R. Within the C_π or C_{σ_s} families, the substitution rate constants can be eliminated, thus giving the relative rate constants for decarboxylation listed in Table II. The rates of decarboxylation decrease with increased branching in the R group: *pivaloxy is more stable than propionoxy* at low temperatures. The failure of the rates of decarboxylation to reflect the stability of the alkyl radical that is produced upon decarboxylation strongly indicates an early transition state for this process, one in which there is little stretching of the carbon–carbon bond.

These results require two hydrogen abstracting carboxylate radicals. By analogy with the assignment made for succinimidyl radicals, method I produces C_π and method II produces C_{σ_s}.[8] This two-state rationalization is in accord with the experimental information and with a state-of-the-art calculation[9] that shows an excited state for acetoxy 12 kcal/mol above ground state. The upper state, $2\text{-}^2A''$ (our C_π), and the ground state $1\text{-}^2A''$ (our C_{σ_s}), both have barriers for loss of carbon dioxide. At the energy minima, the OCO angle is 120° for the upper, 115° for the lower state. Decarboxylation leads ultimately to an OCO angle of 180°. An explanation for the greater stability of pivaloxy depends on assigning to the transition state an increased OCO bond angle and little C–C stretching, from which it follows that the barrier will increase as the bulk of R increases.

Acknowledgment. We thank the National Science Foundation for its financial support of this work.

Registry No. $CH_3CH_2CO_2Br$, 82198-80-9; i-$PrCO_2Br$, 82198-81-0; t-$BuCO_2Br$, 82198-82-1; propionoxy, 24446-96-6; isobutryoxy, 54388-94-2; pivaloxy, 28149-41-9; butane, 106-97-8.

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(8) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381-387.

(9) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. J. Am. Chem. Soc., in press.

Strategy for the Synthesis of Monosubstituted Dodecahedranes and the Isolation of an Isododecahedrane

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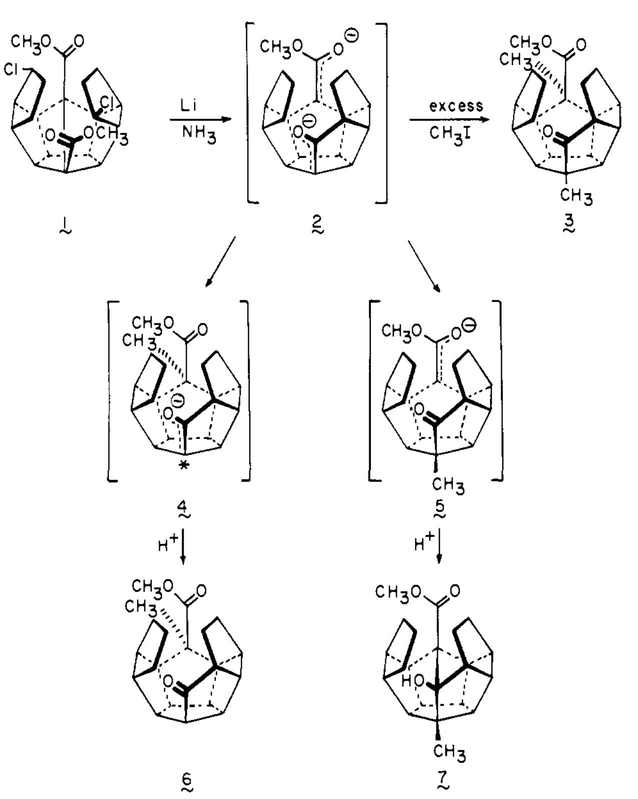
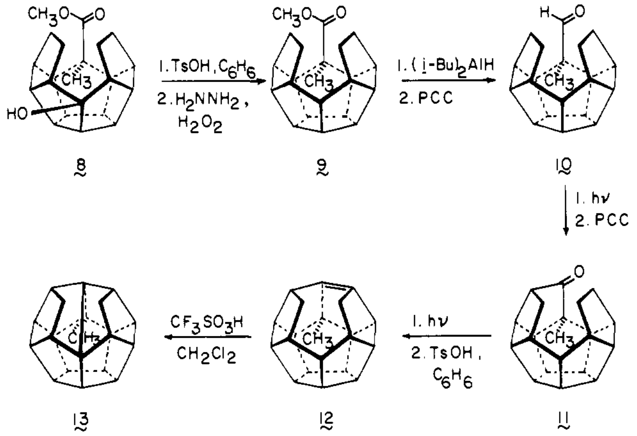
One of the key steps involved in the successful synthesis of 1,16-dimethyldodecahedrane is the dissolving metal reduction of dichloro diester **1** (Scheme I) in liquid ammonia followed by treatment with a large excess of methyl iodide.[2] It was hypothesized that **3** results from exhaustive alkylation of dianion **2**. This intermediate has become a focal point of considerable interest from the standpoint of its reactivity (little information is currently available on the relative nucleophilicities of disconnected ester and ketone enolates[3]) and its possible role as a precursor to monosubstituted dodecahedranes and the parent $C_{20}H_{20}$ hydrocarbon.[4]

When consideration is given to the monoalkylation of **2**, it becomes imperative for our purposes that electrophilic capture be achieved selectively α to the carbomethoxy group to give **4**.

Scheme I



Scheme II



This monoanion was viewed to be a species wherein subsequent intramolecular aldol condensation could be discounted because of the geometrically prohibitive requirement that the asterisked framework carbon experience inversion of configuration. In contrast, the formation of **5** should be rapidly followed by ring closure to **7** since configurational inversion α to the carbomethoxy group now serves to project this substituent to the outer surface of the superstructure and to release numerous other nonbonded steric interactions. Thus, preferential reaction at the ketone enolate center in **2** would seriously frustrate our aims. Given the a priori consideration that ester enolates should be somewhat electronically destabilized because of attachment of a second oxygen atom, a detailed study of **2** appeared to be warranted.[5]

Addition of **1** to a solution containing 6 equiv of lithium in liquid NH_3 at −78 °C followed by 1 equiv of methyl iodide as soon as the blue color began to fade afforded a mixture of **6** (46%) and

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

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

(3) We are aware of a lone example where this issue has been raised. In their attempts to effect chemospecific sulfenylation of methyl 9-oxodecanoate with dimethyl disulfide, Trost et al. (Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887) were never able to attain >30% of the desired α-carbomethoxy sulfenylated product. The extent of reaction that occurred α to the ketone carbonyl was not stated.

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

(5) Only the methyl example is discussed here. For an exhaustive treatment of this subject, consult: Paquette, L. A.; Balogh, D. W.; Ternansky, R. J.; Begley, W. J.; Banwell, M. G., to be submitted for publication.

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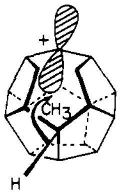
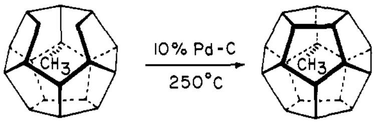
7 (24%).[6,7] With arrival at **6**, fixed endo orientation of a pair of chemically distinguishable carbonyl groups within a monoalkylated product was guaranteed. Photoinduced ring closure at the ketone site proceeded readily with formation of **8** (100%), whose dehydration and diimide reduction delivered 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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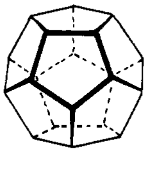
The position of dodecahedrane (**1**) as the structurally most complex, symmetric, and aesthetically appealing member of the C_nH_n convex polyhedra ($n = 20$) has caused its synthesis to be intensely pursued during the last 2 decades.[3] Previously, we have described successful approaches to its monomethyl[4] 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.

0002-7863/82/1504-4503$01.25/0