

We feel that the experimental evidence that we have presented for selective photomobilization and photoaggregation of metal atomic species, as monitored by our mixed metal atomic-bimetallic cluster optical experiments, is overwhelmingly positive. Nevertheless further experimental probes of these new and interesting photophysical-photochemical phenomena, together with an intensive search for still higher clusters are planned for these as well as other metallic and bimetallic systems. The impetus for such "mini-alloy" cluster experiments, besides the intrinsic chemical novelty of "few-atom-bimetallics", is the long-range goal of probing the "molecular metal cluster-bulk metal particle interface",² the objective being a fundamental enquiry into bimetallic cluster electronic, geometric, chemisorptive, and catalytic properties as a function of the size and composition of the cluster.⁹

Acknowledgment. The generous financial assistance of the National Research Council of Canada Operating New Ideas and Strategic Energy Grants Programmes, the Atkinson Foundation, the Connaught Fund, Imperial Oil of Canada, the Lash Miller Chemical Laboratories, and Erindale College are all gratefully appreciated.

References and Notes

- (1) (a) H. Huber and G. A. Ozin, *Inorg. Chem.*, **17**, 155 (1978); (b) W. E. Klotzbucher and G. A. Ozin, *J. Mol. Catal.*, **3**, 195 (1977).
- (2) See, for example, G. A. Ozin, "Cryochemistry", M. Moskovits and G. A. Ozin, Ed., Wiley, New York, N.Y., 1976, and references cited therein.
- (3) (a) W. E. Klotzbucher, H. Kolari, J. Norman, Jr., and G. A. Ozin, *Inorg. Chem.*, **16**, 297 (1977); (b) W. E. Klotzbucher and G. A. Ozin, *ibid.*, **16**, 984 (1977); (c) E. P. Kundlg, M. Moskovits, and G. A. Ozin, *Nature*, **254**, 503 (1975).
- (4) As Cr₂ remains essentially invariant under these circumstances we favor Mo⁺ + CrMo → CrMo₂ rather than Mo⁺ + Cr₂ → Cr₂Mo.
- (5) As Mo₂ remains essentially invariant under these circumstances we favor Cr⁺ + CrMo → Cr₂Mo rather than Cr⁺ + Mo₂ → CrMo₂.
- (6) It is important to note here that, under a wide variety of concentration conditions in separate Cr/Kr(Ar), Mo/Kr(Ar), and Cr/Mo/Kr(Ar) experiments, bulk diffusion incurred by thermal annealing (12–40K for Ar, 12–80K for Kr) leads only to "catastrophic clustering" as seen by the general decay of all Cr_n, Mo_m, and Cr_nMo_m spectral absorbances (presumably arising from nonselective diffusion-aggregation processes, leading mainly to high clusters characterized by broad bulk metal-like, far-UV absorptions). This could imply "thermally activated clustering" for the lower diatomic, triatomic, etc. species which might well be kinetically impeded at the low temperatures employed in our matrix experiments. (Incidentally, this is not the case for silver, where at least Ag_{2,3,4,5} clusters can be generated by thermal-annealing techniques in Ar, Kr, Xe, and CH₄.^{1,7,8}) It is therefore conceivable, that the facile photogeneration of CrMo, Mo₂, Cr₃, Cr₂Mo, CrMo₂, and Mo₃ is, in fact, the outcome of "photoactivated" nucleation events involving either electronically excited or "thermally hot" atomic/cluster moieties. Further research is required to establish this pertinent aspect of photoaggregation.
- (7) W. Schulze, H. U. Becker and H. Abe, *Int. Conf. Matrix Isolation Spectrosc.*, paper 8.5 (June 1977).
- (8) H. Huber, S. Mitchell, and G. A. Ozin, unpublished work.
- (9) J. H. Sinfelt, *Acc. Chem. Res.*, **10**, 15 (1977).

Werner E. Klotzbücher, Geoffrey A. Ozin*

Lash Miller Chemistry Laboratory and Erindale College
University of Toronto, Toronto, Ontario, Canada

Received September 27, 1977

Preparation and Isolation of $\Delta^{1,4}$ -Bicyclo[2.2.0]hexene

Sir:

We wish to report details of the preparation and properties of the highly strained olefin, $\Delta^{1,4}$ -bicyclo[2.2.0]hexene (**1**). Three previous papers have reported evidence for the presence of this compound, but none has described isolation of the pure



material.¹ Bromochloride **2** was prepared as previously described.² Compound **2** can be electrochemically reduced only with difficulty ($E_{1/2} = -2.50$ V vs. saturated calomel electrode in dimethylformamide),^{1b} behavior not characteristic of 1,2-dihalides.³ Dipole moment measurements of **2**^{2b,4} suggest a large intervector angle between the carbon-halogen bonds. Since the molecule may also be twisted, these two effects could explain the observed electrochemical behavior.⁵

Controlled current electroreduction of 400 mg of **2** in 40 mL of dimethylformamide⁶ in a divided cell, with 0.18 M tetramethylammonium hexafluorophosphate⁷ was conducted at -14 °C over a stirred mercury pool cathode⁸ while the apparatus was maintained at 2×10^{-3} Torr pressure in a vacuum line. Volatile effluents were collected in cold traps maintained at -23 , -45 , and -95 °C, respectively, while 2.0 F of current were passed. The current was held at 100 mA, and resulted in an applied voltage of 10–14 V. The -95 °C trap contained 10–30 mg of a white crystalline solid, melting below -60 °C, which could be identified as $\Delta^{1,4}$ -bicyclo[2.2.0]hexene (**1**) from the behavior and properties described below.

In contrast to its behavior in dilute hydrocarbon solution,^{1c} the pure olefin **1** is extremely reactive. It can be transferred from a -45 °C bath to a -200 °C bath over a short path length with some loss to polymer, but at -23 °C the neat olefin polymerizes with a half-time of <10 s. Vapor pressures of >1 Torr have not been obtained, owing to polymerization. The polymer is a clear solid, insoluble in most solvents: IR (cm^{-1}) 3000, 2960, 2880, 1425, 1225, 1010.

The ¹H NMR (CD_2Cl_2) of **1** consisted of a sharp singlet at 3.24 ppm.^{1a} In dilute solution ($\sim 1\%$) in $\text{C}_6\text{D}_5\text{CD}_3$, the olefin disappeared with a half-time of 420 s at 0 °C. The product was an insoluble polymer. The ¹³C NMR of **1** at -50 °C showed peaks at 163.5 and 43.7 ppm (CD_2Cl_2) (relative to Me_4Si). The low field peak, assigned to the olefinic carbon, is significantly further downfield than any other simple olefinic resonance heretofore reported.¹¹ The mass spectrum, recorded at 2.1 kV, show m/e (percent of base peak) of 80 (49) (M^+), 79 (100), 77 (28), and 43 (26).

The Raman spectrum of **1** was recorded at -190 °C using a sample prepared by condensing vapor onto a copper plate. Spectra were recorded of unannealed and annealed (at -110 °C) films excited with ~ 50 mW of 514.5-nm Ar⁺ laser radiation. Both C=C and C—H bands were observed. The C=C band appeared at 1661 cm^{-1} in the solid and was shifted when measured in solution (1664 cm^{-1} in CD_2Cl_2 at -50 °C, 1673 cm^{-1} in cyclopropane at -56 °C). The C—H bands appeared at 2843, 2923, 2951, and 2961 cm^{-1} and were consistent with CH_2 modes in normal strained alicyclic hydrocarbons.^{12a}

The infrared spectrum of a solid film of **1**, obtained by vapor deposition onto a cesium iodide plate at -196 °C, was recorded before and after annealing at -110 °C. The C—H bands appeared at 2832, 2930, and 2965 cm^{-1} ; the latter two appear normal for aliphatic CH_2 .^{12b} Only five bands appear between 650 and 200 cm^{-1} . They were found at 424, 410, 400 (sh), 393, and 288 cm^{-1} and seem to account for the fundamental out-of-plane deformation modes. It was not possible to measure the gas phase infrared spectrum of **1**, even in a 10-m multipass cell, owing to decomposition of the olefin at room temperature. The appearance of strong, low frequency fundamental bands in the infrared and their complete absence in the Raman spectrum are consistent with D_{2h} symmetry, characteristic of a planar skeleton. The unusual downfield ¹³C chemical shift of the olefinic carbon in **1** suggests a tendency toward allenic-like sp character.

Although the olefin is reactive with cyclopentadiene,^{1a,b} it failed to undergo cycloaddition with 2,3-dimethyl-1,3-butadiene in CD_2Cl_2 solution at temperatures below those necessary for polymerization.

The choice of supporting electrolyte for the electrochemical preparation of **1** was critical. Tetraethyl- and tetrabutylammonium salts produced substantial amounts of tertiary amine and olefin, presumably from a Hofmann reaction of the intermediate carbanion.¹³ These products were difficult to separate from **1**. A reaction using platinum cathode with tetraalkylammonium salts followed a different course and gave little or no olefin.

Studies on the mechanism of formation of **1** and its chemical behavior are in progress.

Acknowledgment. The authors are grateful to Ms. Janet Allison for laboratory assistance in preparing samples of the olefin.

References and Notes

- (1) (a) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971); (b) J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 3803 (1974); (c) K. B. Wiberg, W. F. Bailey, and M. E. Jason, *ibid.*, **39**, 3803 (1974).
- (2) (a) K. V. Scherer and T. J. Meyers, Abstract of Papers, the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, Section P-180. (b) K. Katsumoto, Ph.D. Thesis, University of California at Berkeley, 1968; *Diss. Abstr.*, **29**, 3262B (1968–1969). (c) K. V. Scherer, Jr., *Tetrahedron Lett.*, 5685 (1966). (d) K. V. Scherer, Jr., and K. Katsumoto, *ibid.*, 3079 (1967). (e) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Am. Chem. Soc.*, **90**, 1014 (1968).
- (3) J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 2408 (1974).
- (4) K. V. Scherer, private communication.
- (5) J. Zavada, T. Krupička, and J. Sicher, *Collect. Czech. Chem. Commun.*, **28**, 1644 (1963).
- (6) Normally the catholyte volume is 25 mL, anolyte 15 mL.
- (7) The use of this supporting electrolyte was suggested Professor S. Mazur, and its preparation will be described elsewhere.
- (8) The counterelectrode was a 1-cm² platinum foil, and the mercury surface area was 11.3 cm².
- (9) CCl₃ appeared to react with **1** and induce polymerization. Similar behavior has been observed for other strained bridgehead olefins (Professor D. Aue, private communication).
- (10) Using C₆D₅CD₃ the peaks appeared at 163.3 and 44.1 ppm relative to Me₄Si. The low field peak was small compared with the ¹³CH₂ resonance, possibly owing to a long spin-lattice relaxation time.
- (11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, Chapter 3.
- (12) (a) J. Bragin and D. Guthals, *J. Phys. Chem.*, **79**, 2139 (1975); (b) K. Nakaniishi and P. H. Solomon, "Infrared Absorption Spectroscopy", 2nd ed, Holden-Day, San Francisco, Calif., 1977, Chapter 2.
- (13) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **93**, 553 (1971).

J. Casanova,* J. Bragin, F. D. Cottrell

Department of Chemistry
California State University, Los Angeles
Los Angeles, California 90032

Received December 8, 1977

Enthalpy Limit in The Laser-Induced Reaction of CH₃CF₂Cl

Sir:

Recently, Tardieu de Maleissye et al.¹ reported on the pyrolysis of ethylene induced by a CO₂ laser. At a continuous laser intensity of 660 W/cm² and ethylene pressure above 200 Torr, the number of absorbed photons per decomposed molecule reached a limiting value of 16.7, corresponding in total absorbed energy per mole to the thermal activation energy measured by standard pyrolytic techniques. Similar results were claimed for ethane,² with added SF₆ as the laser absorber. The thermodynamic limit is set, however, not by the activation energy E_A , but by the enthalpy difference, ΔH . In the experiments just described, there is energy per mole $E_A - \Delta H$ being lost or unused. We wish to report that in similar experiments on the compound CH₃CF₂Cl the number of photons absorbed per molecule dissociated is considerably less than the activation energy equivalent and approaches ΔH for the reaction.

The pyrolytic elimination of HCl from CH₃CF₂Cl to yield

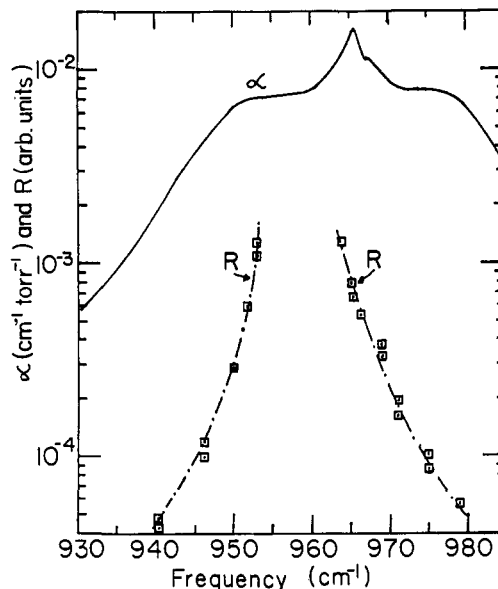


Figure 1. Optical absorption coefficient α and laser-induced reaction rate R for various frequencies over the 966-cm⁻¹ band of CH₃CF₂Cl. The gap in R is due to lack of laser output at those frequencies.

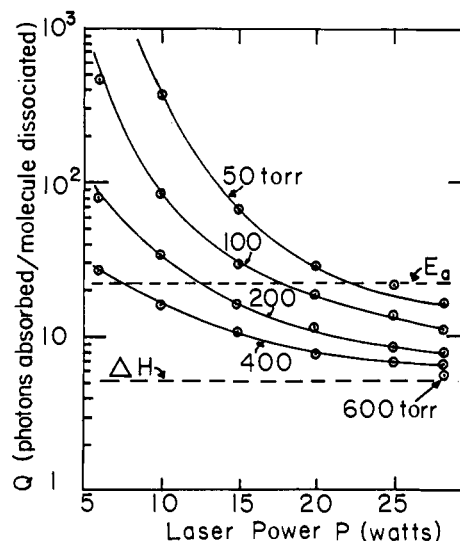


Figure 2. Quantum requirement Q as a function of laser beam power P for several gas pressures. The horizontal dotted lines indicate the activation energy and enthalpy in units of photons/molecule. The laser frequency is 953 cm⁻¹.

CH₂CF₂ occurs with an enthalpy change³ and activation energy⁴ of 59.4 and 252 kJ/mol, respectively. There is a competing reaction, namely HF elimination, which can amount to 30% of the total in reactors with quartz or inconel walls, but only to 2 or 3% of the total for some seasoned Ni-Cr alloy walls.⁴ In our experiments, the beam interaction region is far from the Pyrex cell walls, and we observe only HCl elimination with no evidence of the competing HF elimination reaction.

The laser frequencies used were primarily those in near resonance with the 966-cm⁻¹ absorption band of CH₃CF₂Cl, which has been characterized as a CH₃ rocking mode.⁵ The laser beam diameter was 1 mm, while the reaction cell had an inner diameter of 22 mm and a total volume of 50 cm³. Reaction rates were obtained by observing the growth of the 1731-cm⁻¹ absorption band of the product CH₂CF₂, and only initial rates were recorded, corresponding to small product concentrations. Above 10 W of laser power, rates were too rapid to measure in the pure continuous mode, and pulses of ~10⁻¹-s duration were used. This duration exceeds even the