*, **99**, 5497 (1977); (b) R. S. Brown, A. Tse, and R. C. Haddon, *ibid.*, **101**, 3157 (1979).
- (5) (a) Spectra were determined on a MacPherson 36 ESCA spectrometer with a heated inlet assembly, the details of which will be published. (b) **1a** (**1b**) was a commercial sample purified by distillation. (c) **2b** was prepared by CH_3I -catalyzed rearrangement of **1b** according to the procedure of P. Beak, J. Bonham, and J. T. Lee, *J. Am. Chem. Soc.*, **90**, 1569 (1968).
- (6) (a) It would clearly be desirable to investigate the other blocked derivative **3b** for comparison. Unfortunately, under the conditions of the experiment, heating of **3b** caused it to rearrange cleanly to **4b** and the spectrum which was finally obtained showed only **4b** and no other species. (b) J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 4375 (1957), estimate from analysis of solution-phase IR and UV data that the pyridone form (**4a**) dominates.
- (7) (a) B. E. Mills, R. L. Martin, and D. A. Shirley, *J. Am. Chem. Soc.*, **98**, 2380 (1976); (b) R. L. Martin and D. A. Shirley, *ibid.*, **96**, 5299 (1974); (c) D. W. Davis and J. W. Rabalais, *ibid.*, **96**, 5305 (1974); (d) T. X. Carroll, S. R. Smith, and T. D. Thomas, *ibid.*, **97**, 659 (1975); (e) R. G. Cavell and D. A. Allison, *ibid.*, **99**, 4203 (1977); (f) A. J. Ashe, M. K. Bahl, K. D. Bomben, W.-T. Chan, J. K. Gimzewski, P. G. Sifton, and T. D. Thomas, *ibid.*, **101**, 1764 (1979) (phosphorus bases); (g) F. M. Benoit and A. G. Harrison, *ibid.*, **99**, 3980 (1977) (oxygen bases).
- (8) R. S. Brown and A. Tse, unpublished results. Full results and analysis for the 2-, 3-, and 4-substituted pyridines will be published.
- (9) Corrected gas-phase basicities were generously provided by Professor R. W. Taft.
- (10) Since the difference in gas-phase basicities for **1a** and **2a** is given here as 0.58 kcal/mol, the differences in proton affinity should also be small. The PA of pyridine (relative to that of NH_3 (202.3 kcal/mol)^{1d}) is given as 217.4 kcal/mol,^{1d} and, according to Figure 1, should be close to that for **1a**. For a series of oxygen bases, Benoit and Harrison^{7g} have established a correlation between PA and O_{1s} ionization energies given as PA (eV) = $-0.792 \text{ BE}(\text{O}_{1s}) + 434.6$. For **2a** [$\text{BE}(\text{O}_{1s}) = 536.66$ eV], the predicted PA is 220.6 kcal/mol which, considering the extrapolation, is in gratifyingly close agreement with that expected for **1a**.
- (11) NOTE ADDED IN PROOF. A recent UV PES investigation of the $1a \rightleftharpoons 2a$ equilibrium shows that there are at least six overlapping bands with ionization energies of <11 eV. Deconvolution of the bands gives a $\Delta G^\circ (1a \rightleftharpoons 2a)$ of 0.90 kcal/mol at 110 °C [C. Guimon, G. Garrabe, and G. Pfister-Guilouzo, *Tetrahedron Lett.*, 2585 (1979)].

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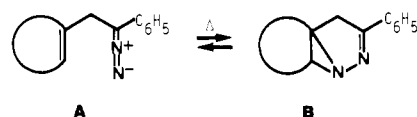
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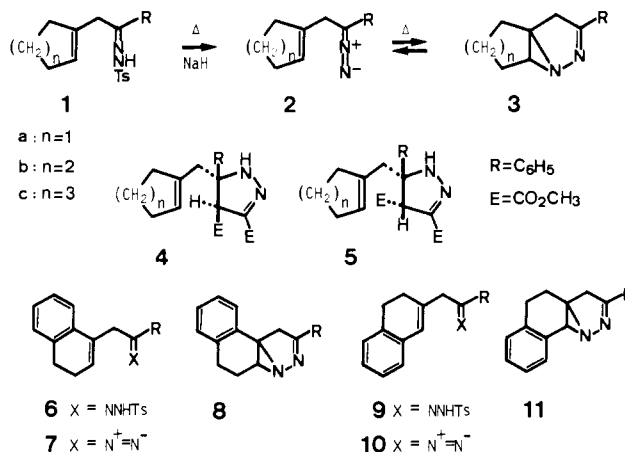
Intramolecular 1,1-Cycloaddition Reactions of Diazomethanes to C=C Double Bonds¹

Sir:

Recently, Padwa² and Steglich³ reported that both photochemically² and thermally³ generated 2-allyl-substituted nitrile ylides underwent a *carbene*-type intramolecular 1,1 cycloaddition to give 2-azabicyclo[3.1.0]hex-2-enes. In connection with those findings and our recent report⁴ on a novel cyclization of allyldiazomethane derivative derived from thermal decomposition of the sodium salt of α -(1,3,5-cycloheptatrien-3-yl)acetophenone to 10-phenyl-1,1,1-diazatricyclo[6.3.0.0^{4,6}]undeca-2,8,10-triene, it was of interest to explore the generality of intramolecular cyclizations of 2-allyl-substituted diazomethanes in which steric restrictions oppose the parallel-plane approach which gives normal 1,3-dipolar adducts, 2,3-diazabicyclo[3.1.0]hex-2-enes. Herein we report our first observation of a formal *nitrene*-type 1,1 cycloaddition of 2-allyl-substituted diazomethanes A leading to 1,2-diazabicyclo[3.1.0]hex-2-enes B.



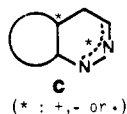
Decomposition of the sodium salt of tosylhydrazone **1a** (mp 123 °C)⁷ in refluxing carbon tetrachloride immediately developed a red coloration which gradually faded during refluxing. Upon cooling to room temperature the color faded completely and **3a** (mp 91 °C) was isolated in 73% yield. The structure of **3a** was unequivocally determined by its spectral properties: m/e (rel intensity) 198 (M^+ , 62), 170 (45), 169 (35), 155 (52), 142 (90), 141 (100); $\nu_{\text{max}}^{\text{IR}}$ 3040, 2950, 1560, 1495, 1445, 760, 690 cm^{-1} ; $\lambda_{\text{max}}^{\text{EIOH}}$ 253.4 nm ($\log \epsilon$ 4.09); $^1\text{H NMR}$ (δ units in toluene- d_8), 1.2~2.2 (m, 7 H), 2.72 (d, 1 H, $J = 17.3$ Hz), 2.91 (d, 1 H, $J = 17.3$ Hz), 7.0~7.2 (m, 3 H), 7.6~7.8 (m, 2 H). Similarly, decomposition of **1b** (mp 127 °C) and **1c** (mp 120 °C) under the same conditions gave the corresponding aziridines **3b** (mp 71.5 °C)⁸ and **3c** (mp 65~67 °C)⁹ in 72 and 86% yields, respectively. Dihydronaphthalene derivative **6** (mp 138 °C) also afforded a quantitative yield of the air-sensitive **8**.¹⁰ The isomer **9** (mp 159 °C dec), on the other hand, afforded in quantitative yield **10**,¹¹ which was found, however, to cyclize slowly to **11** (mp 93.5~95 °C)¹² in 50% yield when allowed to stand at -23 °C.



The generation of diazomethanes as intermediates in the formation of aziridines was substantiated in the case of **2c**¹³ by the formation of the usual 1,3-dipolar adducts,¹⁴ **4c** (58%) and **5c** (18%), and suppression of the yield of **3c** (20%) when **1c** was decomposed in the presence of dimethyl fumarate. Also, the reversibility of the 1,1 cycloaddition between diazomethanes and aziridines was directly observed by temperature-dependent $^1\text{H NMR}$ analyses of these aziridines.¹⁵ Thus, upon heating a solution of **3a** in toluene- d_8 at 101 °C for 10 min in the probe or **3b** at 85 °C, new absorptions appeared due to **2a** and **2b** both in the $^1\text{H NMR}$ ¹⁶ and IR ($\nu_{\text{max}}^{\text{neat}}$ 2040 cm^{-1}) spectra, indicating the formation of the following mixtures, respectively: **2a** (13%) and **3a** (87%) and **2b** (24%) and **3b** (76%). The absorptions due to **2a** and **2b** disappeared upon cooling to room temperature, cleanly reproducing the spectra of **3a** and **3b**. Separate heating of a mixture of **7** (9%) and **8** (91%) at 30 or at 90 °C for 10 min in carbon tetrachloride gave mixtures composed, respectively, of 13% **7** and 87% **8** at 30 °C and 50% **7** and 50% **8** at 90 °C. The latter mixture, when cooled to 30 °C, gave nearly the same composition (10% **7** and 90% **8**) as the starting one. Diazomethane **10**, on the other hand, cyclized rather slowly to **11**; a mixture composed of **10** (74%) and **11** (26%) obtained by heating of **11** at 80 °C for 10 min slowly changed its composition to 45% **10** and 55% **11** after 30 days at room temperature. During the above $^1\text{H NMR}$ analyses, neither an intermediate such as a 2,3-di-

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 Huisgen¹⁷ not to occur during *intermolecular* 1,3-dipolar cycloaddition reactions of diazomethanes and olefins, can take place *intramolecularly*. Since MO calculations¹⁸ 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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References and Notes

- (1) Organic Thermal Reaction. 49; part 48, T. Mukai, *Sci. Rep. Tohoku Univ., Ser. I*, **62**, 21 (1979).
- (2) A. Padwa and P. H. J. Carlsen, *J. Am. Chem. Soc.*, **97**, 3862 (1975); **98**, 2006 (1976); **99**, 1514 (1977).
- (3) J. Fischer and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, **18**, 167 (1979).
- (4) T. Miyashi, Y. Nishizawa, T. Sugiyama, and T. Mukai, *J. Am. Chem. Soc.* **99**, 6109 (1977).
- (5) To the best of our knowledge this ring system is only known in one derivative⁶ which was obtained by the benzophenone sensitized photolysis of a 2,3-diazabicyclo[3.1.0]hex-2-ene derivative.
- (6) M. Franck-Newmann, D. Martina, and C. Dietrich-Buchecker, *Tetrahedron Lett.*, 1763 (1975).
- (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}^{IR} 2950, 1560, 1495, 1450, 750 cm^{-1} ; $\lambda_{\max}^{\text{UV}}$ 254.5 nm ($\log \epsilon$ 4.10); $^1\text{H NMR}$ (δ units in toluene- d_6) 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}^{IR} 2920, 1560, 1494, 1455, 750 cm^{-1} ; $\lambda_{\max}^{\text{UV}}$ 254 nm ($\log \epsilon$ 4.13); $^1\text{H NMR}$ (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**: $^1\text{H NMR}$ (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**: $\nu_{\max}^{\text{CCl}_4}$ 2040 cm^{-1} ; $^1\text{H NMR}$ (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}^{IR} 2930, 1554, 1490, 1442, 935, 790, 744, 723 cm^{-1} ; $^1\text{H NMR}$ (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 **5a**. Similarly, both **1b** and **3b** gave **4b** and **5b**.
- (14) **4c**: $\nu_{\max}^{\text{CCl}_4}$ 3350, 1740, 1713, 1565, 1440, 1210, 692 cm^{-1} ; $^1\text{H NMR}$ (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}^{IR} 3370, 1740, 1677, 1547, 1445, 1210 cm^{-1} ; $^1\text{H NMR}$ (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 $^1\text{H NMR}$ analyses because **3c** was stable up to 130 °C, but decomposed releasing nitrogen over 130 °C.
- (16) During heating in the probe toluene- d_6 solutions turned wine-red. Analyses of diazomethanes **2a** 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 **2a** 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**.
- (17) R. Huisgen, R. Sustmann and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972).
- (18) K. N. Houk, J. Sims, R. E. Duek, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973).
- (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
- (21) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
- (22) In this case, the electron pair from the bonding antisymmetric σ orbital of the aziridine ring and the π orbital 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
- (23) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 159.

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Comment on the Electronic Structure of HAlOH and H₂O·Al

Sir:

The interaction of ground- and excited-state metal atoms with water molecules has attracted considerable experimental¹⁻⁵ and theoretical⁶ interest. Matrix isolation studies by Grandsden and co-workers¹ indicate that aluminum interacts with water to yield the metal hydroxyhydride. Oblath and Gole² have suggested that emission from excited HAlOH may be responsible for the continuum resulting from the reaction of Al with H₂O in the gas phase. In this communication we present the results of theoretical calculations which suggest that insertion of Al into H₂O to yield HAlOH is exothermic by ≈ 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}-H₂O·Al, we have employed the spin-unrestricted Hartree-Fock approximation, together with the effective core potential procedure⁷ 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's⁸ double ζ basis sets were employed for hydrogen and oxygen. We have repeated the calculations at the optimized geometries for HAlOH and the C_{2v}-H₂O·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 ²B₂ state of the C_{2v}-H₂O·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 + H₂O) of 4.4 kcal/mol. In the present study, the optimized C_{2v} geometry has an Al-O separation of 2.12