was extracted out. The combined acidic extracts were neutralized with 10 N NaOH, extracted into ethyl acetate, washed with water and brine, and dried over sodium sulfate. Evaporation of solvents under reduced pressure gave 1-(3-methoxy-2-aminophenyl)pyrene as a brown oil (0.66 g, 68% yield). The amino compound was cyclized as described above for **26**. Flash chromatography on silica gel (10% benzene–hexane) yielded **28** as a yellow residue. Crystallization from hexane afforded pure **28** as yellow needles: 30 mg (5%); mp 209–211 °C; mass spectrum, *m/e* (relative intensity) 306 (100, M^+), 263 (67).

7-Hydroxyindeno[1,2,3-*cd*]pyrene (21). Treatment of **28** (30 mg, 98 μmol) as described above for **22** yielded **21** as yellow needles: 20 mg (69%); mp 226–228 °C dec; mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (45); UV (EtOH) λ_{max} (ε) 399 nm (21 200), 388 (sh, 21 000), 370 (sh, 15 600), 350 sh, 7100), 325 (sh, 8400), 313 (16 500), 297 (34 900), 286 (sh, 27 500), 270 (27 300), 250 (63 800), 239 (67 700), 223 (55 300); high-resolution mass spectrum, exact mass calcd for $C_{22}H_{12}O$ 292.0888, obsd 292.0800.

Acknowledgment. This work was supported in part by Grant ES 02030 from the National Institute of Environmental Health Sciences. We are also grateful to the Chemical and Physical Carcinogenesis Branch of the National Cancer Institute for partial support of this work under Contract NO1-CP-05613. We also thank Debbie Conroy for her assistance in the preparation of this manuscript.

Registry No. **1**, 193-39-5; **2**, 102420-53-1; **3**, 102420-54-2; **4**, 99520-63-5; **5**, 102420-55-3; **6**, 102420-56-4; **7**, 102420-57-5; **8**, 99520-65-7; **9**, 102420-58-6; **10**, 99520-66-8; **11**, 102434-58-2; **12**, 102420-59-7; **13**, 99520-64-6; **14**, 102420-60-0; **15**, 13974-81-7; **16**, 212-54-; **17**, 241-28-1; **18**, 102420-61-1; **19**, 102420-62-2; **20**, 99520-67-9; **21**, 102420-63-3; **22**, 99520-58-8; **25**, 102420-64-4; **26**, 102420-65-5; **27**, 102420-66-6; **28**, 102420-67-7; 1-(4-methoxy-2-aminophenyl)pyrene, 102420-68-8; 3-methoxy-2-nitroaniline, 16554-47-5; 2-fluorenecarboxaldehyde, 30084-90-3; benzyl chloride, 100-44-7; pyrene, 129-00-0; 4-methoxy-2-nitroaniline, 96-96-8.

Supplementary Material Available: UV spectra for 1-, 2-, 6-, 7-, 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene and (±)-*trans*-1,2-dihydro-1,2-dihydroxyindeno[1,2,3-*cd*]pyrene (1 page). Ordering information is given on any current masthead page.

Synthesis of Disiloxanediyl Diamines via a Facile Homocondensation of Amino Silanols

Robert B. Weisenfeld

Monsanto Agricultural Company, St. Louis, Missouri 63167

Received December 17, 1985

1,3-Bis(4-isocyanatophenyl)-1,3-dimethyl-1,3-diphenyldisiloxane (**1a**) and 1,3-bis(4-isocyanatophenyl)-1,1,3,3-tetramethyldisiloxane (**1b**) were synthesized in six steps from 4-bromoaniline (**2**) in 57% and 55% overall yields, respectively. The key step in the process involved the generation of 4,4′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**8a**) and 4,4′-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)bis(benzenamine) (**8b**) via the tetrabutylammonium hydroxide mediated homocondensation of (4-aminophenyl)methylphenylsilanol (**7a**) and (4-aminophenyl)dimethylsilanol (**7b**), respectively.

A method for generating disiloxanediyl diisocyanates **1a,b** in six steps from 4-bromoaniline (**2**) has been developed such that all of the intermediates can be easily isolated in good to excellent yields without the need for chromatography. The key step in this synthesis involves the formation of aminodisiloxanes **8a** and **8b** via a facile homocoupling of the corresponding amino silanols **7a** and **7b**, respectively. The synthetic pathway for the formation of disiloxanediyl diisocyanates **1a,b** is shown below in Scheme I.

The first major step toward the synthesis of diisocyanates **1a** and **1b** involved the generation of (4-aminophenyl)methylphenylsilanol (**7a**) and (4-aminophenyl)dimethylsilanol (**7b**). The synthetic pathway began with 4-bromoaniline (**2**), which when heated at 45 °C for 3 h in the presence of excess Me_3SiCl and Et_3N was converted into *N*-(trimethylsilyl)-4-bromoaniline (**3**)[1] in 95% yield. An attempt was made to add another trimethylsilyl group to amine **3** by extending the reaction time several days. However, only a trace amount of *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**) was formed. Instead, compound **4** was synthesized in 91% yield by first treating amine **3** with excess MeMgCl and then with Me_3SiCl. Previously, aniline **4** was generated in one step from 4-bromoaniline (**2**) by metalating the amine with 2 equiv of *n*-BuLi followed by addition of Me_3SiCl.[2] However, an attempt to reproduce this reaction resulted in the formation of an inseparable mixture of amines **3** and **4**. The synthesis of silanols **7a** and **7b** continued with the formation of silyl compounds **6a** and **6b**. This was accomplished by adding the Grignard reagent[3] generated from compound **4** to $RMeSiCl_2$ (R = Me, Ph) followed by treatment of the solution with MeOH and Et_3N. Both compounds **6a** and **6b** could be conveniently purified by bulb-to-bulb distillation. Although silyl amines **6a** and **6b** could be generated in one step and in good yields from *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**), the intermediate silyl chloride **5a** was isolated and characterized by ^1H NMR. Finally, amino silanes **6a** and **6b** were hydrolyzed to silanols **7a** and **7b**, respectively. The reactions were easily monitored by TLC (7:3 hexanes/ethyl acetate).

While the investigation into the synthesis of amino disiloxanes **8a** and **8b** via silanols **7a** and **7b** was underway, an attempt was made to generate compound **8b** in two steps from *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**). When the Grignard reagent formed in situ from amine **4**

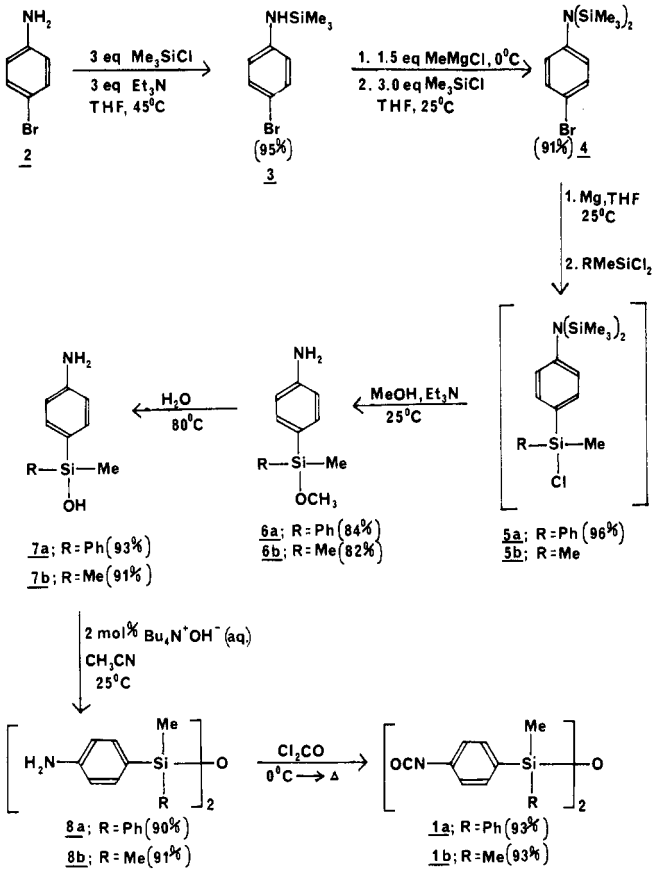
(1) Ando, W.; Tsumaki, H. *Synthesis* **1982**, 263–264.

(2) Breed, L. W.; Wiley, J. C., Jr. *J. Organomet. Chem.* **1975**, *102*, 29–39.

(3) Breed, L. W.; Wiley, J. C., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 83–92.

0022-3263/86/1951-2434$01.50/0

Scheme I



was added to $(ClMe_2Si)_2O$ followed by treatment of the reaction mixture with MeOH and Et_3N, 1-(4-aminophenyl)-3-methoxy-1,1,3,3-tetramethyldisiloxane (**9**) and compound **8b** were isolated in 46% and 25% yields, respectively.[4] Although the desired product **8b** was formed, it was isolated from the reaction mixture as the minor component. This approach to amino disiloxanes **8a,b** was abandoned.

With silanols **7a** and **7b** in hand, a method for generating the disiloxane unit in the presence of the anilinyl group needed to be developed. Addition of (4-aminophenyl)-methylphenylsilanol (**7a**) to a THF solution of silyl chloride **5a** at 50 °C afforded a complex mixture of silanol **7a**, amino disiloxane **8a**, and $MePh(p\text{-}NH_2C_6H_4)SiOSiMe_3$ (**10**). In addition, attempts at coupling silane **6a** and silanol **7a** under neutral and basic conditions were unsuccessful.

Due to the unsuccessful employment of amino silane **6a** as one of the precursors to amino disiloxanes, methodology for the homocondensation of silanol **7a** was sought after. When silanol **7a** was stirred at ambient temperature in the presence of concentrated H_2SO_4, disiloxane **8a** was generated in only 36% yield. Substantial decomposition was noted. As a result of this low yield conversion of amino silanol **7a** to disiloxane **8a** under acidic conditions and due to the prohibitive conditions required for NaOH-mediated[2,3] homocoupling of arylsilanols, another method of homocondensation had to be found. Fortunately, a mild procedure was discovered for generating hexaphenyldisiloxane from triphenylsilanol.[5] This reaction involved treatment of a solution of triphenylsilanol in acetonitrile with a catalytic amount of aqueous tetrabutylammonium hydroxide (TBAH). When amino silanols **7a** and **7b** were exposed to the above conditions, disiloxanes **8a** and **8b** were generated in 90% and 91% yields, respectively. The reactions were conveniently monitored by TLC (6:4:1 hexanes/EtOAc/Et_3N). Finally, disiloxanediyl diamines **8a,b** were easily converted into their corresponding diisocyanates **1a,b** by treatment of the amines with excess phosgene.

Diisocyanates **1a** and **1b** were synthesized in six steps from 4-bromoaniline (**2**) in 57% and 55% overall yields, respectively. The key step in the process involved the generation of amino disiloxanes **8a** and **8b** via the TBAH-catalyzed homocondensation of the corresponding amino silanols.[6] Although the quantity of methods for synthesizing disiloxanes from silanols is rather extensive,[7] no facile method for the homocondensation of silanols containing an anilinyl group appears to exist. Previous syntheses of disiloxanediyl dianilines (i.e., **8b**) involved either generation of the amine functionality on the phenyl ring attached to a disiloxanyl moiety[8] or addition of a metalated arene containing a protected anilino group to a dichlorotetraalkyl(aryl)disiloxane.[2-4] This mild method of homocondensation should be applicable to the formation of the disiloxanyl unit in the presence of acid- or base-sensitive functional groups.

Experimental Section

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. All reactions were performed under N_2. Anhydrous THF was freshly distilled from sodium benzophenone ketyl. IR spectra were obtained on a Nicolet MX-1 FT-IR. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer using Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on a JEOL VX-100 spectrometer (22.5 MHz) using $CDCl_3$ as an internal standard. Chemical shifts are reported in ppm (δ) downfield from Me_4Si. Electron impact mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were recorded on a Finnigan-4535 quadrapole mass spectrometer. Fast atom bombardment mass spectra were recorded on a VG-7070-E mass spectrometer. Column chromatography was performed by the method of Still.[9] Elemental analyses were performed by Atlantic Laboratories.

4-(Methoxymethylphenylsilyl)benzenamine (6a). A solution of *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**) (20.24 g, 0.0641 mol) in 48 mL of THF was added over a 2-h period to a mixture of Mg (1.94 g, 0.0798 mol) and THF (16 mL) at ambient temperature. The reaction was initiated with a crystal of I_2. After 20 min at ambient temperature, the reaction mixture was added over a 20-min period to $MePhSiCl_2$ (11.43 g, 0.0598 mol). The temperature was not allowed to exceed 30 °C. The mixture was stirred overnight at ambient temperature, followed by concentration under reduced pressure and addition of ether. The reaction mixture was filtered and the filtrate was concentrated in vacuo to afford 23.98 g (96%) of 4-[*N,N*-bis((trimethylsilyl)amino)-phenyl]methylphenylsilyl chloride (**5a**): ^1H NMR ($CDCl_3$) δ 0.07 (s, 18 H, $NSiCH_3$), 0.89 (s, 3 H, $SiCH_3$), 6.86 (d, 2 H, J = 8 Hz, *p*-$(Me_3Si)_2NArH$), 7.22-7.66 (m, 7 H, *p*-$(Me_3Si)_2NArH$ + ArH). Compound **5a** was added to MeOH (100 mL) and triethylamine (31.12 g, 0.3081 mol). The solution was stirred for 1.5 h at ambient temperature and then concentrated under reduced pressure. After the addition of ether, the reaction mixture was filtered, and the

(4) Greber, V. G. *J. Prakt. Chem.* **1971**, *313*, 461-483.
(5) Tondeur, J. J.; Vandendunghen, G.; Borghese, A. *React. Kinet. Catal. Lett.* **1981**, *16*, 19-27.
(6) See ref 5. Authors found the rate of homocondensation of triphenylsilanol to hexaphenyldisiloxane to be dependent on water concentration.
(7) Noll, W. *Chemistry and Technology of Silicones*; Academic: New York and London, 1968. Pike, R. M. *J. Org. Chem.* **1961**, *26*, 232-236. Pittman, C. U., Jr.; Patterson, W. J.; McManus, S. P. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1715-1734. McManus, S. P.; Patterson, W. J., Pittman, C. U., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 825-836. Rosenberg, H.; Tsai, T.-T.; Ngo, N. K. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1-13. Breed, L. W.; Elliot, R. L.; Whitehead, M. E. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2745-2755.
(8) Bonnet, J. C.; Marechal, E. *Bull. Soc. Chim. Fr.* **1972**, 3561-3579.
(9) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

filtrate was concentrated in vacuo to afford 13.09 g (84%) of **6a** as a yellow oil: IR (neat) 3465 (s), 3365 (s), 3220 (m), 3065 (m), 3045 (m), 3015 (m), 2955 (s), 2830 (s), 1620 (s), 1600 (s), 1120 (s), 1075 (s), 800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57 (s, 3 H, CH_3), 3.47 (s, 3 H, OCH_3), 3.67 (br s, 2 H, NH_2), 6.58 (d, 2 H, J = 7 Hz, *p*-NH_2ArH), 7.30 (d, 2 H, J = 7 Hz, *p*-NH_2ArH), 7.21-7.41 (m, 3 H, ArH), 7.44-7.64 (m, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 3.5, 51.0, 114.4, 127.7, 129.5, 134.3, 135.7, 148.0; EIMS, *m/e* (relative intensity) 244 (P + 1, 12.2), 243 (P, 55.3), 228 (P - Me, 74.0); high-resolution mass spectrum, *m/e* 243.1086 ($C_{14}H_{17}NOSi$ requires *m/e* 243.1079.

(4-Aminophenyl)methylphenylsilanol (7a). A solution of 4-(methoxymethylphenylsilyl)benzenamine (**6a**) (9.370 g, 38.56 mmol) in 50 mL of 1:1 acetone-water was stirred for 2 days at 80 °C. The mixture was concentrated under reduced pressure, and $CHCl_3$ (30 mL) was added. The reaction mixture was washed with H_2O (30 mL). The aqueous layer was then washed with $CHCl_3$ (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to afford 8.237 g (93%) of (4-aminophenyl)methylphenylsilanol (**7a**) as a dark red, viscous oil: IR (neat) 3625-3100 (br s), 3065 (m), 3045 (m), 3015 (m), 2960 (m), 1620 (s), 1600 (s), 1505 (s), 1430 (s), 1260 (s), 1120 (s), 1065 (br m), 1000 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.55 (s, 3 H, CH_3), 3.42 (s, 2 H, NH_2), 6.51 (d, 2 H, J = 8 Hz, *p*-NH_2ArH), 7.16 (d, 2 H, J = 8 Hz, *p*-NH_2ArH), 7.18-7.35 (m, 3 H, ArH), 7.38-7.58 (m, 2 H, ArH); FAB-MS, *m/e* (230, P + 1).

4,4'-(1,3-Dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (8a). A solution of (4-aminophenyl)methylphenylsilanol (**7a**) (2.276 g, 9.939 mmol) in 3 mL of CH_3CN was treated dropwise with 0.18 mL (0.18 mmol) of 1.0 M aqueous $Bu_4N^+OH^-$. The mixture was stirred for 2 days at ambient temperature, concentrated under reduced pressure, and treated with $CHCl_3$ (30 mL). The reaction mixture was washed with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with H_2O until the color of the organic layer turned from green to brown. The organic extract was dried over $MgSO_4$ and concentrated in vacuo to afford 1.96 g (90%) of 4,4'-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**8a**) as a dark red oil: IR (neat) 3465 (m), 3375 (s), 3205 (m), 3060 (m), 3040 (m), 3010 (s), 2950 (m), 1620 (s), 1595 (s), 1500 (s), 1425 (s), 1115 (s), 1050 (br s), 785 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (s, 6 H, CH_3), 3.66 (br s, 4 H, NH_2), 6.54 (d, 4 H, J = 8 Hz, *p*-NH_2ArH) 7.12-7.36 (m, 10 H, *p*-NH_2ArH + ArH), 7.39-7.56 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$) δ 0.4, 114.3, 127.5, 129.2, 133.3, 133.9, 135.4, 138.5, 147.6; CIMS, *m/e* (relative intensity) 497 (P + 57, 16.4), 441 (P + 1, 100.0), 348 (P - C_6H_6N, 53.7). Anal. Calcd for $C_{26}H_{28}N_2OSi_2$: C, 70.87; H, 6.42; N, 6.36. Found: C, 70.60; H, 6.49; N, 6.29.

1,3-Bis(4-isocyanatophenyl)-1,3-dimethyl-1,3-diphenyldisiloxane (1a). A solution of phosgene (ca. 40 mL) in chlorobenzene (25 mL) at 0 °C was treated dropwise with a solution of 4,4'-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**8a**) (1.96 g, 4.45 mmol) in chlorobenzene (50 mL). The mixture was heated to reflux and maintained at that temperature for 4.5 h while phosgene gas was slowly passed through the reaction mixture. The solution was purged with N_2 (gas) for 45 min and then cooled to ambient temperature. The volatiles were removed in vacuo to afford 2.03 g (93%) of 1,3-bis(4-isocyanatophenyl)-1,3-dimethyl-1,3-diphenyldisiloxane (**1a**) as a dark brown oil: IR (neat) 3070 (m), 3050 (w), 3025 (w), 2960 (m), 2275 (br s), 1595 (s), 1515 (m), 1430 (s), 1260 (s), 1115 (s), 1095 (s), 1060 (br s), 795 (s), 735 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 6 H, CH_3), 7.05, (d, 4 H, J = 8 Hz, *p*-OCNAr*H*), 7.23-7.67 (m, 14 H, *p*-OCNAr*H* + ArH).

Registry No. **1a**, 102368-11-6; **1b**, 102368-12-7; **2**, 106-40-1; **3**, 63911-87-5; **4**, 5089-33-8; **5a**, 102368-04-7; **5b**, 69185-17-7; **6a**, 102368-05-8; **6b**, 102368-06-9; **7a**, 102368-07-0; **7b**, 102368-08-1; **8a**, 102368-09-2; **8b**, 102368-10-5.

Formation of the Tetracyclo[5.4.2.0^{2,6}.0^{2,9}]tridecane Ring System by a Novel Transannular Aldolization Reaction[1]

M. N. Deshpande, S. Wehrli, M. Jawdosiuk, J. T. Guy, Jr., D. W. Bennett, and J. M. Cook*

Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

M. R. Depp

Nicolet Instrument Corporation, Madison, Wisconsin 53711

U. Weiss

Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes, Digestive and Kidney Diseases, Bethesda, Maryland 20892

Received September 20, 1985

Attempts to employ the "aldol approach"[5] to convert 1-(1,5-dioxopentyl)-*cis*-bicyclo[3.3.0]octane-3,7-dione (**7**) into the corresponding [5.5.5.5]fenestrane derivative **8b** were thwarted when the dialdehyde **7** underwent transannular cyclization instead to provide the two diastereomeric diketodiacetates **18a** and **18b**. The structures of the trans,trans isomer **18a** and its cis,trans diastereomer **18b** were assigned, on the basis of 1D and 2D NMR (COSY and ^1H-^{13}C correlated) experiments; moreover, the structure of **18a** was confirmed by X-ray crystallography. The difference between the mode of cyclization of the diacid **5** to provide the [5.5.5.5]fenestrane **6** as compared to the transannular cyclization of dialdehyde **7** to furnish the [5.4.2.0^{2,6}.0^{2,9}] system in **18** is discussed.

The synthesis of saturated [4.4.4.4] and unsaturated [5.5.5.5] derivatives of [*m.n.o.p.*]fenestranes[2-4] has received much attention recently in particular with respect to the deformation of the central carbon atom toward a planar

(1) This paper is based in part on the Ph.D. thesis of M.N.D., University of Wisconsin—Milwaukee, Milwaukee, Wisconsin, 1985.

(2) (a) Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, 315. (b) Richman, J. E.; Simmons, H. E. *Tetrahedron* **1974**, *30*, 1769. (c) Wiberg, K. B.; Olli, L. K.; Golembski, N.; Adams, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 7467. (d) Wolff, S.; Agosta, W. G. *J. Chem. Soc., Chem. Commun.* **1981**, 118. (e) Dauben, W. G.; Walker, D. M. *Tetrahedron Lett.* **1982**, *23*, 711. (f) Rao, V. B.; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1984**, 293. Rao, B.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 5732. (g) Crimmins, M. T.; Mascarella, S. W.; Brendon, L. D. *Tetrahedron Lett.* **1985**, *26*, 997.

(3) (a) Hoffmann, R.; Alder, R.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181. (b) Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921. (c) Wynberg, H.; Hulshof, L. A. *Tetrahedron* **1974**, *30*, 1775. (d) Böhm, M. C.; Gleiter, R.; Schang, P. *Tetrahedron Lett.* **1979**, 2575. (e) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419. (f) Würthwein, E.-U.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 553. (g) Keese, R.; Pfenninger, A.; Roesle, A. *Helv. Chim. Acta* **1979**, *62*, 326.

0022-3263/86/1951-2436$01.50/0