mmol) in THF was slowly added (10 min). A wonderful blue color appeared when the phosphine was added. The mixture was allowed to warm to a temperature depending on the alkylating agent as indicated below. Then, previously degassed water (10 equiv) was added under nitrogen to avoid dialkylation. The solution was decanted and transferred with a flex-needle into a flask containing dried and degassed $MgSO_4$ (0.5 g). The mixture was stirred 15 min under nitrogen and transferred into another flask containing a small amount of hydroquinone (0.05 equiv). Further purification was performed by trap to trap distillation for the volatile compounds **2a**, **2c**, and **2d**.

Methylvinylphosphine (2a). Alkylating agent: methyl iodide. Hydrolysis temperature: −10 °C. Yield: 70%. Purity (>95%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −80.5 (d, $^1J_{PH}$ = 208.7 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (dd, 3 H, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 2.6 Hz); 3.80 (dm, 1 H, $^1J_{PH}$ = 208.7 Hz); 5.62 (m, 1 H, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 1.7 Hz); 5.70 (ddd, 1 H, $^3J_{PH}$ = 24.3 Hz, $^3J_{HH}$ = 11.8 Hz, $^2J_{HH}$ = 1.7 Hz); 6.41 (ddm, 1 H, $^3J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 11.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.0 (qd, $^1J_{CH}$ = 130.2 Hz, $^1J_{CP}$ = 10.0 Hz); 125.7 (tdm, $^1J_{CH}$ = 156.8 Hz, $^2J_{CP}$ = 14.3 Hz); 135.5 (ddm, $^1J_{CH}$ = 157.0 Hz, $^1J_{CP}$ = 14.2 Hz). HRMS calcd for $C_3H_7P^{\cdot+}$: 74.0285. Found: 74.0284.

Benzylvinylphosphine (2b). Alkylating agent: benzyl bromide. Hydrolysis temperature: −30 °C. Yield: 76%. Purity (>85%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −53.4 ($^1J_{PH}$ = 205.0 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 2.7 (m, 2 H); 3.9 (dm, $^1J_{PH}$ = 205.0 Hz); 5.5 (m, 2 H); 6.1 (m, 1 H); 7.0 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.8 (td, $^1J_{CH}$ = 129.5 Hz, $^1J_{CP}$ = 10.8 Hz); 126.1 (td, $^1J_{CH}$ = 160.1 Hz, $^2J_{CP}$ = 14.3 Hz); 130.3 (dd, $^1J_{CH}$ = 158.7 Hz, $^1J_{CP}$ = 20.7 Hz). HRMS calcd for $C_9H_{11}P^{\cdot+}$: 150.0598. Found: 150.059.

Allylvinylphosphine (2c). Alkylating agent: allyl bromide. Hydrolysis temperature: −40 °C. Yield: 62%. Purity (>95%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −62.5 (d, $^1J_{PH}$ = 209.0 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (m, 2 H); 3.7 (dm, 1 H, $^1J_{PH}$ = 209.0 Hz); 4.95 (m, 2 H); 5.78 (m, 3 H); 6.36 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9 (td, $^1J_{CH}$ = 132.0 Hz, $^1J_{CP}$ = 10.7 Hz); 115.4 (td, $^1J_{CH}$ = 161.1 Hz, $^3J_{CP}$ = 6.7 Hz); 128.6 (td, $^1J_{CH}$ = 160.1 Hz, $^2J_{CP}$ = 19.5 Hz); 132.8 (dd, $^1J_{CH}$ = 159.8 Hz, $^1J_{CP}$ = 15.9 Hz); 135.8 (dd, $^1J_{CH}$ = 160.0 Hz, $^2J_{CP}$ = 1.1 Hz). HRMS calcd for $C_8H_9P^{\cdot+}$: 100.044. Found: 100.043.

Registry No. **1a**, 63314-88-5; **1b**, 89222-11-7; **1c**, 77697-52-0; **1d**, 7766-52-1; **2a**, 141850-64-8; **2b**, 141850-65-9; **2c**, 141850-66-0; **2d**, 90006-08-9; **3**, 58436-39-8; **4a**, 756-79-6; **4b**, 1080-32-6; **4c**, 1067-87-4; **5a**, 1066-52-0; **5b**, 41760-95-6; **5c**, 41760-96-7; **5d**, 41761-00-6; **6a**, 141850-67-1; **6b**, 141850-68-2; phenylphosphonic dichloride, 824-72-6; vinylmagnesium bromide, 1826-67-1.

The Isolation of a Bi(2,4,6,8-tetraazabicyclo[3.3.0]octane) from the Reaction of Glyoxal with Benzylamine

Michael Chaykovsky,* William M. Koppes, and Thomas P. Russell

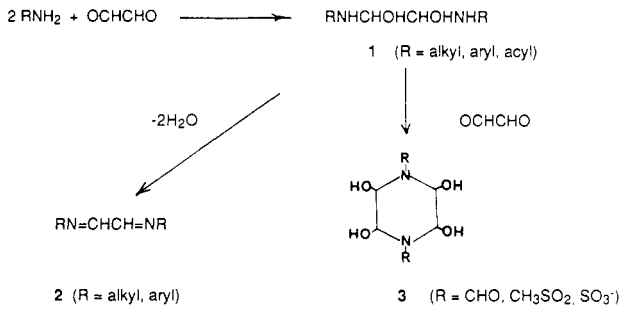
Energetic Materials Division, Naval Surface Warfare Center, Silver Spring, Maryland 20903-5000

Richard Gilardi, Clifford George, and Judith L. Flippen-Anderson

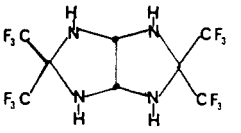
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375-5000

Received October 10, 1991 (Revised Manuscript Received April 6, 1992)

The reactions of primary amines and amides (RNH_2) with glyoxal give a variety of products depending upon the nature of R and, in certain cases, upon the reaction conditions.[1-5] Primary aliphatic amines usually form dicarbinolamines **1** or conjugated diimines **2**, while aromatic primary amines form these and other products.[1,2] Primary aliphatic amides give primarily adducts of type **1**,[6] but in some cases, further reaction with glyoxal occurs to give tetrahydroxypiperazines **3**.[3-5]



Ethylenediamine and N,N′-disubstituted ethylenediamines react with glyoxal to give *cis*- and *trans*-1,4,5,8-tetraazadecalins and 2,2′-biimidazolidines.[7] We have shown that the *gem*-diamine 2,2-diaminohexafluoropropane reacts with glyoxal to give the 2,4,5,8-tetraazabicyclo[3.3.0]octane **4** in high yield.[8]



4

Recently, Nielsen and co-workers have reported, in this journal, the facile condensation of glyoxal with benzylamine (and certain phenyl-substituted benzylamines) to produce the new polyazapolycyclic caged ring system **5**, to which they have assigned the semisystematic name hexabenzylhexaazaisowurtzitane.[1] In this report, we describe the isolation of another compound produced in this reaction as a byproduct in low but significant yield, whose structure was determined to be that of **6**. The production of **6**, a bi(2,4,6,8-tetraazabicyclo[3.3.0]octane), further illustrates the diversity of products formed in amine–glyoxal reactions and is consistent with the mechanism of formation of **5**, as proposed by Nielsen.[1]

Our experimental conditions for the condensation of glyoxal with benzylamine were essentially the same as those reported (procedure A in ref 1), with the exception of some variations in solvent volume (800 mL CH_3CN vs 1100 mL), added water (40 mL vs 100 mL), and time of addition of glyoxal (30 min vs 1 h).[9] The crude reaction product, mp 149–152 °C, was recrystallized from a large volume of CH_3CN to give colorless needles of almost pure **5**, mp 153–155 °C. Repeated recrystallizations (5×) of a sample gave pure **5**, mp 155–157 °C. Pure **6**, mp 174–175 °C, was isolated from the original CH_3CN recrystallization

(1) Nielsen, A. T.; Nissan, R. A.; Vanderah, D. J.; Coon, C. L.; Gilardi, R. D.; George, C. F.; Flippen-Anderson, J. *J. Org. Chem.* **1990**, *55*, 1459 and references cited therein.

(2) Whitfield, G. F.; Johnson, R.; Swern, D. *J. Org. Chem.* **1972**, *37*, 95 and references cited therein.

(3) Vail, S. L.; Moran, C. M.; Barker, R. H. *J. Org. Chem.* **1965**, *30*, 1195.

(4) Currie, A. C.; Dinwoodie, A. H.; Fort, G.; Thompson, J. M. C. *J. Chem. Soc. C* **1967**, 491.

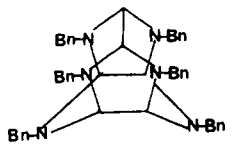
(5) Dinwoodie, A. H.; Gibson, J. A.; Parker, J. B. *J. Chem. Soc.* **1967**, 496.

(6) American Cyanamid, Belgian Patent 615,320; *Chem. Abstr.* **1963**, *59*, 8603c.

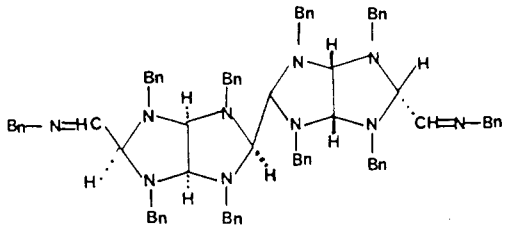
(7) Willer, R. L.; Moore, D. W.; Vanderah, D. J. *J. Org. Chem.* **1985**, *50*, 2365 and references cited therein.

(8) Koppes, W. M.; Chaykovsky, M.; Adolph, H. G.; Gilardi, R.; George, C. *J. Org. Chem.* **1987**, *52*, 1113.

(9) We thank Dr. A. T. Nielsen for providing us with technical reports on the preparation of **5** prior to his publication.



5



6

filtrate as detailed in the Experimental Section.

Quantitative analyses for the determination of the amount of **6** present in the crude reaction product and in the once-recrystallized product were performed using diffuse reflectance FTIR spectroscopy utilizing a partial least-squares method. In this manner, it was found that the crude product from typical runs contained about 5–6% by weight of **6** and that the once-recrystallized product still retained **6** to the extent of 2.5–3%. HPLC analysis on a silica gel column confirmed these results and showed that compounds **5** and **6** were the major products of the reaction, with only minor amounts of impurities (ca. 1% total) which were not isolated or identified (see Experimental Section).

X-ray crystallographic analysis was used to determine the crystal molecular structure of **6**, which is shown in Figure 1.

The benzyl-substituted nitrogen atoms in **6** are each bonded to three fully saturated carbon atoms and are thus expected to be pyramidal in conformation. In solutions, these pyramids may invert (if the overall steric situation allows), but in the crystal the bend at each nitrogen atom is frozen at a particular value by the close packing of the molecules. In a similarly substituted polyamine, 3,5,12-tribenzyl-3,5,12-triazawurtzitane,[10] the angle between the *N*-methylene bond and the adjacent C–N–C ring plane ranged from 36 to 44° and averaged 40.8° for the three distinct amino nitrogen atoms. For pure tetrahedral geometry, this bend would be 54.8°. In molecule **6**, there are eight benzyl-substituted amines, but because of the center of symmetry, only four of them are conformationally distinct. The bend angles (defined above) at N2, N4, N6, and N8 are 57.0, 14.0, 49.8, and 52.0°, respectively. All bends are away (exo) from the cleft of the *cis*-bicyclooctane system except the one at N4, which is near-planar, but is slightly endo. We propose that the reason N4 is nearly planar is because of steric interference stemming from the junction of the two bicyclic systems.

It has been proposed[1] that the mechanism of formation of **5** involves the trimerization, in discrete steps, of the conjugated dipolar diimine **2** (R = benzyl) to give, as an intermediate, the bicyclic dication **9** (Scheme I). Intramolecular cyclization in **9** leads to the caged structure **5** after loss of two protons. However, if **9** were to react further with two more molecules of **2**, one adding at each of the rings to give **10**, then cyclization and loss of two

(10) Nielsen, A. T.; Christian, S. L.; Moore, D. W.; Gilardi, R. D. *J. Org. Chem.* 1987, *52*, 1656.

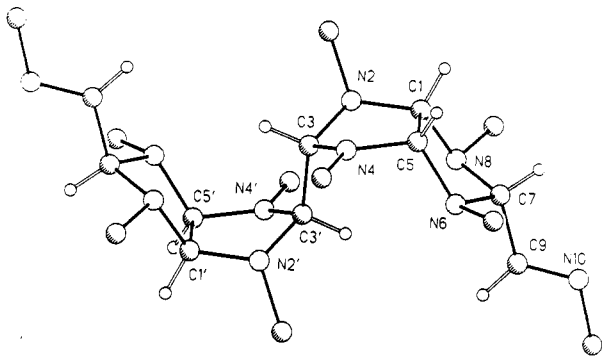
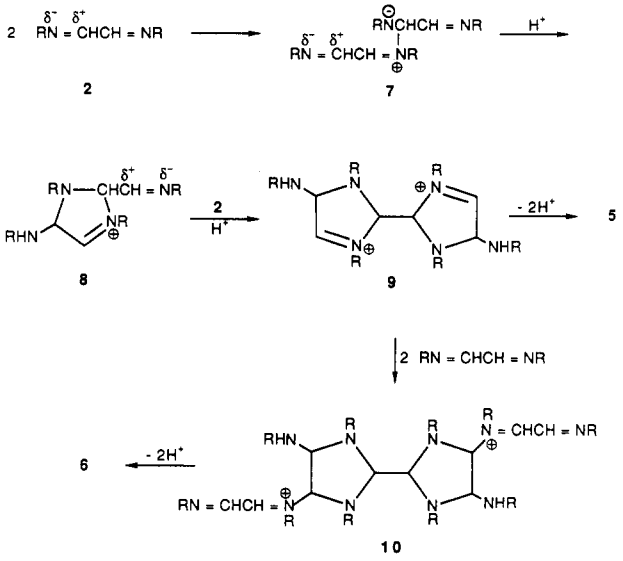


Figure 1. Molecular structure and numbering scheme for compound **6**. The center of the molecule lies on a center of symmetry in the crystal. The unlabeled atoms bonded to N2, N4, N8, and N10 are methylene carbon atoms of the substituent benzyl groups; the rest of the atoms of the benzyl groups were omitted for clarity.

Scheme I. Formation of 5 and 6 from 2 (R = Benzyl)



protons leads to the bi(tetraazabicyclooctane) **6**. Thus, the same bicyclic trimer **9**, which Nielsen proposes as an intermediate in the formation of **5**, may also be the intermediate for the formation of **6**. This mechanism also explains the low yield of **6**, since intramolecular cyclization in **9**, to give **5**, would be expected to be more rapid than the subsequent reactions leading to **6**.

Experimental Section

^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer with a pulsed Fourier transform system (Me_4Si internal standard). IR spectra were recorded on a Nicolet 20SX FTIR spectrometer with a Nicolet 1280 data acquisition system, utilizing a Harrick PMM diffuse reflectance accessory cell. Melting points were taken on a Thomas-Hoover capillary apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of Benzylamine with Glyoxal To Give 5 and 6. Glyoxal (72.5 g of 40% aqueous solution, 0.50 mol) was added dropwise over 30 min to a stirred solution of benzylamine (112 g, 1.045 mol), formic acid (5.5 g of 95%, 0.113 mol), and water (40 mL) in CH_3CN (800 mL), keeping the temperature between 10 and 20 °C. A white solid began to precipitate after about half of the glyoxal had been added. After being stirred at room temperature for 18 h, the mixture was filtered and the solid washed with cold CH_3CN (100 mL) and dried to yield 83.7 g of crude product: mp 149–152 °C. This material was dissolved in 2.7 L of boiling CH_3CN, cooled to room temperature overnight, and filtered to give 77 g of colorless needles: mp 152–155 °C. A sample of this material was recrystallized five times from CH_3CN to give pure **5**: mp 155–157 °C, (identified by ^{1}H NMR).[1]

The CH_3CN filtrate from the first recrystallization (2.7 L) was evaporated at a water pump to leave a mixture of oil and solid. This was triturated with ether (50 mL), cooled in ice, and then filtered to give a white solid (3.0 g): mp 146–158 °C, consisting of a mixture of **5** and **6**. The solid was heated in boiling ether (200 mL), cooled to room temperature, and filtered to give crude **6** (1.05 g): mp 170–173 °C. Recrystallization twice from ethyl acetate–isopropyl ether gave pure **6**: mp 174–175 °C; ^1H NMR (CD_2Cl_2) δ 7.74–6.78 (m, 52 H), 5.02 (s, 2 H, CHC=N), 4.47–3.36 (m, 26 H). Anal. Calcd for $C_{80}H_{80}N_{10}$: C, 81.31; H, 6.83; N, 11.86. Found: C, 80.93; H, 6.84; N, 11.77.

Quantitative FTIR Analysis. Throughout the IR spectral regions for compounds **5** and **6**, numerous differences were observed. These differences consisted of mostly overlapping absorbances; however, a sharp individual imine band at 1669 cm^{-1} was present for **6**. Other major distinguishable peaks for **6** occur at 3320 (w), 2847 (s), 2772 (w), 1735 (w), 1437 (s), 1247 (w), 1158 (s), 967 (s), 885 (w), 865 (w), and 610 cm^{-1} (w). Analytical standards were prepared with known weight percentages of pure **6** to pure **5** (0–15% by weight of **6**). Standards and samples were ground with KBr and loaded into the PPM-DRA cell. Quantitative analyses were determined on the recorded IR spectra (200 summed scans at 2 cm^{-1} resolution) utilizing the Nicolet partial least-squares (PLS) program version 2.1. Samples of the crude product and the once-recrystallized product from typical synthetic runs, as described above, were found to contain 5–6% and 2.5–3% of **6**, respectively.

HPLC Analysis. The crude reaction product from a typical run was analyzed on a Waters Model 990 HPLC system using a photodiode array detector (254 nm), a 712 WISP automatic injector, and a Model 510 pump. The adsorption column was a Varian MicroPak SI-10 (silica; 30 cm × 4 mm). Mobil phase: 90:10 $CHCl_3/CH_3CN$; flow rate: 1.0 mL/min; injection volume: 5.0 μL; run time: 10 min; sample size: 0.01 g/10 mL dissolved in mobil phase. Compounds **5** and **6** had retention times of 3.43 and 2.83 min, respectively. Minor impurities (*ca.* 1% total) were observed at retention times of 2.42, 4.39, and 6.74 min.

Single-Crystal X-ray Diffraction Analysis of Compound 6. $C_{80}H_{80}N_{10}$, FW = 1181.5, triclinic space group, $P\bar{1}$, a = 11.464 (2) Å, b = 12.172 (2) Å, c = 13.267 (3) Å, α = 114.57 (2)°, β = 95.30 (2)°, γ = 97.47 (2)°, V = 1647.2 (6) Å^3, Z = 1 ($^1/_2$ molecule per asymmetric unit), ρ_{calc} = 1.191 mg/mm^3, λ (MoKα) = 0.710 73 Å, μ = 0.066 mm^{-1}, $F(000)$ = 630, T = 293 K.

A clear colorless 0.22- × 0.36-mm crystal, in the shape of a prism, was used for data collection on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator. Lattice parameters were determined from 28 centered reflections within $24.3 \le 2\theta \le 33.4°$. The data collection range of hkl was $-12 \le h \le 12$, $-12 \le k \le 13$, $-14 \le l \le 1$, with $[(\sin\theta/\lambda]_{max}$ = 0.54. Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to +2.5% during the data collection. A set of 4922 reflections was collected in the $\theta/2$ scan mode, with scan width $[2\theta(K_{\alpha1}) - 1.0]$ to $[2\theta(K_{\alpha2}) + 1.0]°$ and ω scan rate (a function of count rate) from 6.0°/min to 29.3°/min. There was 4326 unique reflections, and 3198 were observed with $F_o > 3\sigma(F_o)$. The structure was solved and refined with the aid of the SHELXTL system of programs.[11] The full-matrix least-squares refinement varied 462 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms and coordinates and isotropic thermal parameters for the hydrogen atoms bonded to the fused rings. Remaining H atoms were included by using a riding model [coordinate shifts of C applied to attached H atoms, C–H distance set to 0.96 Å, H angles idealized]. Final residuals were R = 0.058 and wR = 0.055 with final difference Fourier excursions of 0.28 and −0.23 eÅ^{-3}.

Acknowledgment. This work was supported by the Office of Naval Research, Mechanics Division. We thank Ms. Sibyl Turner (NSWC) for the HPLC analyses.

Registry No. **5**, 124782-15-6; **6**, 141663-57-2; glyoxal, 107-22-2; benzylamine, 100-46-9.

(11) Sheldrick, G. M. *SHELXDTL80. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Univ. of Gottingen, Germany, 1980.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Nucleophilic and Photochemical Reactions of *F*-Adamantanone

James L. Adcock* and Huimin Luo

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received January 13, 1992

Introduction

The successful synthesis of perfluorinated diamondoids has been a synthetic challenge most successfully met by direct fluorination.[1-5] However, the high stability of C–F bonds has made such compounds difficult to functionalize or derivatize. This prompted us to search for a more direct route to functionalized perfluorodiamondoid derivatives. Adamantanone was synthesized many years ago,[6] is commercially available, and has been widely used as a starting material for preparing numerous adamantane derivatives;[7,8] therefore, we sought to synthesize *F*-adamantanone and study some of its reactions. In this paper, we report the synthesis, solution equilibria, and photochemical reactions of *F*-adamantanone.

Results and Discussion

With the help of spectroscopic techniques (vide infra), the major product (98% by weight) collected from the aerosol direct fluorination of adamantanone was identified as the analogous perfluoro ketone. Based on input of adamantanone, the yield of *F*-adamantanone was in the range of 50–73% which varied with the number of hours the product trap was pumped with the vacuum line. The longer the trap was pumped, the higher was the yield. This implies that there exists some kind of interaction between the carbonyl group of *F*-adamantanone and the NaF pellets in the product trap. Although direct fluorination of hydrocarbons into their perfluoro analogues with little carbon framework rearrangement or fragmentation has been achieved by other techniques, these synthesis methods have met with diminished success with diamondoid compounds because of the sensitivity of the compounds to HF generated during the fluorination.[2] In our case possible photolysis of the carbonyl group during photochemical finishing of the fluorination was a concern.[9] The successful synthesis of *F*-adamantanone with almost no fragmentation suggests that photolysis of the perfluoro ketone occurs too slowly to be important on the reactor time scale of about 1 min.

(1) Maraschin, N. J.; Catsikis, B. D.; Davis, L. H.; Jarvinen, G.; Lagow, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 513.
(2) Robertson, G.; Liu, E. K. S.; Lagow, R. J. *J. Org. Chem.* **1978**, *43*, 4981.
(3) Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 3128.
(4) Adcock, J. L.; Luo, H. *J. Org. Chem.* **1992**, *57*, 2162.
(5) Huang, S.; Klein, D. H.; Adcock, J. L. *Rapid Commun. Mass Spectr.* **1988**, *2*, 204.
(6) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182.
(7) Cuddy, B. D.; Grant, D.; Karim, A.; McKervey, M. A.; Rea, E. J. F. *J. Chem. Soc., Perkin Trans I* **1972**, 2701.
(8) Faulkner, D.; McKervey, M. A. *J. Chem. Soc.* **1971**, 3906.
(9) Giacometti, G.; Okabe, H.; Price, S. J.; Steacie, E. W. R. *Can. J. Chem.* **1960**, *38*, 104.

0022-3263/92/1957-4297$03.00/0