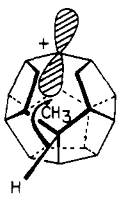
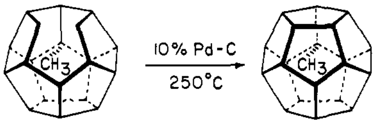
7 (24%).[6,7] With arrival at 6, fixed endo orientation of a pair of chemically distinguishable carbonyl groups within a monoalkylated product was guaranteed. Photoinduced ring closure at the ketone site proceeded readily with formation of **8** (100%), whose dehydration and diimide reduction delivered the triseco ester **9** (92%) (see Scheme II).

With construction of the front portion of the developing sphere completed, ester **9** was next transformed into the photoreactive aldehyde **10** (94%). Because of the neopentyl nature of the carbonyl group in **10**, ready decarbonylation was anticipated from its photoexcited state. Although this pathway proved difficult to curtail, partial success was achieved by performing the irradiation in a 9:1 toluene–ethanol solvent system at −78 °C. These conditions provided the desired homo-Norrish alcohol in 25% yield. Following oxidation to **11**, it proved an easy matter to install yet another C–C bond by photochemical means. Heating of the tertiary alcohol so formed with *p*-toluenesulfonic acid in benzene resulted in smooth dehydration and formation of seco olefin **12** (85% overall).

In earlier work, a dimethyl seco olefin related to **12** was found to be subject to rapid acid-catalyzed isomerization in the presence of trifluoromethanesulfonic acid at room temperature, the multistep rearrangement culminating in formation of 1,16-dimethyldodecahedrane.[2] Not yet elucidated is the timing of the methyl shift vis-à-vis closure of the final framework bond. In any event, the obvious complexity of this cyclization process was further manifested when **12** was analogously treated. Not only did a myriad of products result, but the most prevalent of these was the beautifully crystalline "isododecahedrane" **13** (55–60% of the volatile constituents). The lone methyl substituent is seen to destroy the otherwise symmetric nature of this unusual ring system and to make recourse to X-ray crystal structure analysis essential. The total polyquinane nature[8] of **13** was thereby revealed.[9] Furthermore, the twinned norbornyl character of its methano bridges was noted to project the associated internal hydrogens well beyond intramolecular contact range. Evidently, the very severe nonbonded interaction between the same hydrogen atoms in **12** provides the necessary steric driving force for transannular electrophilic attack at the unactivated methine carbon with *apparent* inversion of configuration. Carbonium ion **14** represents the shortest pathway to product.[10] However, this reaction course need not be favored relative to a multistep process, and the inoperability of any of the numerous alternative cationic equilibrium mechanisms is *not* implied.



14



15 16

Following this unexpected development, we examined the possible catalytic dehydrogenation of **15** (produced by diimide reduction of **12**) in the hope that an efficient route to the monosubstituted dodecahedrane would result. Success was realized upon heating an intimate mixture of **15** with 50 times its weight of 10% Pd–C (previously exposed to 50 psi of H_2) at 250 °C for 7 h in a sealed stainless steel chamber. Although capillary gas chromatography clearly indicated that a variety of byproducts are also formed under these conditions, **16** is present to the extent of 35–40% and can be separated from the mixture by recrystallization from benzene. The reluctance of **16** to experience melting and especially its ^{1}H NMR[11] and mass spectra leave no doubt as to the identity of this material, the structural assignment to which has been confirmed by X-ray analysis.[9]

The dehydrogenation procedure highlighted here provides an important, previously unavailable, practical solution to the acquisition of dodecahedranes from seco precursors.[12]

Registry No. 1, 82400-15-5; **2**, 82400-16-6; **6**, 82390-84-9; **7**, 80317-84-6; **8**, 82390-85-0; **9**, 82390-86-1; **10**, 82390-87-2; **11**, 82390-88-3; **12**, 82390-89-4; **13**, 82390-90-7; **15**, 82390-91-8; **16**, 82400-17-7.

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(6) Comparable 2:1 partitionings were routinely observed with other electrophiles as well.[5]

(7) All new compounds exhibited compatible infrared, proton magnetic resonance, and mass spectroscopic data. In addition, the elemental composition of all key intermediates has been substantiated by combustion analysis. Yields refer to isolated chromatographically homogeneous materials.

(8) Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

(9) Christoph, G. G., private communication.

(10) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588 and references cited therein.

(11) In $CDCl_3$ at 200 MHz: δ 3.38 (br s, 16 H), 2.92 (narrow m, 3 H), 1.14 (s, 3 H).

(12) This research has been made possible by the generous financial support of the National Institutes of Health (Grant AI-11490). We thank Dr. Ole Mols for his invaluable assistance in recording the high-field NMR data.

Dodecahedrane[1]

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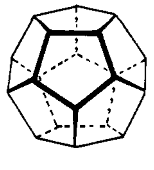
The position of dodecahedrane (**1**) as the structurally most complex, symmetric, and aesthetically appealing member of the C_nH_n convex polyhedra (n = 20) has caused its synthesis to be intensely pursued during the last 2 decades.[3] Previously, we have described successful approaches to its monomethyl[4] and 1,16-dimethyl derivatives.[5] In this communication, we provide details of a protocol that makes the parent spherical hydrocarbon available for the first time.



1

In view of our ability to achieve clean reduction of dichloro diester **2** (Scheme I) to keto alcohol **3**[6] and subsequent conversion to **4** by sequential photoinduced homo-Norrish cyclization, regiospecific acid-catalyzed dehydration, and olefin saturation with diimide,[7] studies designed to transform **4** into **1** were undertaken. Unfortunately, these efforts were thwarted because **4** proved particularly sensitive to overoxidation, presumably as a direct consequence of the high enol content of the derived aldehyde. Furthermore, the α,β-unsaturated aldehyde that was routinely produced (**5**) readily polymerized on standing.

For this reason, the decision was made to engage **2** in reduction–monoalkylation[4] in order to install a blocking group that

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(1) The IUPAC name for dodecahedrane is undecacyclo[$9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}$]eicosane: Eckroth, D. R. *J. Org. Chem.* **1967**, *32*, 3362.

(2) (a) The Ohio State University Fellow, 1977–1978. (b) Presidential Fellow, The Ohio State University, 1979–1980.

(3) Review: Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

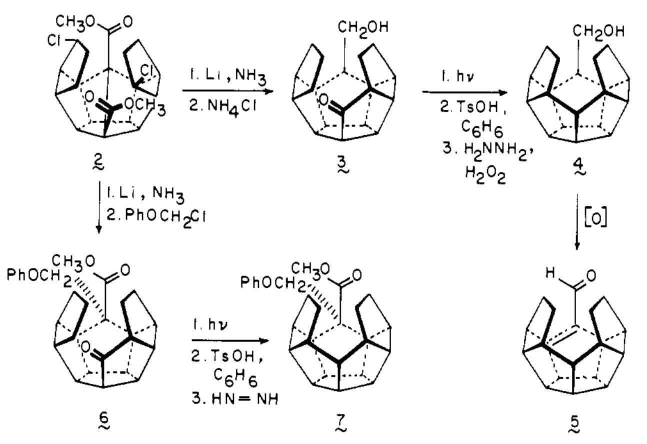
(4) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W., preceding communication in this issue.

(5) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, D.C.)* **1981**, *211*, 575. Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774.

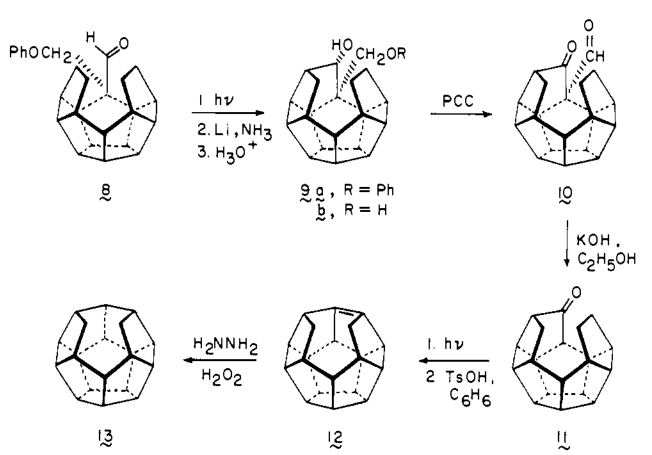
(6) All new compounds exhibited compatible infrared, proton magnetic resonance, and mass spectroscopic data. In addition, the elemental composition of all key intermediates has been substantiated by combustion and/or accurate mass analysis. Yields refer to isolated chromatographically homogeneous materials.

(7) Paquette, L. A.; Balogh, D. W.; Ternansky, R. J.; Begley, W. J.; Banwell, M. G., to be submitted for publication.

Scheme I



Scheme II



would effectively deter enolization of the carboxaldehyde functionality yet prove readily removable at a later stage. The selection of a pendant side chain had to be made judiciously since its role was necessarily multifaceted. Thus, its introduction must be achieved via S_N2 methodology, and it must survive those steps required for construction of two framework bonds on the opposite molecular surface as well as alteration of the carbomethoxy oxidation level. Most importantly, the R group in question must not foster added photodecarbonylation of the aldehyde nor engage in capture of this photoexcited carbonyl group.

Chloromethyl phenyl ether[8] satisfies all of these requirements. As indicated in the formulas, lithium-liquid ammonia reduction of **2** and immediate addition of 1 equiv of the electrophile gave **6** (48%). The phenoxymethyl side chain causes interference neither during the three-step conversion to **7** nor during the ensuing Dibal-H reduction and PCC oxidation of this triseco ester. With **8** (Scheme II) in hand, it was determined that the $PhOCH_2$-residue likewise does not become entangled with proximate functionality during photochemical cyclization to **9a** (36%). As always, the lowered yield observed in this step results from competitive photodecarbonylation.

Reduction of **9a** under Birch conditions delivered a dihydrobenzene product, aqueous acid hydrolysis of which furnished **9b** in 99% isolated yield. This diol undergoes efficient oxidation to β-keto aldehyde **10** upon treatment with pyridinium chlorochromate. This intermediate conforms to the susceptibility of this class of compounds to retroaldol cleavage in alkaline solution and provides diseco ketone **11** in 37% overall yield. The risk of complications due to enolization α to a carbonyl site was now behind us.

The conversion of **11** to **13** via **12** proved to be quite uneventful and satisfyingly efficient (65% overall). Upon being heated with H_2-presaturated 10% palladium on carbon at 250 °C for >4.5 h as described earlier,[4] **13** was transformed with 40–50% efficiency into dodecahedrane (**1**). The colorless crystalline hydrocarbon can be rountinely obtained in >98% purity after a *single* recrystallization of such product mixtures from benzene.

As fully expected, the ^1H and ^{13}C NMR spectra of **1** (in $CDCl_3$) are characterized by singlets, the former at δ 3.38 and the latter at 66.93 ppm. The ^{13}C–H coupling constant of 134.9 Hz is somewhat larger than the value earlier calculated by Mislow (128.1 Hz),[9] but entirely comparable to those of the dimethyl derivative (131.2, 135.0 Hz).[5] The vibrational frequencies exhibited by this I_h symmetric molecule (120 identity operations) agree fully with a highly rigid network of interlinked methine units. Three infrared-active bands are observed at 2945, 1298, and 728 cm^{-1}; its eight Raman-active frequencies occur at 2954, 2938, 1324, 1164, 1092, 840, 676, and 480 cm^{-1}.[10] In general, these findings compare reasonably well with values calculated by Ermer.[11] The hydrocarbon gives no visible evidence of melting at temperatures up to 450 °C.

In summary, the total synthesis of dodecahedrane has been achieved in 23 steps from cyclopentadienide anion. While this already brief sequence is certain to see improvement in the future, quantities of this most exquisite of polycondensed ring systems are now available for further experimentation. In ongoing research, we intend to address some of the many questions relating to its possibly distinctive physical and chemical properties.[12]

Registry No. 1, 4493-23-6; **2**, 71342-50-2; **6**, 82390-75-8; **7**, 82390-76-9; **8**, 82390-77-0; **9a**, 82390-78-1; **9b**, 82390-79-2; **10**, 82390-80-5; **11**, 82390-81-6; **12**, 82390-82-7; **13**, 82390-83-8; chloromethyl phenyl ether, 6707-01-3.

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(8) Barber, H. J.; Fuller, R. F.; Grea, M. B.; Zwartouw, H. T. *J. Appl. Chem.* **1953**, *3*, 266.

(9) Mislow, K., private communication. For a discussion of the method used, see: Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *23*, 31.

(10) We are indebted to Mark Wisnowsky (Owens-Corning Co.) for the determination of these spectra.

(11) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *6*, 411.

(12) This research was made possible by the generous financial support of the National Institutes of Health (Grant AI-11490). We thank Dr. Ole Mols for his invaluable assistance in recording the high-field NMR data.

Total Synthesis of (±)-Pentalenene

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The antibiotic properties of pentalenolactone,[1] an agent active against Gram-positive/negative bacteria and pathogenic fungi as a consequence of its ability to inhibit glyceraldehyde 3-phosphate dehydrogenase,[2] served to elicit extensive investigation of its biosynthesis. Soon to follow was evidence in support of its mevalonoid origin[3] and isolation of the acidic biosynthetic intermediates pentalenolactone E,[4] G,[5] and H,[6] as well as pentalenic

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(1) (a) Isolation: Koe, B. K.; Osbin, B. A.; Celmer, W. D. *Antibiot. Ann.* **1956–1957**, 672. Takeuchi, S.; Ogawa, Y.; Yonehara, H. *Tetrahedron Lett.* **1969**, 2737. Martin, D. G.; Slomp, G.; Mizsak, S.; Duchamp, D. J.; Chidester, C. G. *Ibid.* **1970**, 4901. Duchamp, D. J.; Chidester, C. G. *Acta Crystallogr., Sect. B* **1972**, *B28*, 173. (b) Synthesis: Danishefsky, S.; Hirama, M.; Gombatz, K.; Harayama, T.; Berman, E.; Schuda, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 6536; **1979**, *101*, 7020. Parsons, W. H.; Schlessinger, R. H.; Quesada, M. L. *Ibid.* **1980**, *102*, 889.

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(3) Cane, D. E.; Rossi, T.; Pachlatko, J. P. *Tetrahedron Lett.* **1979**, 3639.

(4) (a) Isolation: Cane, D. E.; Rossi, T. *Tetrahedron Lett.* **1979**, 2973. (b) Synthesis: Paquette, L. A.; Schostarez, H.; Annis, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 6526.

(5) Seto, H.; Sasaki, T.; Yonehara, H.; Uzawa, J. *Tetrahedron Lett.* **1978**, 923.

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