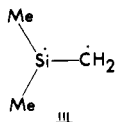


previously obtained estimates of 12–29 kcal mol⁻¹ ^{2a,d,3} and 15.5 ± 5 kcal mol⁻¹.²² Estimating the heat of formation of the related biradical (III) to be 54 kcal mol⁻¹ (on the basis of an



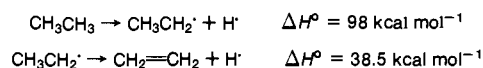
experimental value of -29.6 kcal mol⁻¹ for the heat of formation of trimethylsilane^{4b} and estimates of CH and SiH bond energies of 99¹⁶ and 89^{4b} kcal mol⁻¹, respectively), we arrive at a π -bond energy of ≈ 34 kcal mol⁻¹. This is both significantly less than the π -bond energy associated with a C=C linkage (e.g., 60–65 kcal mol⁻¹ in ethylene^{8,9}) and the estimate of 46 kcal mol⁻¹ obtained theoretically for parent silaethylene.⁶ It is in somewhat better accord with the 30–42-kcal mol⁻¹ range of values provided by Walsh^{2d} on the basis of pyrolysis of 1,1-dimethyl-1-silacyclobutane and of trimethylsilane and of the estimate of 28 ± 8 kcal mol⁻¹ suggested by Gusel'nikov and Nametkin²² based on the analysis of their data.

Acknowledgments. This research was supported in part by a grant from the National Science Foundation. The authors are indebted to Professor K. Shea and to Mr. J. Bramblet for useful suggestions during the course of this work.

References and Notes

- Reviews: (a) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1974); (b) *Russ. Chem. Rev.*, **43**, 620 (1974); (c) M. Ishikawa, *Pure Appl. Chem.*, **50**, 11 (1978).
- (a) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, **419**, 1396 (1968); (b) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971); (c) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 1972, 861 (1972); (d) R. Walsh, *J. Organomet. Chem.*, **38**, 245 (1972); (e) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Am. Chem. Soc.*, **94**, 7626 (1972); (f) R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, *J. Organomet. Chem.*, **80**, 37 (1974); (g) C. M. Golino, R. D. Bush, D. N. Roak, and L. H. Sommer, *ibid.*, **66**, 29 (1974); (h) S. P. Hopper and J. S. Fine, *ibid.*, **80**, 21 (1974); (i) Y. Nakadaira, Sikanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5621 (1974); (j) R. D. Bush, C. M. Golino, and L. H. Sommer, *ibid.*, **96**, 7105 (1974); (k) C. M. Golino, R. D. Bush, and L. H. Sommer, *ibid.*, **97**, 7371 (1975); (l) W. Ando, A. Sekiguchi, J. Ogiwara, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 145 (1975); (m) M. Ishikawa, F. Ohii, and M. Kumada, *J. Organomet. Chem.*, **86**, C23 (1975); (n) M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada, *J. Am. Chem. Soc.*, **97**, 5923 (1975); (o) P. B. Valkovich and W. P. Weber, *J. Organomet. Chem.*, **99**, 231 (1975); (p) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Am. Chem. Soc.*, **98**, 7424, 7453 (1976); (q) A. K. Mal'tsev, V. N. Khanbashsky, and O. M. Nefedov, *Dokl. Akad. Nauk. SSSR*, 1165 (1976); (r) M. Ishikawa, T. Fuchikami, and K. Kumada, *J. Organomet. Chem.*, **117**, C52, **118**, 155, 139, and **127**, 261 (1976); (s) N. Ishikawa, T. Fuchikami, and K. Kumada, *Tetrahedron Lett.*, 1299 (1976); (t) M. Ishikawa, T. Fuchikami, and K. Kumada, *J. Am. Chem. Soc.*, **99**, 245 (1977); (u) M. Ishikawa, T. Fuchikami, and K. Kumada, *J. Organomet. Chem.*, **133**, 19 (1977); (v) M. Ishikawa, T. Fuchikami, and K. Kumada, 11th Organosilicon Symposium, Kansas City, Mo., March 18–19, 1977; (w) L. E. Gusel'nikov, K. S. Konobeevski, V. M. Vdovin, and N. S. Nametkin, *Dokl. Akad. Nauk. SSSR*, **235**, 1086 (1977); (x) A. G. Brook, J. W. Harris, J. Lennon, and M. El Sheikh, *J. Am. Chem. Soc.*, **101**, 83 (1979); (y) T. J. Barton, W. D. Wulff, E. V. Arnold, and J. Cardy, *ibid.*, **101**, 2733 (1979); (z) L. E. Gusel'nikov and N. S. Nametkin, *J. Organomet. Chem.*, **169**, 155 (1979).
- This paper^{2d} suggests an enthalpy for reaction 1 of between 35 and 52 kcal mol⁻¹. Estimating the heat of formation of 1,1-dimethyl-1-silacyclobutane to be -10.6 kcal mol⁻¹ ⁴ and using a value of 12.5 kcal mol⁻¹ for ΔH° for ethylene,^{4a} this leads to a range of 12–29 kcal mol⁻¹ for the heat of formation of 1,1-dimethylsilaethylene.
- From bond additivity. Bond energies from (a) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969), except for C–Si from (b) P. Potzinger, A. Ritter, and J. Krause, *Z. Naturforsch. A*, **30**, 347 (1975).
- (a) A. K. Mal'tsev, V. N. Khabashsky, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1193 (1976); (b) A. K. Mal'tsev, V. N. Khabashsky, and O. M. Nefedov, *Dokl. Akad. Nauk SSSR*, **223**, 421 (1977); (c) O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tuney, *J. Am. Chem. Soc.*, **98**, 7844 (1976); (d) M. R. Chedekel, M. Shoglund, R. L. Kreeger, and H. Shechter *ibid.*, **98**, 7846 (1976).
- R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, **99**, 7452 (1977).
- Other related theoretical work: (a) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975); (b) O. P. Strausz, L. Gammie, G. Theodorakopoulos, P. G. Mezey, and I. G. Czidmadia, *J. Am. Chem. Soc.*, **98**, 1622 (1976); (c) D. M. Hood, and H. F. Schaefer III, *J. Chem. Phys.*, **68**, 43 (1978).
- J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

- Alternatively, a π -bond energy of 59.5 kcal mol⁻¹ for ethylene may be given as the difference in energy of the two bond dissociation processes:



Thermochemical data from S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.

- R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971); (d) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978).
- For examples of the use of similar techniques in the elucidation of the thermodynamic stabilities of transient neutrals, see the following. Free radicals: (a) D. J. DeFrees, W. J. Hehre, R. T. McIver, Jr., and D. H. McDaniel, *J. Phys. Chem.*, **83**, 232 (1979). Enols of stable ketones: (b) S. K. Pollack and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 4845 (1977). Singlet carbenes: (c) J. Vogt and J. L. Beauchamp, *ibid.*, **97**, 6682 (1975); (d) S. G. Lias and P. Ausloss, *Int. J. Mass Spectrom. Ion Phys.*, **22**, 135 (1976); (e) B. A. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 8454 (1977); (f) P. Ausloss and S. G. Lias, *ibid.*, **100**, 4594 (1978). Methyleneimine: (g) D. J. DeFrees and W. J. Hehre, *J. Phys. Chem.*, **82**, 391 (1978).
- Except for *i*-PrEtNH and *i*-Pr₂NH data from R. W. Taft in "Proton Transfer Equilibria", E. F. Caldin and V. Gold, Ed., Wiley-Interscience, New York, 1975, p. 31. These basicities have been slightly modified to account for higher ambient temperatures in the ICR spectrometer than previously believed. Data for *i*-PrEtNH and *i*-Pr₂NH from R. W. Taft, unpublished work.
- The value of 202.3 kcal mol⁻¹ for the proton affinity of ammonia derived from ICR spectroscopy ((a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, J. L. Beauchamp, R. T. McIver, Jr., and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977)), has been revised upward by more recent work: 203.6 kcal mol⁻¹ ((b) S. T. Ceyer, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 14 (1979); 207 kcal mol⁻¹ ((c) F. Houle and J. L. Beauchamp, unpublished results).
- From appearance potential measurements on trimethylsilane and on tetramethylsilane.^{4b}
- D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 37* (1971).
- Estimated on the basis of 98 kcal mol⁻¹ for the bond dissociation energy of CH in ethane, corrected by 1 kcal mol⁻¹ for the theoretical (3–21G level¹⁷) energy for the reaction:

$$\text{SiH}_3\text{CH}_2^\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{SiH}_3\text{CH}_3 + \text{CH}_3\text{CH}_2^\cdot$$
- (a) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 4085 (1979); (b) M. S. Gordon, W. J. Hehre, J. S. Binkley, and J. A. Pople, manuscript in preparation.

William J. Pietro, Steven K. Pollack, Warren J. Hehre*

Department of Chemistry, University of California
Irvine, California 92717

Received June 14, 1979

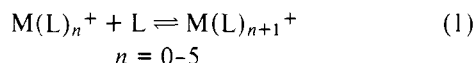
Coordination Chemistry of Copper(I) in the Gas Phase

Sir:

Coordination complexes comprise a large and important class of inorganic compounds. Comprehensive equilibrium studies on these species in solution have yielded extensive compilations of formation constants which, together with theoretical models, have provided insight into the covalent properties of metal centers as well as into the nature of specific metal–ligand interactions. Only recently, however, have a few of the corresponding complexes been studied in the gas phase by mass spectrometric methods.^{1–5} These studies are of particular fundamental importance in that they yield the intrinsic properties of the metal center with various ligands in the absence of any solvation effects. Similar studies on organic molecules, for example, have in some instances drastically altered previously accepted principles such as in understanding the intrinsic effect of alkyl substitution on acid–base properties.⁶ While such dramatic results may not be obtained with coordination complexes, it is evident that gas-phase studies are required for a complete understanding of the chemistry of these species.

Kebarle and co-workers, using variable-temperature–high-pressure mass spectrometry, have been on the forefront of this area.⁷ Their studies have yielded accurate values of ΔH

and ΔS for the sequential addition of ligands to a metal center in the generalized reaction



for the alkali metal ions Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ to ligands such as H_2O , NH_3 , and CH_3CN . One of the significant findings of these studies was that distinct inner and outer coordination spheres are not apparent as evidenced by gradual decreases in ΔH beyond attachment of the first ligand.

Thus far these studies have been limited mainly to alkali metal ions owing to the relative ease of generating these species by thermionic emission. Transition metal ions, however, cannot readily be formed by this method and, although in some instances they can be generated by electron impact on volatile inorganic complexes,¹⁻⁵ the presence of the parent gas as well as other fragment ions can present complications. We have found that laser ionization provides a convenient method for preparing virtually any metal ion from its metal for study by ion cyclotron resonance (ICR) spectroscopy. The pulsed nitrogen laser and ICR spectrometer combination has been described previously.⁸ The present studies on Cu^+ were conducted at room temperature and monitored reaction products as a function of pressure. The pressure was measured using a Baratron capacitance manometer. Figures 1-3 plot ion intensity, starting with Cu^+ as the sole reactant ion, as a function of NH_3 , C_3H_6 , and CH_3CN pressure, respectively. In each case termolecular reactions are observed, as evidenced by the high pressures required to observe products, leading to varying degrees of complexation. Essentially no complexation is observed with H_2O , with the intensity of $Cu(H_2O)^+$ <1% of the Cu^+ intensity. The results in Figures 1-3 clearly indicate that sequential addition of two molecules of NH_3 and C_3H_6 to Cu^+ occurs, and that at least three molecules of CH_3CN complex to form $Cu(CH_3CN)_3^+$. In the latter case, the upper mass range of the instrument prevented us from observing whether any additional complexation occurs.

These results contrast with that for the alkali ions in which multiple ligand binding with H_2O and NH_3 is observed, and at the same time bear a remarkable correspondence to the solution chemistry of monovalent copper. The diammine-copper(I) complex, for example, observed in solution does not complex further with NH_3 presumably because the third NH_3 is unable to displace coordinated H_2O .⁹ The gas-phase results are dramatic in that a third NH_3 does not bind despite the absence of H_2O , suggesting an intrinsically weak interaction. In addition, the cuprous ion is very effectively solvated by CH_3CN ; the cuprous salts have relatively high solubilities in CH_3CN compared with their negligible solubilities in H_2O . Notably, CH_3CN differs from NH_3 and H_2O in that it has substantial π -bonding ability.² The gas-phase results, however, are somewhat tempered by the possibility of a kinetic as well as an energetic influence. Owing to the exothermicity of the coordination reactions and the excess kinetic energy of the laser-generated Cu^+ ,⁸ ligands having a greater number of degrees of freedom may bind more rapidly because of their increased ability to absorb the energy. This kinetic effect diminishes, however, as the number of ligands attached to the metal center increases since the exothermicity of additional ligand attachment lessens, the ion continues to acquire a greater number of vibrational degrees of freedom, and any excess kinetic energy that the Cu^+ may have had originally is dissipated by multiple collisions. While the failure of one H_2O to complex with Cu^+ may be kinetically controlled, therefore, the lack of complexation of Cu^+ with more than two molecules of NH_3 and C_3H_6 is most assuredly not.

In summary, this technique shows great promise for the elucidation of the details of the coordination and charge-transfer chemistry of virtually all of the metal ions. Equilibrium

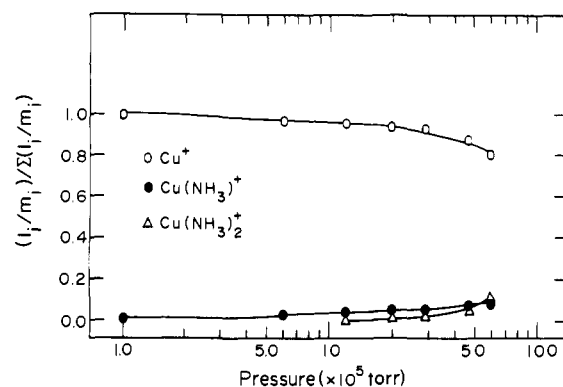


Figure 1. Variation of ion abundance with pressure of NH_3 .

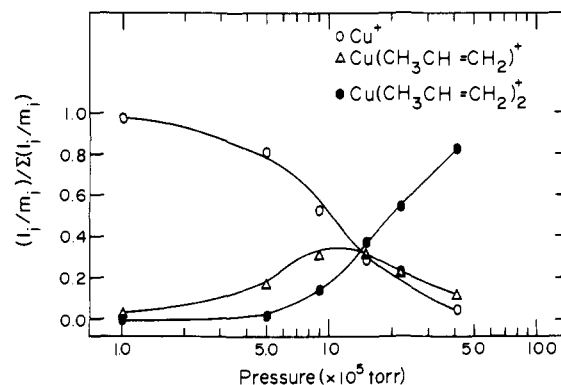


Figure 2. Variation of ion abundance with pressure of C_3H_6 .

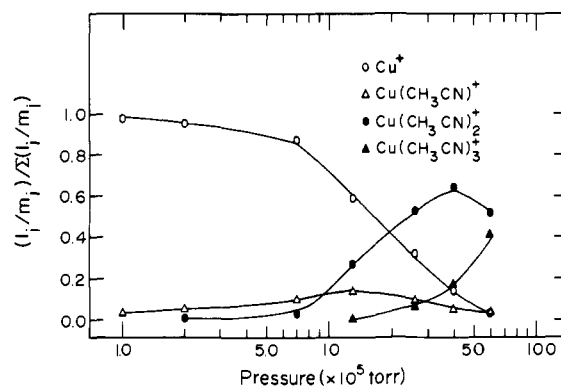


Figure 3. Variation of ion abundance with pressure of CH_3CN .

studies between two ligands will provide significant quantitative data. Such studies are being actively pursued in our laboratory.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to the Research Corporation under a Cottrell Research Grant, and to Du Pont for support administered through Purdue University.

References and Notes

- (1) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 4924-4926.
- (2) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998-4000.
- (3) Hemberger, P. H.; Dunbar, R. C. *Inorg. Chem.* **1977**, *16*, 1246-1247.
- (4) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998-5009.
- (5) Comisarow, M.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413-420.
- (6) Brauman, J. I. *J. Am. Chem. Soc.* **1968**, *90*, 6561-6562.
- (7) (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445-476. (b) Kebarle, P. "Modern Aspects of Electrochemistry", Conway, B. E., Brockis, M., Ed.; Plenum: New York; Number 9, Chapter 1.

- (8) Cody, R. B.; Burnier, R. C.; Reents, Jr., W. D.; Carlin, T. J.; McCreery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass. Spectrom. Ion Phys.*, in press.
 (9) Fisher, J. H.; Hall, S. C. *Anal. Chem.* **1967**, *34*, 1550-1556.

R. C. Burnier, T. J. Carlin, W. D. Reents, Jr.
 R. B. Cody, R. K. Lengel, B. S. Freiser*

Department of Chemistry, Purdue University
 West Lafayette, Indiana 47907

Received May 24, 1979

A Regiospecific and Highly Stereoselective Approach to the Synthesis of Linearly Fused Tricyclopentanoids. Intramolecular Diyl Trapping Reactions

Sir:

We report herein the first example of an intramolecular 1,3-diyl trapping reaction and the application of the reaction to the construction of the linearly fused tricyclopentanoid skeleton common to a class of naturally occurring sesquiterpenes which possess antibiotic and antitumor activity.¹ The key reaction in our route involves the formation of two new carbon-carbon bonds with simultaneous creation of two of the three five-membered rings in a highly stereoselective process which serves to generate four asymmetric centers with the proper relative stereochemical relationship required for elaboration to the naturally occurring systems.

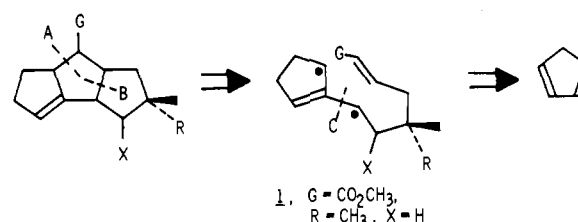
In the discussion which follows attention will be focused upon (1) the synthesis and trapping of 1,3-diyl **1** (note the relationship of **1** to trimethylenemethane) [The basic synthetic plan involves three important disconnections (labeled A, B, and C) and is illustrated in Scheme I.]; (2) a rationale for the observed high degree of stereoselectivity; and (3) a comparison of inter- and intramolecular diyl trapping reactions for the construction of linearly fused tricyclopentanoids.

The bicyclic azo compound **8**, a convenient source of diyl **1**, was synthesized starting with commercially available 3,3-dimethylglutaric anhydride (**2**) following the route outlined in Scheme II. Successive reduction of **2** with sodium borohydride and diisobutylaluminum hydride (Dibal) afforded the cyclic hemiacetal **3**.^{2,3} Wittig condensation of carbomethoxyethylidene triphenylphosphorane with **3**, followed by oxidation of the resulting primary alcohol using the Corey-Suggs procedure, afforded aldehyde **5**.^{4,5}

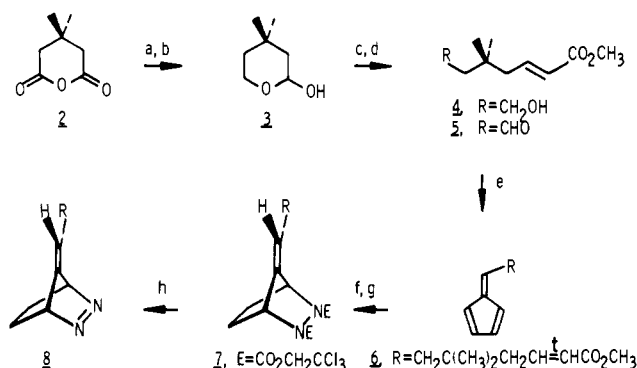
The conversion of **5** into the α,β -unsaturated fulvene **6** proved to be a troublesome task at first, but, after considerable exploration, it was found that uniformly acceptable yields could be obtained using a modification of an approach developed by Freiesleben.⁶ Thus, the dropwise addition of a methanolic solution of diethylamine (1.5 equiv) to freshly distilled cyclopentadiene (2.5 equiv) and aldehyde **5** (1.0 equiv) in absolute methanol at 5-10 °C followed by stirring at room temperature for 2 h, recooling to 0-5 °C, addition of acetic acid, removal of the methanol, ether extraction, successive washing with 10% sodium bicarbonate and brine, drying (MgSO₄), concentration and chromatography over neutral alumina afforded a 91% yield of the desired fulvene: UV λ_{\max} (C₂H₅OH) 258 nm (ϵ 20 600). The Diels-Alder reaction of fulvene **6** and di(2,2,2-trichloroethyl) azodicarboxylate proceeded efficiently at 0 °C in ether and was followed immediately by selective monohydrogenation of the endocyclic π bond to form the bicyclic biscarbamate **7** in 70% yield from **6**.⁷ Conversion of **7** into the desired azo compound **8** was achieved electrochemically using our recently developed method (note Scheme II).^{8,9}

To test the viability of using an intramolecular diyl trapping reaction as a route to linearly fused tricyclopentanoids, azo

Scheme I

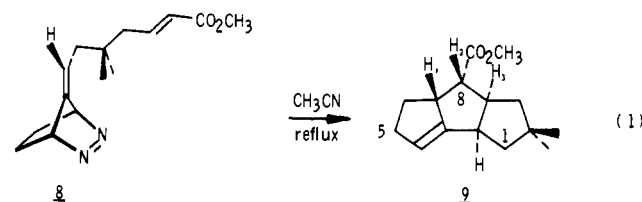


Scheme II^a



^a (a) NaBH₄, THF, 0 °C and then raise to room temperature, 74%; (b) Dibal, ether, -20 °C and then raise to room temperature, 74%; (c) Ph₃P=CHCO₂CH₃, benzene, reflux, 40%;¹⁴ (d) C₅H₅N⁺HCrO₃Cl⁻ (PCC), CH₂Cl₂, room temperature, 92%; (e) 2.5 equiv of cyclopentadiene, 1.5 equiv of Et₂NH, 1.0 equiv of aldehyde **5**, absolute methanol, 5-10 °C and then warm to room temperature, 91%; (f) Cl₃CCH₂O₂CN=NC₂H₄CCl₃, ether, 0 °C, and then (g) H₂, 10% Pd/C, CHCl₃/EtOAc, atmospheric pressure, room temperature, 70% from **6**; (h) e⁻ (1.75 V vs. a silver/silver chloride reference electrode), DMF, 0.1 N LiClO₄, room temperature followed by cooling to 0 °C, and the addition of 3.0 equiv of K₃Fe(CN)₆.

compound **8** was refluxed in acetonitrile for 6 h. A highly stereoselective reaction ensued and, after chromatographic purification, linearly fused tricyclopentanoid **9** was isolated in 50% overall (nonoptimized) yield from biscarbamate **7**^{10,11} (eq 1).



The stereochemical assignment shown in eq 1 follows from ¹H NMR studies. In particular, it was found that the methine hydrogen α to the ester group (H₂, δ 2.58) was split into a clean doublet with $J = 8$ Hz thereby implying a 0-Hz coupling between H₂ and one of the bridgehead protons. Molecular models reveal that, of the four possible linearly fused tricyclopentanoids which could have been formed, only **9** has a dihedral angle of 90° between H₂ and H₃. Europium shift reagent experiments corroborate the assignment.

The observed high degree of stereoselectivity can be rationalized by noting that there exist bonding secondary orbital interactions between C_A and C_B of the diyl and the carbonyl carbon of the unsaturated ester unit (note Scheme III).¹² To the extent that these interactions lower the transition state energy of the path leading to **9** relative to the other possible linearly fused tricyclopentanoids, one would predict its preferential formation.

We recently reported that linearly fused tricyclopentanoids can be synthesized using an intermolecular diyl trapping reaction.¹³ Of the two methods (inter- vs. intra-), the intramo-