J. Org. Chem. 1986, 51, 3219–3221

placed in a dry 10-mL flask equipped with a rubber stopper and magnetic stirrer. The flask was evacuated and flushed with dry N_2 several times, and $CHCl_3$ (3.0 mL) was introduced by means of a syringe. The suspension was stirred for 2 h and, after the addition of 2 drops of methanol, became a clear solution. The solvent was evaporated in vacuo, and the oily residue was dissolved in 2 mL of dry $CHCl_3$. This solution was added dropwise to a chloroform solution (5 mL) of 0.10 g (0.26 mmol) of compound 2 at room temperature and the mixture was stirred for 5 h. After the reaction was complete (TLC), the solvent was evaporated in vacuo, and the residue was purified by flash chromatography on a silica gel column using AcOEt–hexane (50:50) and affording a quantitative yield of 4 (0.083 g) as white crystals: mp 145–146 °C; R_f 0.19 ($CHCl_3$); IR (KBr) 3415, 2985, 1805, and 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$), 1.22 (s, 12 H), 1.51 (s, 3 H), 3.73 (s, 3 H), 4.03 (d, 1 H, J = 1.6 Hz), 5.20 (br s, 1 H), 5.75 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 5.94 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 7.63 (d, 1 H, J = 6.4 Hz); mass spectrum, m/e (relative intensity) 345 (M^+, 2), 85 (25), 57 (100).

Acknowledgment. We thank CONICET and Fundación Alberto J. Roemmers for financial support. We also thank Prof. L. F. Cafferata (Universidad Nacional de La Plata) for a generous gift of fluorosulfonic acid, Prof. M. G. Sierra for recording the ^{1}H and ^{13}C NMR spectra and for helpful discussions, and Prof. O. S. Giordano (Universidad Nacional de San Luis) for the low-resolution mass spectral data.

Registry No. **2**, 81658-78-8; **3a**, 74772-34-2; **3b**, 74772-33-1; **3c**, 74772-35-3; **4**, 102871-09-0; (pivaloyloxy)methyl 6β-aminopenicillanate, 25031-08-7.

A Silver Ion Catalyzed [3.1.1]Propellane Rearrangement. 2,4-Methano-2,4-didehydroadamantane Retro-Carbene Ring Opening

Zdenko Majerski* and Kata Mlinarić-Majerski

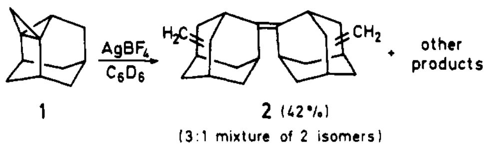
Rudjer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

Received February 18, 1986

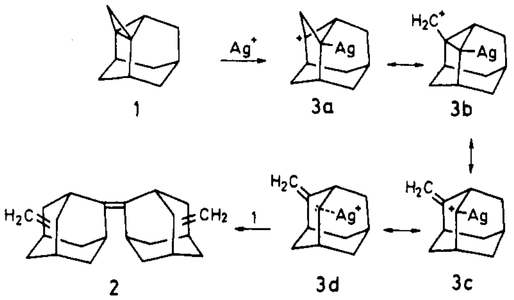
We report the first silver ion catalyzed retro-carbene rearrangement of a carbocyclic [3.1.1]propellane: 2,4-methano-2,4-didehydroadamantane (1).

Propellane 1 was readily prepared by an intramolecular cycloaddition of 4-methylene-2-adamantylidene to the olefinic bond.[1] It was thermally stable and completely inert toward nucleophiles but highly reactive toward electrophiles and free radicals.[1] This was explained by a high electron density at the reaction site, i.e., at the backside of the inverted carbon atoms, and a decrease in electron density between them. Such an electron density distribution in the central bond of 1 is in accord with theoretical considerations,[2] and X-ray,[3] vibrational,[4a] and electron-diffraction[4b] analyses, as well as with chemical behavior of other small propellanes.[5-8] Hence, small propellanes should readily interact with transition metals having high electron affinities.

Scheme I



Scheme II



Transition metal catalyzed reactions of small propellanes have been only sparingly studied,[5,6,9] although such reactions of other small-ring organic molecules have been subjects of numerous investigations.[10] In the early 1970s, Gassman and Armour[9] reported a rearrangement of the parent [3.2.1]propellane to a mixture of diolefins, 4- and 5-methylenecycloheptenes, catalyzed by iridium, rhodium, or ruthenium chlorocarbonyl complexes. Recently, Szeimies and Szeimies-Seebach reported ring openings of a carbocyclic [4.1.1]propellane[5,6] and an oxa[3.1.1]propellane[6] to the structurally related conjugated diolefins catalyzed by silver ion or rhodium, palladium, or copper complexes. The same products were formed by the propellane thermolyses, presumably, via the respective carbene intermediates.

The main purpose of this investigation was to provide a further insight into the specific electron distribution in

---

[1] Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7389. Mlinarić-Majerski, K.; Majerski, Z. *Ibid.* **1980**, *102*, 1418.

[2] (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. (b) Jackson, J. E.; Allen, L. C. *Ibid.* **1984**, *106*, 591. (c) Zilberg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 358. (d) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. (e) Stohrer, W.-D.; Hoffmann, R. *Ibid.* **1972**, *94*, 779.

[3] Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schlüter, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378.

[4] (a) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247. (b) Hedberg, L.; Hedberg, K. *Ibid.* **1985**, *107*, 7257.

[5] Szeimies-Seebach, U.; Szeimies, G. *J. Am. Chem. Soc.* **1978**, *100*, 3966.

[6] Baumgart, K.-D.; Harnisch, H.; Szeimies-Seebach, U.; Szeimies, G. *Chem. Ber.* **1985**, *118*, 2883.

[7] [1.1.1]Propellane: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. [2.1.1]Propellane: Wiberg, K. B.; Walker, F. K.; Pratt, W. E.; Michl, J. *Ibid.* **1983**, *105*, 3638. [2.2.1]Propellane: Walker, F. H.; Wiberg, K. B.; Michl, J. *Ibid.* **1982**, *104*, 2056. [3.1.1]Propellane: Gassman, P. G.; Proehl, G. S. *Ibid.* **1980**, *102*, 6862. Vinković, V.; Majerski, Z. *Ibid.* **1982**, *104*, 4027. Reference 1. Reference 6. [2.2.2]Propellane: Eaton, P. E.; Temme, G. H., III. *Ibid.* **1973**, *95*, 7508. [3.2.1]Propellane: Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317. Gassman, P. G.; Topp, A.; Keller, J. W. *Ibid.* **1969**, 1093. Wiberg, K. B.; Burgmaier, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 7396. Wiberg, K. B.; Connon, H. A.; Pratt, W. E. *Ibid.* **1979**, *101*, 6970. Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *Ibid.* **1977**, *99*, 2297. Aue, D. H.; Reynolds, R. N. *J. Org. Chem.* **1974**, *39*, 2315. [4.1.1]Propellane: Hamon, D. P. G.; Trenerry, V. C. *J. Am. Chem. Soc.* **1981**, *103*, 4962. Reference 5. Reference 6. [4.2.1]Propellane: Warner, P.; LaRose, R. *Tetrahedron Lett.* **1972**, 2141. Baumgärtel, O.; Harnisch, J.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *Chem. Ber.* **1983**, *116*, 2205. [3.2.2]Propellane: Eaton, P. E.; Nyi, K. *J. Am. Chem. Soc.* **1971**, *93*, 2786. [3.3.1]Propellane: Warner, P.; LaRose, R.; Schleis, T. *Tetrahedron Lett.* **1974**, 1409. Kogay, B. E.; Sokolenko, W. A. *Ibid.* **1983**, 613. Sokolenko, W. A.; Kishkan, L. N.; Kogay, B. E. *Zh. Org. Khim.* **1976**, *12*, 906. Pincock, R. E.; Torupka, E. J. *J. Am. Chem. Soc.* **1969**, *91*, 4593. Scott, W. B.; Pincock, R. E. *Ibid.* **1973**, *95*, 2040. Pincock, R. E.; Schmidt, J.; Scott, W. B.; Torupka, E. J. *Can. J. Chem.* **1972**, *50*, 3958.

[8] Reviews: Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, 1975. Also see its sequels I and II; Department of Chemistry, Technion: Haifa, 1981 and 1985, respectively.

[9] Gassman, P. G.; Armour, E. A. *Tetrahedron Lett.* **1971**, 1431.

[10] Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; pp 245–277.

0022-3263/86/1951-3219$01.50/0

the central bond of small propellanes such as **1**. In addition, our object was also to display intermediacy and fate of metal–carbene complexes in the transition metal catalyzed rearrangements of such propellanes. Propellane **1** was anticipated to be a good model for these investigations, since any isomerization to a diolefin(s) is highly improbable owing to the unique structure of the adamantane skeleton.

Treatment of propellane **1** in dry benzene-d_6 solution with a catalytic amount of $AgBF_4$ at room temperature led to a mixture of products (Scheme I). The reaction was instantaneous and exothermic. The products were separated by column chromatography on neutral alumina by using successively pentane, ether, and benzene as the eluents. The benzene fraction gave a white polymeric material (by ^{13}C NMR and ^{1}H NMR) and the ether fraction yielded a small amount of a mixture of, at least, four GC low retention time products. The major, pentane, fraction (42% with respect to **1**) contained two sublimable products in a ratio of 3:1 (by GC and ^{13}C NMR). These products were separated by column chromatography on $AgNO_3$-pretrated silica gel and identified as two isomeric 4-methylene-2-adamantylidene dimers (**2**) by ^{13}C NMR, ^{1}H NMR, IR, and mass spectra. No methylene-2,4-didehydroadamantane isomer was detected by ^{13}C NMR in an appreciable amount. A catalytic amount of $AgBF_4$ suspended in dry benzene-d_6 was also treated with a 1:4 mixture of propellane **1** and cyclohexene or 2,3-dimethyl-2-butene; virtually the same product mixtures as before were obtained and no appreciable amounts of new products were detected (by ^{13}C NMR).

The mechanism presumably involves an interaction of the silver cation with back lobe electrons of the propellane central bond orbitals leading to the intermediary metallo-carbocation–carbene **3** (Scheme II).[11] Simultaneous formation of cyclobutyl, cyclopropylcarbinyl, and exclusively anti homoallyl products in reactions of **1** with other electrophiles[1] strongly indicate that this intermediate is bridged. Consequently, **3** may be represented by a resonance hybrid of four canonical forms: **3a**, **3b**, **3c**, and **3d**. The last one is a silver(I)–carbene complex. Although silver ion has a rather high promotion energy it can still dontate electrons to the neighboring electron-deficient center,[10] transforming the silver(I)–carbocation form **3c** to the silver(I)–carbene form **3d**. An interaction of the silver ion in the carbene complex **3** with another molecule of propellane **1** will lead to 4-methylene-2-adamantylidene dimers (**2**) by reductive loss of the metal from the respective bis(4-methylene-2-adamantylidene)–silver(I) complexes. Theoretically four isomeric 4-methylene-2-adamantylidene dimers could be formed, but only two of them were actually found in the product mixture. This can easily be explained. Molecular models of four possible spatial orientations of two 4-methylene-2-adamantylidene units complexed with a silver ion indicate that two anti orientations should be energetically favored[12] over the other two because of weaker hydrogen–hydrogen repulsions. The reaction of carbenoid **3** with **1** is favored over intramolecular insertions into γ-C,H bonds as well as over intermoledular cycloadditions to olefinic bonds. The electrophilic complex **3** preferably interacts with the propellane central bond electrons than with the olefinic π-electrons. This indicates the relative nucleophilicities of such two bonds provided that their steric hindrances are equal.

In summary, 2,4-methano-2,4-didehydroadamantane (**1**), a prototype carbocylic [3.1.1]propellane, rearranges instantaneously in the presence of $AgBF_4$, yielding 42% of a 3:1 mixture of two isomeric 4-methylene-2-adamantylidene dimers (**2**). The mechanism appears to involve a silver ion attack at an electron-rich back lobe of the propellane central bond orbitals leading to a bridged silver(I)–carbocation–carbene complex. Interaction of this intermediate with another propellane molecule eventuates in reductive loss of the metal, giving rise to the two dimers.

Experimental Section

^{13}C NMR and ^{1}H NMR spectra were taken on a JEOL FX90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were obtained on a Varian CH-7 mass spectrometer. The quantitative analyses with ^{13}C NMR were performed by a combination of long-pulse intervals (120 s) to assure complete relaxation of all ^{13}C nuclei and a gated decoupling, which eliminated the nuclear Overhauser enhancement. GC analyses were carried out on a Varian Aerograph 1800 gas chromatograph on stainless-steel analytical columns. Melting points were determined in sealed capillary tubes completely immersed in oil by using a Thiele apparatus and were uncorrected. Benzene-d_6 (≥99% *d*, Merck) was dried over molecular sieves prior to use. $AgBF_4$ was purchased from Fluka and kept under dry nitrogen.

2,4-Methano-2,4-didehydroadamantane (1) was prepared in 70% yield by pyrolysis of the dry 4-methylene-2-adamantanone tosylhydrazone sodium salt at 180–190 °C in vacuo as described previously.[1] The sodium salt was obtained from the tosylhydrazone (775 mg, 2.35 mmol) by treatment with sodium hydride (50% suspension in mineral oil, 130 mg, 2.70 mmol) in dry tetrahydrofuran (7 mL) at room temperature.

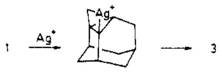
Reaction of Propellane 1 with $AgBF_4$. Propellane **1** was dissolved under dry N_2 gas in anhydrous benzene-d_6 (0.8 mL), and the resulting solution was transferred via a syringe into a small flask, which was previously flushed with dry N_2 gas. A catalytic amount of $AgBF_4$ (~25 mg, 0.13 mmol, 8 mol %) was added in one portion to the solution at room temperature. The color of the solution instantaneously turned dark brown. The reaction was exothermic. The mixture was filtered through a short neutral alumina column. ^{13}C NMR and GC analyses indicated a complex mixture of products. The products were separated by column chromatography on neutral alumina (activity I) using successively pentane, ether, and benzene as the eluents.

The pentane fractions of two pyrolyses were combined. Evaporation of the solvent yielded 200 mg (42% with respect to **1**) of a white sublimable solid, which was shown to be a 3:1 mixture [by GC (FS-1265, 150 °C) and ^{13}C NMR] of two 4-methylene-2-adamantylidene dimers (**2**) [mass spectrum, *m/z* (relative intensity) 292 (M^+, 100), 148 (11), 105 (15), 91 (25)]. Other possible products, such as methylene 2,4-didehydroadamantane isomers or 2,4-methanodamantane, were not detected by ^{13}C NMR in appreciable amounts. The former would exhibit olefinic methylene signals other than those of **2**, while the later is a known compound the ^{13}C NMR data of which were published.[13] The dimers were separated by column chromatography on $AgNO_3$-pretreated (10%) silica gel using pentane as eluent.

The Major Product: 35 mg; mp 115–116 °C; ^{13}C NMR ($CDCl_3$) δ 158.2 (s, 2 C), 133.3 (s, 2 C), 100.3 (t, 2 C), 43.1 (d, 2 C), 41.3 (t, 2 C), 40.6 (t, 2 C), 39.2 (t, 2 C), 39.0 (t + d, 4 C), 32.0 (d, 2 C), 28.5 (d, 2 C); ^{1}H NMR ($CDCl_3$) δ 4.52 (d, *J* = 2.3 Hz, 2 H), 4.45 (d, *J* = 2.3 Hz, 2 H), 3.58 (br s, 2 H), 2.93 (br s, 2 H),

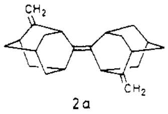
---

[11] An oxidative addition of the metal to one of the external cyclopropane bonds would also eventuate in **3**.

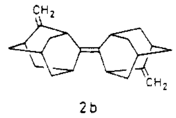


4

[12] These orientations would lead to the anti dimers **2a** and **2b**.



2a



2b

[13] Sasaki, T.; Eguchi, S.; Hirako, Y. *J. Org. Chem.* **1977**, *42*, 2981.

2.53 (br s, 2 H), 2.12–1.37 (m, 18 H); IR (KBr) 3060 (w), 2900 (s), 1650 (m), 1460 (w), 1445 (m), 875 (s) cm^{-1}; MS, *m/z* (relative intensity) (M^+, 100), 148 (5), 105 (15), 91 (30). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.24; H, 9.85.

The Minor Product: 10 mg; ^{13}C NMR ($CDCl_3$) δ 157.6 (s, 2 C), 133.3 (s, 2 C), 100.7 (t, 2 C), 43.0 (d, 2 C), 42.0 (t, 2 C), 40.5 (t, 2 C), 39.2 (2 t, 4 C), 38.9 (d, 2 C), 32.0 (d, 2 C), 28.5 (d, 2 C); ^1H NMR ($CDCl_3$) δ 4.49 (d, J = 2.2 Hz, 2 H), 4.45 (d, J = 2.2 Hz, 2 H), 3.57 (br s, 2 H), 2.89 (br s, 2 H), 2.51 (br s, 2 H), 2.09–1.46 (m, 18 H).

The ether fractions gave 25 mg of a mixture of, at least, four products (by gas chromatography on a FS-1265 column at 100 °C; the retention times were quite short at these conditions). The benzene fractions yielded 67 mg of a white polymeric material (by ^{13}C NMR and ^1H NMR) poorly soluble in pentane or ether.

Acknowledgment. We gratefully acknowledge support of this work by the Research Council of the Republic of Croatia and the U.S.–Yugoslav Cooperative Program PN-531, NSF.

Registry No. 1, 73586-31-9; **2a**, 102780-95-0; **2b**, 102918-62-7; 4-methylene-2-adamantanone tosylhydrazone, 102780-96-1; 4-methylene-2-adamantanone tosylhydrazone sodium salt, 102780-94-9.

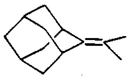
Electron-Transfer Chain Oxidation of 4,5-Dimethylhomoadamant-4-ene

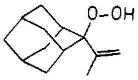
Stephen F. Nelsen* and Mark F. Teasley

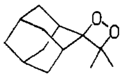
S. M. McElvain Laboratories of Organic Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

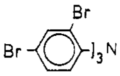
Received January 22, 1986

A dichotomy of products has been observed for oxygenation reactions of isopropylideneadamantane (1) with


1


2

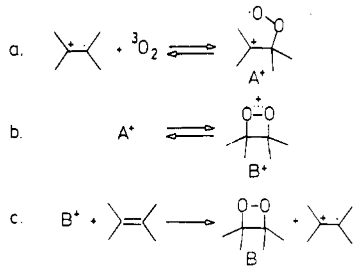

3



4

various reagents.[1] Both singlet oxygen[2] and the olefin cation, O_2^- pairs produced by use of 9,10-dicyanoanthracene as a photosensitizer[3] gave exclusively the ene product 2, but dioxetane 3 was produced by treatment of 1 in oxygen-saturated CH_2Cl_2 with a catalytic amount of 4^+ $SbCl_6^-$ at −78 °C. Because conversion of 1 to 3 by both the Kopecky method[4] and peroxymercuration[5] failed (the latter because debromination of brominated 3 could not be accomplished),[6] this result suggests that electron-transfer chain oxidation of hindered olefins having abstractable α-hydrogens might have practical importance for dioxetane preparation.

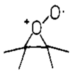
Scheme I



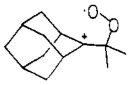
The three-step chain reaction shown in Scheme I has been suggested as the mechanism for conversion of tetraalkylolefins to dioxetanes catalyzed by one-electron oxidants. The two CO bonds of the dioxetane are apparently formed in separate steps as shown, because oxygenation of *anti*-8,8′-bis(bicyclo[3.2.1]octylidene) gives the *syn*- as well as the *anti*-dioxetane, and the CC bond rotation required has been shown not to occur in the absence of oxygen.[7] Much more rapid formation of one CO bond to give A^+ than two at once to give B^+ directly is also predicted by MNDO calculations for the reaction of ethylene cation radical with O_2.[8]

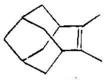

A⁺

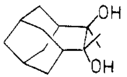

B⁺


C⁺

If A^+ is accepted as an intermediate in the addition of $^3O_2$ to 1^+, however, conversion of 1 to 3 does not provide a reasonable test of whether A^+ would undergo closure to B^+ in preference to internal hydrogen atom transfer to give ene products. On both steric and electronic grounds, the A^+ intermediate formed either from 1^+ and $^3O_2$ or by single CO bond cleavage of 3^+ should be 5^+, which is Bredt's rule


5⁺


6



7

protected against intramolecular hydrogen transfer from the bridgehead carbons α to the cation. We have therefore prepared the symmetrical isomer of 1, 4,5-dimethylhomoadamantene (6), which can only give a single A^+ intermediate having an unprotected methyl group attached to the formally cationic carbon atom to provide such a test.

Preparation of 6 without contamination by 1 (a serious problem in methods which involve carbocation intermediates) was achieved by addition of methyllithium to homoadamantane-4,5-dione[9] to give the *trans*-4,5-dimethylhomoadamantane-4,5-diol (7) in 97% yield and subsequent deoxygenation of 7 using low-valent titanium to give 6 in 68% yield. The ^{13}C NMR spectrum of 7 showed seven signals, establishing it as the trans isomer because the cis isomer would display eight signals. Use of HMPA had no effect on the addition and 7 was still the only product. Since most deoxygenation methods require *cis*-diols, low-valent titanium reagents were tried instead. McMurray's reagent[10] has Ti^0 stoichiometry but failed to

---

(1) Nelsen, S. F.; Kapp, D. L.; Teasley, M. F. *J. Org. Chem.* **1984**, *49*, 5974.

(2) For reviews, see: (a) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (b) Frimer, A. A. *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 7, pp 201–34.

(3) (a) Ericksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Spada, L. T.; Foote, C. S. *Ibid.* **1980**, *102*, 391. (c) Erickson, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083. (d) Steichen, P. S.; Foote, C. S. *Ibid.* **1981**, *103*, 1855. (e) Jiang, Z. Q.; Foote, C. S. *Tetrahedron Lett.* **1983**, *24*, 461. (f) Schaap, A. P.; Zaklika, K. A.; Kasker, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389. (g) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154.

(4) (a) Kopecky, K. R.; Munford, C. *Can. J. Chem.* **1969**, *47*, 709. (b) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockward, P. A.; Ding, J. Y. *Ibid.* **1975**, *53*, 1103.

(5) Adam, W.; Sakanishi, K. *J. Am. Chem. Soc.* **1978**, *100*, 3935.

(6) Adam, W.; Encernacion, L. A. A. *Chem. Ber.* **1982**, *115*, 2592.

(7) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 1265.

(8) (a) Chen, C.-C.; Fox, M. A. *J. Comput. Chem.* **1983**, *4*, 488. (b) Unpublished calculations with T. Clark show the problems of trying to go to higher level ab initio calculations but agree fully with the conclusions of Chen and Fox at the MNDO level.

(9) Schlatmann, J. L. M. A.; Korsloot, J. G.; Schut, J. *Tetrahedron* **1972**, *26*, 949.