was removed in vacuo, and the residue was subjected into flash column chromatography (hexane then hexane–ethyl acetate (3:1)) to give β-amino alcohol **16** in 64% yield (515 mg) as a colorless oil. Compound **15** was also prepared in the same procedure in 30%.

15: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.77–5.93 (m, 1 H), 5.16 (d, J = 11.0 Hz, 1 H), 5.15 (d, J = 16.5 Hz, 1 H), 4.72 (s, 3 H), 3.61 (d, d, J = 4.3, 9.8 Hz, 1 H), 3.50 (s, 3 H), 3.37–3.44 (m, 1 H), 2.52–2.60 (m, 1 H), 2.17–1.24 (m, 2 H), 1.61–2.03 (m, 9 H).

16: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.71–5.88 (m, 1 H), 5.20 (d, d, J = 1.2, 17.1 Hz, 1 H), 5.18 (d, J = 8.5 Hz, 1 H), 4.77 (t, J = 3.7 Hz, 1 H), 4.64 (d, J = 7.4 Hz, 1 H), 4.59 (d, J = 7.4 Hz, 1 H), 3.74 (t, J = 4.8 Hz, 1 H), 3.63 (d, d, J = 6.1, 11.6 Hz, 1 H), 3.48 (s, 3 H), 2.32–2.39 (m, 2 H), 2.11–2.17 (m, 1 H), 1.55–2.00 (m, 9 H).

Dibenzoylation of 11b. The amino diol monoether **11b** (193 mg, 0.84 mmol) and benzoyl chloride (316 mg, 2.25 mmol) were dissolved in pyridine (5 mL), and the reaction mixture was stirred for 2 days at room temperature. The solution was poured into aqueous $NaHCO_3$ (30 mL), and the resulting solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with 1 M HCl and brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent in vacuo, the residue was purified by flash column chromatography (hexane–ethyl acetate (3:1) v/v) to give **17** in 71% yield (260 mg) as white crystals: mp 100–101 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.10 (d, J = 7.3 Hz, 2 H), 7.83 (d, J = 7.9 Hz, 2 H), 7.44–7.60 (m, 6 H), 6.51 (d, J = 10.4 Hz, 1 H), 5.47–5.56 (m, 2 H), 4.93 (d, J = 17.1 Hz, 1 H), 4.77 (d, J = 6.7 Hz, 1 H), 4.68 (d, J = 6.7 Hz, 1 H), 4.64 (d, d, J = 2.4, 10.4 Hz, 1 H), 4.62–4.72 (m, 1 H), 3.77 (d, d, J = 4.6, 8.9 Hz, 1 H), 3.43 (s, 3 H), 2.25–2.41 (m, 2 H), 1.85–2.20 (m, 6 H), 1.58–1.70 (m, 1 H). Anal. Calcd for $C_{26}H_{31}NO_5$: C, 71.37; H, 7.14; N, 3.20. Found: C, 71.52; H, 7.42; N, 3.03.

Acknowledgment. The authors wish to thank Dr. Hideki Sugihara for measuring MS spectra. The authors thank the Computer Center, Institute for Molecular Science at the Okazaki National Research Institutes, for the use of the HITAC M-600 and S-820/80 computers.

Supplementary Material Available: X-ray crystallographic data for compounds *syn*-**2a** and **17** (20 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.

The Dodecahedryl Radical. Reactivity Analysis by Conjugate Addition to π-Electron-Deficient Acceptors and Structural Investigation by Electron Spin Resonance Spectroscopy

Leo A. Paquette,*,† Dean R. Lagerwall,†,[1] and Hans-Gert Korth‡

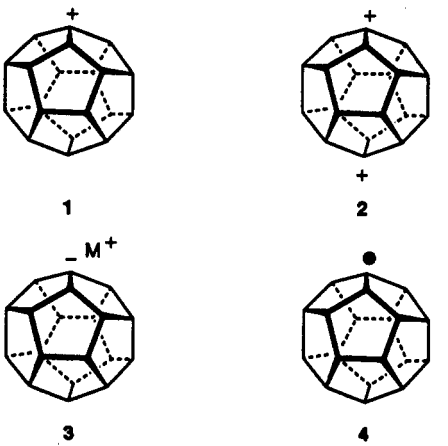
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and the Institut für Organische Chemie, Universität-GH Essen, D-4300 Essen 1, Germany

Received November 22, 1991

The bromo and phenylseleno derivatives of dodecahedrane have been identified as suitable precursors to the dodecahedryl radical (**4**). This reactive intermediate exhibits only modest reactivity, lending itself to capture by the most powerful radical traps, which include acrylonitrile, 2-cyclopentenone, and allyltri-*n*-butylstannane. ESR studies performed on the same two starting materials have provided additional striking evidence that **4** and its closest model, the 1-adamantyl radical, differ widely in their properties. Reaction conditions that result in smooth generation of the adamantyl species did not lead to ESR spectra that can be related to **4**.

The exquisite I_h symmetry of dodecahedrane stems from a highly rigid spherical structure[2] in which each methine carbon experiences minimal deformation from ideal tetrahedral character. The out-of-plane bending angle (θ) for any of the 20 sp^3-hybridized corners is approximately 21°. Ionization to generate monocation **1** is accompanied by considerable deformation of the cationic center toward planarity, which cannot be fully realized because of structural constraints. Counterbalancing bond-angle distortions materialize at the flanking centers to reduce θ to about 11°.[3] Notwithstanding the energetic costs of these substantive geometric changes, **1** can be readily generated,[3,4] the electrophilic chemistry of dodecahedrane serving as a notably useful means for achieving functionalization of the hydrocarbon.[5] Remarkably, the dodecahedryl cage is also quite tolerant of conversion to the 1,16-dication (**2**), despite the onset of added structural deformation, intense Coulombic repulsion, and adverse through-space interactions.[3,4]

The dodecahedryl anion has proven somewhat more elusive.[6] A reduced capability for the formation of **3** was indicated by the half-wave potential for reduction of the bromide, which at −2.16 V (vs SCE) is considerably more

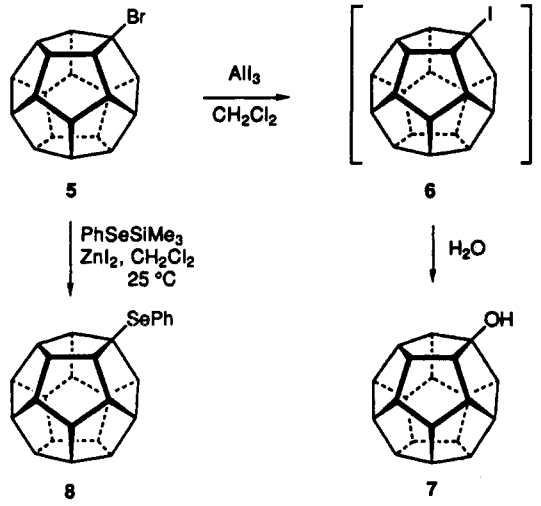


† The Ohio State University.
‡ Universität-GH Essen.

(1) National Needs Fellow, 1990; Procter and Gamble Fellow, 1988–1989.
(2) Gallucci, J. C.; Doecke, C. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 1343.
(3) Olah, G. A.; Surya Prakash, G. K.; Fessner, W.-D.; Kobayashi, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 8599.

0022-3263/92/1957-5413$03.00/0

Scheme I



positive than the $E_{1/2}$ values of other tertiary bromides.[7] Transmetalation of the bromide with *tert*-butyllithium or reduction of the phenyl sulfide with lithium di-*tert*-butyldiphenylide[8] does afford dodecahedryllithium. However, both conversions are only moderately efficient because of competing hydrogen abstraction and oxidation–reduction processes.[6] Similar complications are not unknown in the adamantane series.[9]

General agreement exists that tertiary carbon-centered radicals tolerate nonplanarity to a greater extent than their cationic counterparts.[9a,10] The relative ease with which cubyl radicals can be formed,[11] including direct generation by homolytic cleavage of cubyl C–H bonds,[12] is in line with this conclusion. In a similar vein, studies directed toward the generation of bridgehead radicals abound.[13] Should the dodecahedryl radical **4** prove as readily accessible, an avenue would be open for the production of derivatives not available via polar S_N1 substitution reactions.[14]

One aim of the present undertaking was to determine the feasibility of generating and trapping **4**. In line with the properties of the 1-adamantyl radical,[15] the odd-electron dodecahedryl species was expected to be nucleophilic, with steric effects limiting its reactivity in bimolecular addition reactions. Another objective was to characterize this reactive intermediate by ESR spectroscopic techniques.

Generation and Capture of the Dodecahedryl Radical. Beckwith and Pigou have quantified the reactivity of groups X toward S_H2 attack by tri-*n*-butyltin radicals when the attached R group is kept constant.[16] They found the order to be I > Br > PhSe > Cl > ArS > MeS, indicating a decided preference for the right side of the periodic table. Nitro[17] and xanthate precursors[18] were not seriously considered in the present context because of their lesser reactivity[19] and relative inaccessibility.[20] Instead, the known bromide[5] and the still unknown iodo and phenylseleno derivatives were accorded attention because of their anticipated ease of homolytic cleavage and high potential as radical precursors.

Although the conversion of **5** to the chloride or fluoride proceeds readily and efficiently under electrophilic conditions ($FeCl_3$ or $AgBF_4$),[5] comparable treatment with freshly prepared AlI_3[21] did not lead to the isolation of **6** (Scheme I). Dodecahedranol (**7**) was obtained instead. Evidently, iodide **6** is sufficiently S_N1-reactive that ionization to the carbenium ion and capture by water occurs during workup. Direct analysis of these reaction mixtures by capillary gas chromatography prior to the aqueous quench indicated four components to be present: DDH-H (8.6 min), DDH-Cl (11.9 min), DDH-Br (15.2 min), and (possibly) DDH-I (19.0 min). After processing with water to remove the aluminum salts, the peak of longest retention time is not seen and is replaced by another due to **7**. In light of this development, iododododecahedrane was deemed too labile to be a serviceable radical precursor.

In contrast, room-temperature treatment of **5** with (phenylseleno)trimethylsilane[22,23] in dry CH_2Cl_2 containing anhydrous zinc iodide as catalyst readily provided **8**. Use of a 10-fold excess of $PhSeSiMe_3$ and a reaction time of 3 days resulted in the complete consumption of **5** and isolation of **8** in 62% yield.

The first test of possible radical generation was performed with acrylonitrile as the trap. The conditions

(4) Olah, G. A.; Surya Prakash, G. K.; Kobayashi, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 1304.

(5) (a) Paquette, L. A.; Weber, J. C.; Kobayashi, T. *J. Am. Chem. Soc.* **1988**, *110*, 1303. (b) Weber, J. C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 5315. (c) Paquette, L. A.; Weber, J. C.; Kobayashi, T.; Miyahara, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8591. (d) Paquette, L. A.; Lagerwall, D. R.; King, J. L.; Niwayama, S.; Skerlj, R. *Tetrahedron Lett.* **1991**, *32*, 5259.

(6) Paquette, L. A.; Lagerwall, D. R.; King, J. L.; Niwayama, S. *Tetrahedron Lett.* **1991**, *32*, 6529.

(7) (a) Dubois, J.-E.; Bauer, P.; Kaddani, B. *Tetrahedron Lett.* **1985**, *26*, 57. (b) Dubois, J.-E.; Bauer, P.; Briand, S. *Tetrahedron Lett.* **1988**, *29*, 3935.

(8) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924; **1983**, *48*, 4705; *Tetrahedron Lett.* **1976**, 1849.

(9) (a) Fort, R. C., Jr.; Schleyer, P. v. R. *Adv. Alicyclic Chem.* **1966**, *1*, 283. (b) Molle, G.; Bauer, P.; Dubois, J.-E. *J. Org. Chem.* **1983**, *48*, 2975. (c) Dubois, J.-E.; Molle, G.; Tourillon, G.; Bauer, P. *Tetrahedron Lett.* **1979**, *20*, 5069. (d) Molle, G.; Bauer, P.; Dubois, J.-E. *J. Org. Chem.* **1982**, *47*, 4120.

(10) Fort, R. C. *Adamantane-The Chemistry of Diamond Molecules* Dekker: New York, 1976; pp 233–265.

(11) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157. (b) Della, E. W.; Patney, H. K. *Synthesis* **1976**, 251. (c) Abeywickrema, R. S.; Della, E. W. *J. Org. Chem.* **1980**, *45*, 4226. (d) Moriarty, R. M.; Khosrowshahi, J. S.; Dalecki, T. M. *J. Chem. Soc., Chem. Commun.* **1987**, 675. (e) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230. (f) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. (g) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1989**, *42*, 61. (h) Luh, T.-Y.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 3712. (i) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271.

(12) Reddy, D. S.; Maggini, M.; Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1990**, *31*, 805.

(13) For example: (a) Beckhaus, H.-D.; Flamm, M. A.; Rüchardt, C. *Tetrahedron Lett.* **1982**, *23*, 1805. (b) Lomas, J. S.; Dubois, J.-E. *Tetrahedron Lett.* **1983**, *24*, 1161. (c) Engel, P. S.; Chae, W.-K.; Baughman, S. A.; Marschke, G. E.; Lewis, E. S.; Timberlake, J. W.; Luedtkae, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 5030. (d) Lomas, J. S. *J. Org. Chem.* **1985**, *50*, 4291. (e) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162. (f) Schmittel, M.; Rüchardt, C. *J. Am. Chem. Soc.* **1987**, *109*, 2750.

(14) For free radical functionalization of adamantanes, consult: (a) Smith, G. W.; Williams, H. D. *J. Org. Chem.* **1961**, *26*, 2207. (b) Tabushi, I.; Hamuor, J.; Oda, R. *J. Org. Chem.* **1968**, *33*, 2108. (c) Tabushi, I.; Okada, T.; Aoyama, Y.; Oda, R. *Tetrahedron Lett.* **1969**, 4069. (d) Tabushi, I.; Aoyama, Y.; Kojo, S.; Yoshida, Z. *J. Am. Chem. Soc.* **1972**, *94*, 1177. (e) Perkins, R. R.; Pincock, R. E. *Can. J. Chem.* **1978**, *56*, 1269. (f) Crich, D.; Fortt, S. M. *Synthesis* **1987**, 35. (g) Tabushi, I.; Kojo, S.; Fukunishi, K. *J. Org. Chem.* **1978**, *43*, 2370. (h) Tabushi, I.; Fukunishi, K. *J. Org. Chem.* **1974**, *39*, 3748. (i) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1603. (j) Fukunishi, K.; Tabushi, I. *Synthesis* **1988**, 826. (k) Ohno, M.; Ishizaki, K.; Eguchi, S. *J. Org. Chem.* **1988**, *53*, 1285.

(15) Testaferri, L.; Tiecco, M.; Tingoli, M.; Fiorentino, M.; Troisi, L. *J. Chem. Soc., Chem. Commun.* **1978**, 93.

(16) Beckwith, A. L. J.; Pigou, P. E. *Austr. J. Chem.* **1986**, *39*, 77.

(17) Ono, N.; Miyake, H.; Kaji, A. *Chem. Lett.* **1985**, 635.

(18) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553 and relevant references cited therein.

(19) Curran, D. P. *Synthesis* **1988**, 417.

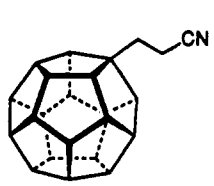
(20) Dodecahedranol is highly insoluble in most solvents and lends itself poorly to functionalization except toward the most reactive reagents. Both we and Olah (private communication) have failed to accomplish the mononitration of dodecahedrane. The possible oxidation of aminododecahedrane[5b] was not considered practical.

(21) Bhatt, M. B.; Baba, J. R. *Tetrahedron Lett.* **1984**, *25*, 3497.

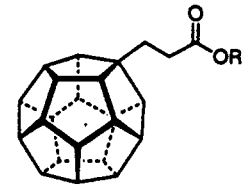
(22) Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 300.

(23) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1981**, *46*, 1283.

utilized by Eguchi[14k] were modified to accommodate the considerably smaller reaction scale. Heating **8** with excess Bu_3SnH and a catalytic quantity of AIBN in benzene containing several equiv of acrylonitrile led to the desired **9** as the major product (GC and GC/MS analysis). Recourse to bromododecahedrane (**5**) as starting material made for easier isolation of **9** (65%). The next most dominant constituent of the reaction mixture was the parent hydrocarbon. Evidently, the well-known[14k] cyclic radical chain process operates, with some of the dodecahedryl radical being diverted from conversion to **9** by virtue of competing hydrogen atom abstraction.



9



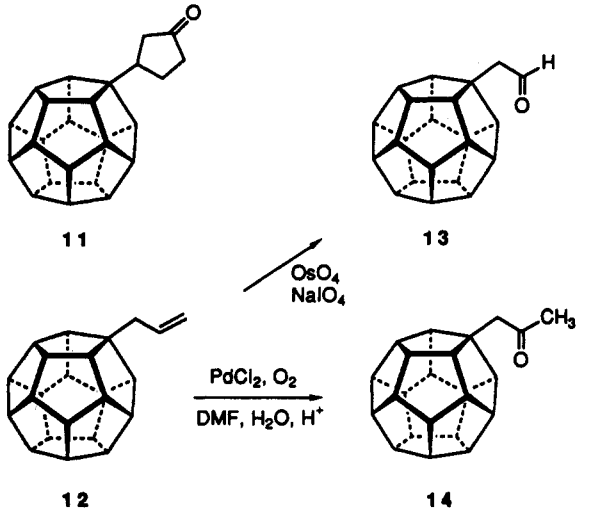
10a, R = CH_3
b, R = CH_2CH_3

At this point, bromide **5** was selected as the radical precursor of choice for several reasons: (a) the loss of material associated with the production of **8** was skirted; (b) purification of the bromide is substantially more convenient; (c) bromide **5** gives a better defined, sharp peak when analyzed by capillary GC, resulting in simplified analysis of reaction mixtures; and (d) selenium residues proved difficult to remove completely when **8** was utilized.

Application of tin hydride technology[24] to **5** in the presence of methyl or ethyl acrylate resulted in polymerization of the monomer with accompanying reduction to dodecahedrane. Since the acrylates generally exhibit radical reactivity comparable to acrylonitrile,[25] attempts were made to retard competing reduction by producing Bu_3SnH in situ under catalytic conditions. Notwithstanding, **10a** and **10b** could be detected only as minor constituents of complex reaction mixtures in which dodecahedrane remained the major nonpolymeric component. Recourse to bis(trimethylstannyl)benzopinacolate[26] did not resolve the complications due to telomerization even when only 1 equiv of the acrylate was added.

Although maleic anhydride has been successfully trapped by the 1-adamantyl[14j] and other radicals,[27] no success was achieved presently under a wide variety of conditions.[28] Nor was *N*-phenylmaleimide[27] adequately reactive. With these developments, wide differences in the reactivity of the 1-adamantyl and dodecahedryl radicals were becoming apparent. Generation of **4** was not considered to be problematic. A reduced level of nucleophilicity was deemed more likely. If so, a more reactive radical trap having an abated tendency for polymerization should prove equally effective as acrylonitrile. On the basis of precedent, 2-cyclopentenone appeared to fit these criteria,[27] although thermal activation had to be avoided. Use of photoactivated tin hydride methodology (**5**, Bu_3SnH, AIBN, $h\nu$) once again afforded predominantly dodecahedrane. Reduction could, however, be considerably minimized by deployment of a catalytic tin hydride alternative ($Bu_3SnSnBu_3$, $NaBH_4$, C_6H_6, $h\nu$). Under these conditions, a 35% yield of **11** was realized if reaction time was controlled, since the resultant cyclopentanone underwent conversion to an unidentified more polar product on prolonged exposure to light.

As a consequence of the systematic studies of Keck and co-workers,[29] free radical allylation with allylstannanes has come to be recognized as a useful functionalization reaction. A tin hydride reagent is not required. The lifetime of the initially formed radical is consequently not now limited by the rate of hydrogen atom transfer from R_3SnH. Nevertheless, irradiation of **5** with 20 equiv of allyltri-*n*-butylstannane and a catalytic quantity of AIBN resulted in very little chemical change. Migita et al. have subjected various organic halides to reaction with allyltin reagents and have determined the efficiency of the chain reactions to be dependent on the nature of the halide and on the ease of halogen abstraction by the stannyl radical.[30] Electrophilic radicals were found to attack the π-bond of allylstannanes readily, whereas aralkyl and alkyl radicals were less reactive, requiring excess tin reagent to maintain a successful chain reaction. For these reasons, recourse was ultimately made to a 200:1 ratio of $CH_2{=}CHCH_2SnBu_3$ to **5**. Allyldodecahedrane (**12**) was now obtained as the major product (30%, GC/MS) but proved difficult to rid completely of tin-containing impurities.[31,32] A cleaner and more expedient route to **12** consists of stirring **5** with allyltrimethylsilane and ZnI_2 in CH_2Cl_2 for 3 days in the dark.[33]



11 **13** **12** **14**

The availability of **12** made possible the acquisition of aldehyde **13** and ketone **14**. The preferred means for arriving at **13** (63%) involved in situ generation of the diol with catalytic OsO_4 in the presence of sodium periodate.[34] Highly efficient delivery of **14** (95%) was achieved by Wacker oxidation.[35]

(24) (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon Press: Oxford, 1986.
(25) Giese, B.; Gonzalez-Gomez, J. A.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69.
(26) Hart, D. J.; Seely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 1631.
(27) Ramaiah, M. *Tetrahedron* **1989**, *43*, 3541.
(28) Lagerwall, D. R. Ph.D. Thesis, The Ohio State University, 1991.
(29) (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829.
(30) Migita, T.; Nagai, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2480.
(31) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636. (b) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.
(32) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140.
(33) This electrophilic alternative was adapted from the adamantane literature [Sasaki, T.; Usuki, A.; Ohno, M. *J. Org. Chem.* **1980**, *45*, 3559; *Tetrahedron Lett.* **1978**, *19*, 4925].
(34) Shue, Y.-K.; Carrera, G. M., Jr.; Nadzan, A. M. *Tetrahedron Lett.* **1987**, *28*, 3225.
(35) (a) Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 80. (b) Tsuji, J. *Synthesis* **1984**, 369.

Since *tert*-butyl peresters of carboxylic acids have served well as thermal and photochemical precursors to radicals, considerable effort was expended in attempts to prepare this derivative of dodecahedranecarboxylic acid. Success was not realized, however, presumably as a consequence of the substantial steric bulk presented by the spherical hydrocarbon in the immediate vicinity of reaction.

ESR Spectroscopic Measurements. Bromides and phenyl selenides are often suitable substrates for the preparation of carbon-centered radicals for subsequent observation by ESR spectroscopy. Therefore, attempts were initially made to generate **4** in the cavity of an ESR spectrometer by photolytically-initiated Br$^{\bullet}$ or PhSe$^{\bullet}$ abstraction from **5** and **8**, respectively, with trialkyltin and -silyl radicals.

$$\underset{\text{X = Br, SePh}}{\text{DDH–X}} \xrightarrow{\text{Me}_3\text{Sn}^{\bullet} \text{ or } \text{Et}_3\text{Si}^{\bullet}} \text{DDH}^{\bullet}$$

Preliminary optimization experiments with 1-bromoadamantane (as the closest available model for DDHBr) indicated the photolysis of hexamethylditin in cyclopropane solution, preferably in the presence of di-*tert*-butyl peroxide (DTBP) (to improve the quantum efficiency of $Me_3Sn^{\bullet}$ generation) to be best suited for this purpose.

UV photolysis of a cyclopropane solution of **5** and Me_6Sn_2 at temperatures between −100 and +20 °C, however, did not give any detectable ESR signals. Since the efficiency of Br abstraction by $Me_3Sn^{\bullet}$ radicals was thought to be unfavorable in competition with decay of the dodecahedryl radical (preferably by hydrogen abstraction from the tin compound), the foregoing experiments were repeated with some added DTBP in order to achieve a higher production rate of $Me_3Sn^{\bullet}$ radicals.[36] Again, no signals were detected immediately after switching on the irradiation of fresh samples. However, a strong, broad "singlet" feature (overall width ca. 15 G) with g = 2.0025 "grew in" within a few (2–3) minutes of irradiation. Continued photolysis led to the formation of additional quite weak pairs of "satellite" lines of ca. 32 and 55 G separation, respectively. All signals, the intensity of which increased with increasing photolysis time, were very persistent, decaying within 2 days at room temperature when the light was cut off. The additional satellite features certainly were not ^{13}C or Sn isotope satellites, since their relative intensity varied strongly with sample preparation, temperature, and/or duration of irradiation. Thus, they represent individual species. The unusual shape of the central signal could be satisfactorily reproduced by spectral simulation, assuming an unresolved quintet splitting of ca. 1.3–1.4 G due to four (nearly) equivalent hydrogen atoms.[37] Additional small, unresolved hyperfine splittings (hfs) were also seen in the satellite features. Virtually identical ESR spectra were also generated by the same initiation method (Me_6Sn_2 + DTBP) in fluorobenzene solution at room temperature from −40 to 25 °C (Figure 1) when the triethylsilane/DTBP couple for the generation of halogen-abstracting triethylsilyl radicals was employed.[38]

The similarity of the spectra from the two different methods of radical generation in different solvents could imply that the DTBP, which was present in both systems, might actually be responsible for their generation. Indeed, this proved to be the case. When a solution of **5** and DTBP (ca. 5 vol %; no other radical initiator present) was irradiated in cyclopropane at −103 °C, a fairly broad (ΔH_{pp} ca. 4 G) "singlet" at g = 2.00243 was built up within a few minutes (Figure 2a). At higher temperatures, line sharpening reveals the presence of the above-mentioned unresolved quintuplet hyperfine structure of ca. 1.3 G. Continued photolysis also led to increasing formation of

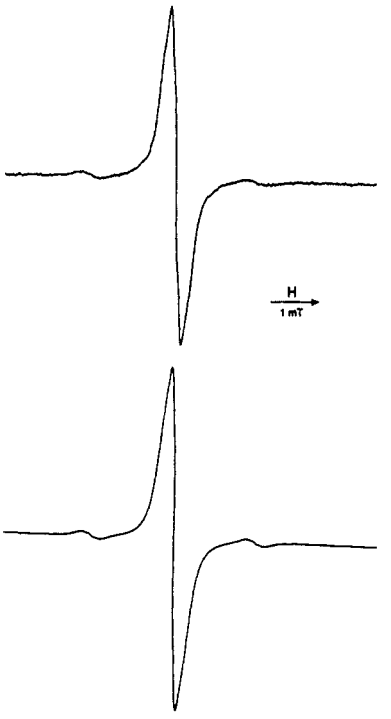


Figure 1. ESR spectrum obtained on UV irradiation of **5**, Me_6Sn_2, and DTBP in fluorobenzene at 293 K (top) and simulation assuming the superposition of two radicals (ratio 20:1) with hfs of a_H = 1.3 G (4 H) and a_H = 16.9 G (2 H) and 1.3 G (4 H), respectively (bottom).

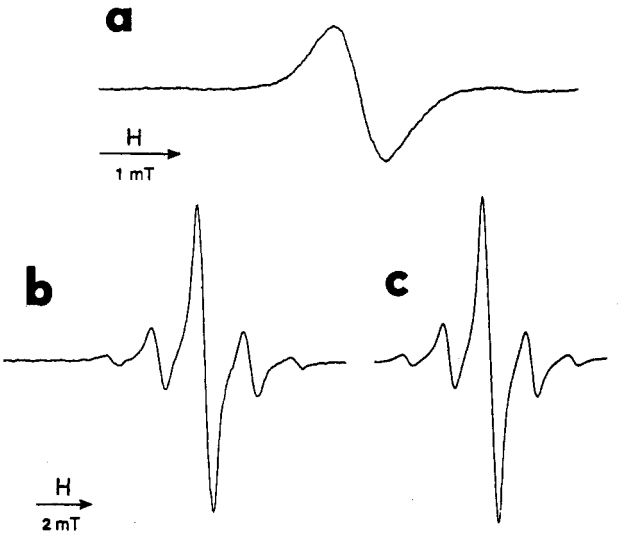


Figure 2. (a) ESR spectrum obtained after 2-min UV irradiation of **5** and DTBP in cyclopropane solution at 170 K. The buildup of an additional 35 G species during recording of the spectrum under continuous irradiation is indicated by the small upfield line. (b) Spectrum obtained after 1 h irradiation at 185 K, recorded at 282 K, (c) simulation assuming the superposition of three radicals with hfs of a_H = 1.3 G (4 H), a_H = 17.7 G (2 H), and a_H = 17.8 G (4 H) and 0.17 G (1 H), respectively, in the mole ratio 1.9:1:2.6 and with the same g value.

(36) We are indebted to Drs. A. G. Neville and K. U. Ingold (NRC of Canada, Ottawa) for performing this initial experiment with this method.

(37) Trial simulations reveal that an even number of unresolved lines (= odd number of hydrogens) can safely be excluded. Also, assumption of other odd multiplicities led to less satisfactory simulations.

(38) By this method, an intense, highly resolved spectrum of the 1-adamantyl radical was obtained from 1-bromoadamantane under otherwise identical conditions.

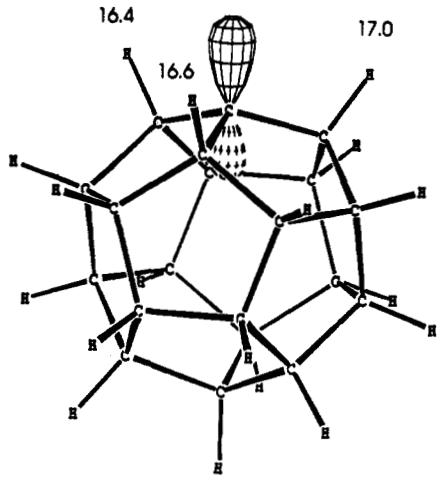


Figure 3. Optimized structure and SOMO of the dodecahedryl radical as calculated by the AM1/PM3-UHF method (annihilated $\langle S^2 \rangle = 0.75$). AM1-UHFQ hyperfine splittings in G are indicated.

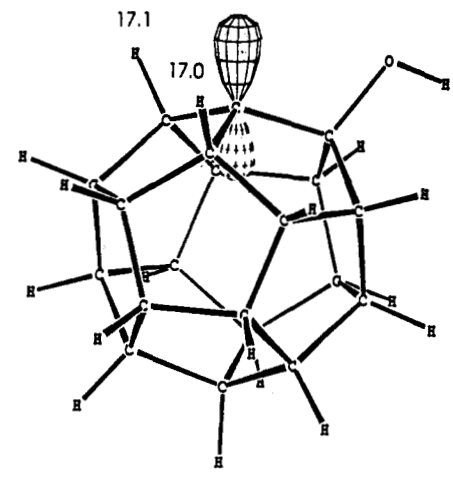


Figure 4. Optimized structure and SOMO of the 2-hydroxydodecahedryl radical as calculated by the AM1/PM3-UHF method (annihilated $\langle S^2 \rangle = 0.75$). AM1-UHFQ hyperfine splittings in G are indicated.

additional "doublet" features of ca. 35 and 71 G overall separation (Figure 2b), the "35 G" feature being formed more rapidly than the "71 G". As before, all signals persisted (half-life ca. 17 h at room temperature) when the light was switched off and had approximately the same g value. After complete decay (3 days), the original spectrum could be regenerated by further photolysis. Identical ESR signals were also observed when **5** was replaced by **8** as a precursor. Interestingly, photolysis of **8** in the presence of Me_6Sn_2 (no DTBP) also produced the now familiar ESR signals described above, though with a ca. 10-fold lower intensity (after comparable irradiation time). This experiment proved that the observed ESR signals do not derive from DTBP itself or products formed from it.

Blank experiments established that (under otherwise identical conditions) *no* ESR signals could be detected from solutions solely of **5**, **8**, or DTBP in cyclopropane. Likewise, no ESR signals were obtained during photolysis of unsubstituted dodecahedrane and DTBP in cyclopropane.

The foregoing experiments led to serious doubt that the central quintuplet can be attributed to the dodecahedryl radical (**4**). The small, unresolved splitting patterns are especially incompatible with the presence of three equivalent β-hydrogens. For the dodecahedryl radical, a basic 1:3:3:1 quartet from the three equivalent β-hydrogens with hfs somewhat larger than those of the 1-adamantyl radical (ca. 6.6 G) was anticipated.[39]

The delayed buildup of ESR signals after switching on the initiating UV light clearly indicates that they do not derive directly from the original monosubstituted dodecahedranes but rather from products formed during the photolysis. Furthermore, even if the dodecahedryl radical would have unexpectedly small β-hfs (<2 G), the high persistency of the observed central quintuplet implies that due to the accumulation effect we should have been able to detect **4** even under conditions unfavorable to its formation. The experiments where Me_6Sn_2 was employed or where hydrogen abstraction from dodecahedrane by *tert*-butoxy radical was attempted are good examples. Presently, we are unable to provide a reasonable structural assignment to the species responsible for the strong ESR quintuplet. However, because it is observed from different precursors in different solvents, it is most likely that it is produced from (monosubstituted) dodecahedrane moieties. The experimental g values of 2.0025 ± 0.0001 are typical for carbon-centered radicals having no heteroatom (O, Sn, Si) bonded directly to the radical center.

Calculations were performed by the AM1/PM3-UHF method in order to gain independent evidence of the magnitude of the hfs to be expected from **4**.[40,41] The fully optimized structure (Figure 3) ($\Delta H_f = -6.7$ kcal mol^{-1}) represents (largely) a σ-type bridgehead radical of a slightly distorted geometry (out-of-plane bending angle of the radical center = 20.7°). Calculation of the hfs by the AM1-UHFQ procedure[42] yielded β-H splittings of 16.4 (1 H), 16.6 (1 H), and 17.0 G (1 H), respectively; all other splittings amounted to <0.2 G. Thus, this calculation provided no confirmation of the fact that the dodecahedryl radical should have β-H splittings within the linewidth of the major experimentally observed ESR signal.

According to semiempirical calculations, almost no change in the magnitude of the β-H hfs is to be expected if one of the β-H's is replaced by a different atom, viz., C, O, Si, or Sn.[43] For instance, AM1-UHFQ calculations of the 2-hydroxydodecahedryl radical ($\Delta H_f = -35.2$ kcal mol^{-1}) gave β-H hfs of 17.0 (1 H) and 17.1 G (1 H) (Figure 4).

It should be noted that hyperfine splittings approximating 17 G are quite characteristic in the reported ESR spectra. The satellite lines of 31–35 G separation observed in all experiments might well be due to 1:2:1 triplets of 16.5–17.5 G hyperfine splitting. The sometimes observed "65–71 G" features might also be interpreted as quadruples of 15–18 G splittings, where two of the inner lines are covered by the "31–35 G doublet" which is always of higher intensity[44] (see Figure 2b). The varying line distances of these satellite features in the various experiments might be related to the incorporation of the initiator and/or solvent into the corresponding radical species. In the

(39) (a) *Landolt-Börnstein, New Series, Magnetic Properties of Free Radicals*, Fischer, H., Hellwege, K. H., Eds.; Springer: Berlin, 1977; Vol. II/9b, p 303. (b) The syn-oriented β-hydrogens of the (configurationally frozen) cyclopropyl radical ($a_H = 17.6$ G) may be regarded as a moded for the β-H's in the (presumably σ-type) dodecahedryl radical.

(40) Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(41) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 109, 221.

(42) Nelsen, S. F. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1005.

(43) The same conclusion can be drawn by inspection of the ESR data of other β-heterosubstituted alkyl radicals from the Landolt-Börnstein collection (ref 39a). Also, no significant shift of the g values compared to a "pure" hydrocarbon radical should be expected.

(44) Attempts to "bleach out" one or another of the various signals by microwave power saturation (in order to obtain simpler spectra) failed. All signals showed a similar saturation behavior.

5/Et_3SiH/DTBP experiment, a most persistent 17.7 G doublet has also been observed after prolonged UV irradiation. The fact that the spectral features are governed by multiples of ca. 17 G might be regarded as an indication of a close relationship between the corresponding species and the dodecahedryl radical structure. However, definite assignments would be highly speculative at the present time.

An attempt was also made to generate 4 by gas-phase reaction of 5 with sodium vapor and to observe by matrix isolation ESR spectroscopy.[45] Cocondensation at 12 K of the vapor of 5 and sodium in a stream of argon gave a matrix showing an intense methyl radical spectrum (often observed in such experiments) and a broad, ca. 20 G wide, anisotropic signal in the center of the methyl spectrum. Weak, anisotropic lines spreading over a ca. 150 G field range were also present. The latter disappeared irreversibly when the matrix was warmed to 30 K. A broad central signal (g ca. 2.002–3) corresponds to what has been reported above. However, unequivocal assignment of its structure has not yet proven possible.

Conclusions. Derivatization of the dodecahedryl nucleus by free radical means has been accomplished. The reactivity of 4 does not, however, lend itself to the broad use of this intermediate in synthesis. The limited range of acceptors that can trap 4 effectively and the lower yields that have been realized when compared to the 1-adamantyl system can be rationalized in terms of reduced nucleophilicity and increased front strain steric shielding in 4. Notwithstanding, this analysis must be tempered by the realization that 4 cannot be directly observed by ESR spectroscopy under a variety of conditions ideally suited to the generation of the 1-adamantyl radical. In those instances where distinct odd-electron species were clearly evident, one component of the signals and their associated hyperfine splittings appears fully consistent with the formation of a monosubstituted dodecahedryl radical. Semiempirical calculations performed on the 2-hydroxy derivative provide some support of the experimental observations. Formation of a monosubstituted dodecahedryl radical can best be explained by rapid conversion of 4 to dodecahedrene followed by recapture of the extraneous radical species (R•) to generate a 2-substituted dodecahedryl radical. This capability is unprecedented in bridgehead radical chemistry. However, this interpretation can only be regarded as provisional.

Experimental Section

(Phenylseleno)dodecahedrane (8). A solution of 5 (5.2 mg, 0.015 mmol) in dry CH_2Cl_2 (5 mL) was treated with anhydrous zinc iodide (15 mg, 0.047 mmol) and trimethylsilyl phenyl selenide (500 mg, 2.18 mmol). The reaction mixture was stirred at room temperature for 1.5 days, at which point additional ZnI_2 (5 mg, 0.016 mmol) and TMSSePh (250 mg, 1.09 mmol) were added and stirring was continued for a total of 3 days. Water (2 mL) was introduced and the mixture was extracted with $CHCl_3$ (2 × 5 mL). After the combined organic layers were dried, filtered, and evaporated, air was blown over the yellow oil for 1 day. The resulting solid diphenyl diselenide could be removed from the desired 8 either by sublimation (100 °C, house vacuum, 3 to 5 days) or more conveniently by trituration with ether (3 × 0.3 mL). Selenide 8 remained as a faintly yellow crystalline solid, which may be used directly or further purified by preparative TLC (silica gel, 5:10:85 Et_2O/CH_2Cl_2/hexane) to yield 8 as an off-white powder (4 mg, 63%), mp 226–227 °C (sealed tube): IR (film, cm^{-1}) 3040, 2940, 2850, 1260, 1100, 1010, 820–720; ^1H NMR (300 MHz, C_6D_6) δ 7.68 (m, 2 H), 7.09–7.07 (m, 3 H), 3.74–3.65 (m, 3 H), 3.26–3.2 (br s, 6 H), 3.2–3.12 (s, 10 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 134.7, 133.6, 129.0, 127.4, 96.5, 82.5, 76.7, 67.1, 66.9, 66.6; MS *m/z* calcd (M^+) 416.1043, obsd 416.1062.

(2-Cyanoethyl)dodecahedrane (9). A 6.8-mg (0.02 mmol) sample of 5 in a flame-dried 1.0-mL Wheaton vial equipped with a magnetic stirring bar and Teflon-coated cap was blanketed with nitrogen and covered with dry benzene (0.15 mL), acrylonitrile (0.1 mL, excess), and tri-*n*-butyltin hydride (80 μL, excess). AIBN (0.1 mg) was added and the mixture was capped and heated at 75 °C for 6 h. After being cooled and diluted with benzene (0.5 mL) and ether (0.2 mL), the reaction mixture was treated with a solution of $KF_{(aq)}$ (1 mL) and stirred vigorously. Extraction of the resulting mixture with CH_2Cl_2 (2 × 3 mL), passage of the combined organic layers through a short silica gel plug (elution with CH_2Cl_2), drying, and solvent removal returned crude 9, which was further purified by preparative TLC (silica gel; 5% ether in hexanes) to yield 4.1 mg (65%) of pure 9, mp 174–175 °C dec (sealed tube): IR (film, cm^{-1}) 2942, 2620, 2242, 1730, 1444, 1422, 1344, 1294, 1260, 1160, 904; ^1H NMR (300 MHz, $CDCl_3$) δ 3.38 (br s, 16 H), 3.00 (br s, 3 H), 2.28 (t, *J* = 6 Hz, 2 H), 1.80 (t, *J* = 6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 120.5, 79.0, 71.3, 67.1, 67.0, 66.5, 66.4, 38.5, 14.0; MS *m/z* calcd (M^+) 313.1831, obsd 313.1817.

3-Dodecahedrylcyclopentanone (11). Dry benzene (0.4 mL) containing 5 (4.7 mg, 0.014 mmol), 2-cyclopentenone (40 μL, excess), $NaBH_4$ (1 mg, excess), and hexabutylditin (2 μL) was irradiated at 10 °C in a dry NMR tube for 18 h. The solution was diluted with ether (0.3 mL) and benzene (0.1 mL) and then treated with $HF_{(aq)}$ solution (4–5 drops). The mixture was stirred until the $NaBH_4$ had been consumed and the organic layer was passed through a short silica gel column containing some anhydrous $MgSO_4$ and Na_2SO_4 and evaporated. Preparative TLC purification (silica gel; elution with 1:8 ethyl acetate/hexanes) provided 1.7 mg (35%) of 11, mp 205 °C dec: IR (film, cm^{-1}) 2938, 1737, 1296, 1158, 739; ^1H NMR (300 MHz, $CDCl_3$) δ 3.5–3.2 (br s, 16 H), 3.15–2.95 (br s, 2 H, 2.4–2.0 (m, 4 H), 1.9–1.75 (m, 1 H), 1.5–1.3 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 220.3, 82.6, 67.2, 67.1, 66.6, 66.51, 66.48, 47.1, 42.0, 39.3, 25.5; MS *m/z* calcd (M^+) 342.1983, obsd 342.2022.

Allyldodecahedrane (12). To a nitrogen-blanketed sample of 5 (4.1 mg, 0.012 mmol) in a flame-dried 1.0-mL Wheaton vial equipped with a magnetic stirring bar and Teflon-coated cap were added dry CH_2Cl_2 (0.1 mL), allyltrimethylsilane (100 μL, excess) and anhydrous zinc iodide (50 mg). The reaction mixture was capped and stirred at room temperature for 3 days. After dilution with CH_2Cl_2 (0.4 mL) and addition of enough water to dissolve the ZnI_2 (0.2 mL), the mixture was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic layers were passed through a short silica gel plug and dried prior to solvent evaporation. There was obtained 3 mg (65%) of 12 as a light tan powder, mp 190 °C dec: IR (film, cm^{-1}) 3069, 2936, 1296, 990, 734; ^1H NMR (300 MHz, $CDCl_3$) δ 5.8–5.7 (m, 1 H), 5.1–4.95 (m, 2 H), 3.35 (br s, 16 H), 3.05 (br s, 3 H), 2.25 (d, *J* = 7.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 137.3, 116.4, 79.1, 71.8, 67.2, 66.6, 66.5, 65.3, 48.1; MS *m/z* calcd (M^+) 300.1855, obsd 330.1866.

Dodecahedrylacetaldehyde (13). A solution of 12 (11 mg, 0.037 mmol) in THF (6 mL) and water (1 mL) was treated with sodium periodate (40 mg, 0.186 mmol) and a catalytic amount of OsO_4 in pyridine (5 μL of a 0.157 M solution). After being stirred for 2 days at room temperature, the reaction mixture was diluted with CH_2Cl_2 (5 mL), washed with brine, and dried. Solvent removal and trituration with ether produced 7 mg (63%) of 13. Further purification was achieved by short column chromatography (elution with 10% ether in petroleum ether), mp 202–205 °C: IR (film, cm^{-1}) 2938, 1690, 1430, 1300, 1250; ^1H NMR (300 MHz, C_6D_6) δ 9.47 (t, *J* = 2.0 Hz, 1 H), 3.40–3.15 (br m, 16 H), 2.80 (br s, 3 H), 2.08 (d, *J* = 2.0 Hz, 2 H); ^{13}C NMR (125 MHz, C_6D_6) ppm 201.5, 73.3, 72.9, 67.21, 67.19, 66.9, 66.8, 66.7; MS *m/z* calcd (M^+) 302.1670, obsd 302.1650.

1-Dodecahedryl-2-propanone (14). Into a 5-mL, two-necked pear-shaped flask (prerinsed with 1% HCl) were placed a magnetic stirring bar, $PdCl_2$ (1 mg), $CuCl_2$ (2 mg), and 2 mL of a DMF/H_2O (3:1) solution. Oxygen was introduced and the initially black solution slowly turned green as the O_2 was absorbed. To the green solution was added 12 (8 mg, 0.026 mmol) in DMF (0.1 mL). Oxygen was bubbled through the mixture for 2 h and the mixture

(45) Korth, H. G.; Lange, F.; Lübbe, F.; Müller, W.; Seidel, M.; Sustmann, R. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1293.

was stirred under O_2 for another day. The reaction mixture was diluted with 10% HCl and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with water (10 mL), dried, and evaporated. The remaining DMF was removed by dissolving the crude mixture in ether, washing the resulting solution with water, drying the solution, and evaporating the solvent to leave pure **14** (7.8 mg, 95%). Further purification could be achieved by preparative TLC (silica gel, 1:2:7 CH_2Cl_2/ether/hexanes), mp 159–161 °C (sealed tube): IR (film, cm^{-1}) 2940, 1715, 1395, 1160; ^1H NMR (300 MHz, C_6D_6) δ 3.48 (br s, 6 H), 3.27 (br s, 10 H), 2.97 (br s, 3 H), 2.17 (s, 2 H), 1.63 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 206.0, 76.8, 73.3, 67.23, 67.16, 67.0, 66.9, 57.0, 30.2; MS m/z calcd (M^+) 316.1827, obsd 316.1805.

ESR Spectroscopic Studies. A Bruker ER-420 X-band spectrometer equipped with a variable temperature unit was used. Data acquisition and spectral simulations were performed on a DEC PDP-11/34 computer.

ESR samples were prepared in 4-mm o.d. quartz tubes, degassed by three freeze–pump–thaw cycles, and sealed under vacuum. Typically, the samples were composed of 2–3 mg of highly purified precursor (**5** or **8**), 10–50 μL of initiator (DTBP, Me_6Sn_2, Et_3SiH), and 0.5–1 mL of solvent (cyclopropane or fluorobenzene). Radicals were generated by direct UV photolysis of the samples with the filtered (UG–5; Schott) output of a 1000-W high-pressure Hg/Xe lamp (Hanovia 977B-1). The g values were determined with the aid of a home-built device, using the digital readout from a frequency counter and a gauss meter.

Matrix-isolation experiments were carried out using an Air Products closed-cycle helium cryostat CV 202. Most of the experimental setup has been described elsewhere.[45] The sample of **5** was evaporated in a vacuum of 10^{-6} mbar at ca. 220 °C; sodium was evaporated at ca. 260 °C. A DDHBr/argon ratio of 1:100 was employed.

AM1/PM3-UHF calculations were performed using the SCAMP 4.20 package[46] on a MicroVax GPX-II workstation. Graphical output was produced by the PERGRA program.[47]

Acknowledgment. This research was supported by the National Institutes of Health (Grant AI-11490 to LAP).

(46) SCAMP, Erlangen Molecular Orbital Package, Version 4.20 (based on AMPAC 1.0 and MOPAC 4.0), Universität Erlangen, Germany. We thank Dr. T. Clark for a copy of this program.

(47) Sustmann, R.; Sicking, W. Universität-GH Essen, Germany, 1990.

Rearrangement of Dimethyl(furylmethyl)ammonium and Dimethyl(thienylmethyl)ammonium *N*-Methylides. Isolation and Reaction of Nonaromatic Intermediates

Takeshi Usami, Naohiro Shirai, and Yoshiro Sato*

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

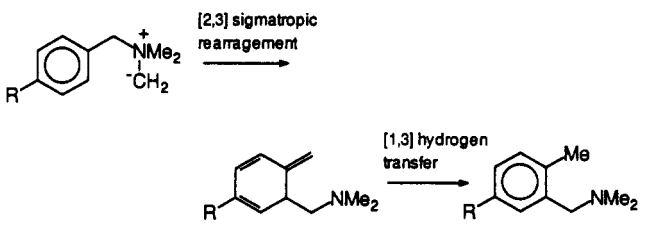
Received May 20, 1992

3-[(Dimethylamino)methyl]-2-methylene-2,3-dihydrofuran (**5o**) and 2-[(dimethylamino)methyl]-3-methylene-2,3-dihydrofuran (**12o**) and their thiophene analogues **5s** and **12s** were prepared in high yields by fluoride-ion induced desilylation of *N,N*-dimethyl-*N*-[(trimethylsilyl)methyl](2-furylmethyl)ammonium (**3o**) and -(3-furylmethyl)ammonium iodides (**10o**) and their thienylmethyl analogues **3s** and **10s**. Compound **5s** or **12s** was successfully converted to 3-[(dimethylamino)methyl](2-thienylmethyl)lithium (**23s**) or 2-[(dimethylamino)methyl](3-thienylmethyl)lithium (**26s**), which reacted with aldehydes to give [(dimethylamino)methyl](2-hydroxyalkyl)thiophenes **25s** or **27s**, respectively.

Introduction

N,N-Dialkylbenzylammonium *N*-methylides rearrange to *N,N*-dialkyl-2-methylbenzylamines (Sommelet–Hauser rearrangement) and/or *N,N*-dialkyl-2-phenylethylamines (Stevens rearrangement).[1] The Sommelet–Hauser rearrangement is the main path from the ylide having an electron-donating or weak electron-releasing substituent on the benzene ring.[2a,b,g] This rearrangement proceeds by a [2,3] sigmatropic rearrangement followed by a [1,3] hydrogen transfer via an intermediate, 6-[(dialkylamino)methyl]-5-methylene-1,3-cyclohexadienes (conjugated triene compounds) (Scheme I). The stability of the conjugated triene compounds increases with the increasing electron-releasing ability of the substituents;[2b,d-f] e.g., 6-[(dimethylamino)methyl]-2-methoxy-5-methylene-1,3-cyclohexadiene was stable at room temperature.[2b] This result seems to suggest that the rearrangement of ylides to an electron-rich aromatic ring may stop at the intermediate compound.

Scheme I



Paul and Tchelitcheff[3] reported that treatment of trimethyl(3-furylmethyl)ammonium or trimethyl(3-thienylmethyl)ammonium salt with sodium amide in liquid ammonia gave 3-methyl-2-[(dimethylamino)methyl]furan or -thiophene (Sommelet–Hauser rearrangement product), but no product was obtained from a similar treatment of

(1) (a) Pine, S. H. *Org. React. (N.Y.)* **1970**, *18*, 403. (b) Lepley, A. R.; Giumanini, A. G. *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, p 297.

(2) (a) Nakano, M.; Sato, Y. *J. Org. Chem.* **1987**, *52*, 1844. (b) Shirai, N.; Watanabe, Y.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 2767. (c) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Org. Chem.* **1989**, *54*, 836. (d) Machida, Y.; Shirai, N.; Sato, Y. *Synthesis*, **1991**, 117. (e) Kitano, T.; Shirai, N.; Sato, Y. *Synthesis*, **1991**, 996; *Chem. Pharm. Bull.* **1992**, *40*, 768. (f) Okazaki, S.; Shirai, N.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 334. (g) Tanaka, T.; Shirai, N.; Sugimori, J.; Sato, Y. *J. Org. Chem.*, in press.

(3) Paul, R.; Tchelitcheff, S. *Bull. Soc. Chim. Fr.* **1968**, 2134.

0022-3263/92/1957-5419$03.00/0