Is the dimerization a triplet–triplet reaction? The chemically induced nuclear polarization (CIDNP) signals previously observed[4] in the dimerization of **1** could arise from either a triplet–triplet or a triplet–singlet combination.[16] Moreover, the second-order rate-law now found for the dimerization is a necessary but insufficient condition for a triplet–triplet reaction. A triplet–singlet reaction also would produce this behavior if the singlet (S) were generated from the triplet (Tr) by a rapid equilibrium $\mathrm{Tr} \rightleftharpoons \mathrm{S}$, with equilibrium constant K. The observed rate constant, k_2, then would be related by eq 1 to the S + Tr mechanistic reaction rate constant k by the rate law $-\mathrm{d}[\mathrm{Tr}]/\mathrm{d}t = kK[\mathrm{Tr}]^2$.

$$k_2 = kK \tag{1}$$

However, the energy of the singlet conservatively may be placed at least 600 cal/mol above that of the triplet,[15] which means that the singlet concentration at 143.5 K would be small. Quantitatively, $K = [\mathrm{S}]/[\mathrm{Tr}] = (1/3)[\exp(-\Delta E/RT)] \lesssim 0.041$, taking into account the statistical factor favoring the triplet. Since we already know that $k_2 = 0.13k_\mathrm{d}$, we may calculate from eq 1 that $k \gg 3k_\mathrm{d}$. In other words, the alleged S + Tr reaction would have to occur much faster than the diffusion-controlled encounter frequency. This suggests that at least under the conditions in this study, the reaction Tr + Tr is the major dimerization pathway.[17]

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(12) *The technique is essentially that of K. Adamic, J. A. Howard, and K. U. Ingold*, *Can. J. Chem.*, **47**, 3803 (1969).

(13) High light intensities lead to a high steady-state concentration of triplets, whereupon dimerization becomes competitive and the reaction order in triplet becomes >1.

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(15) From the linearity of the Curie plot[5] over the range 14–268 K. A gap smaller than 600 cal/mol would have led to at least 10% deviation from the Curie line.

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(17) The possibility remains that a small amount of S + Tr reaction could account for some or all of the CIDNP effect. Also, since the cycloaddition of olefins is much slower than diffusion-controlled, a singlet–olefin reaction cannot be ruled out on kinetic grounds alone.

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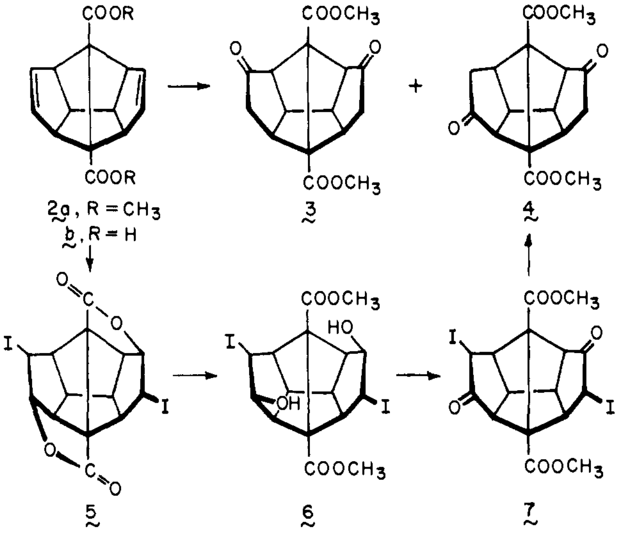
A Functionalized Trisecododecahedrane Having C_2 Symmetry

Sir:

From among the regular polyhedral hydrocarbons based upon the perfect solids of antiquity, dodecahedrane (**1**) holds a preeminent position because its relatively strain-free array of 12 polyfused cyclopentane rings generate the highest known point group symmtery (I_h), a completely enclosed cavity lacking solvation capacity, and an aesthetically appealing topology. Although numerous synthetic approaches to **1** are conceivable, some of which have already been reduced to practice in part,[1] we have viewed with especial interest a scheme which would capitalize on the inherent symmetry of the target molecule. We now describe the essence of this plan as it relates to the ready elaboration of the functionalized trisecododecahedrane **14**, the most highly condensed precursor of **1** presently known.

Diester **2a**, available in one step by Domino Diels-Alder reaction of 9,10-dihydrofulvalene with dimethyl acetylenedicarboxylate,[2] possesses four suitably arrayed cyclopentanoid rings and adequate symmetry (C_{2v}) to serve as our molecular cornerstone. The unnecessary central bond in **2** may be cleaved by a variety of methods but is presently retained to maintain norbornene character and thereby guarantee excellent stereochemical control in later stages. Elaboration of the pivotal diketo diester **4** (C_2 symmetry) was initially attempted by reaction of **2a** with disiamylborane followed by sequential alkaline peroxide and Jones oxidation. However, the principal product proved to be the unwanted isomer **3** (49%) rather than **4** (30%).

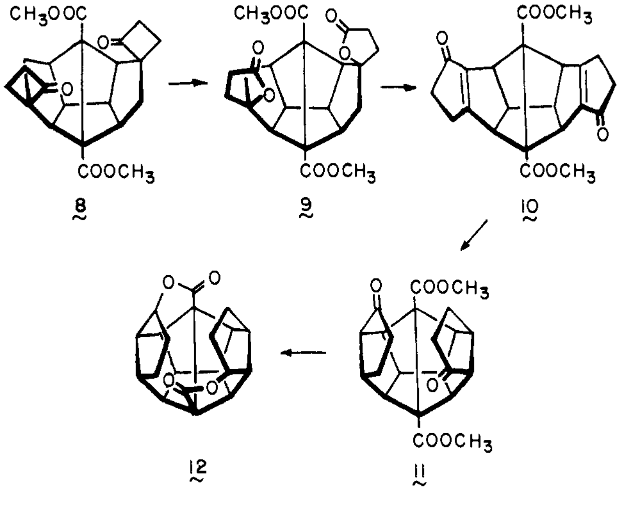


To circumvent this complication, the following "cross-corner" oxygenation sequence was developed. Iodolactonization of diacid **2b**, available in 98% yield from alkaline hydrolysis of **2a**, proceeded with high efficiency (96%) to give **5** ($\nu_\mathrm{max}{}^\mathrm{KBr}$ 1780 and 1792 cm^{-1}) which underwent cleavage to **6** in the presence of methanolic sodium methoxide at room temperature. Importantly, the iodohydrin part structures survive such treatment because intramolecular S$_\mathrm{N}$2 displacement of iodide by the transient alkoxide ions (epoxide formation) is precluded by the rigid superstructure which maintains these groups in a geometric relationship approaching 120°. The oxidation of **6** was brought about with Jones reagent (92% from **5**) and reductive removal of the iodine atoms in **7** was conveniently effected with zinc-copper couple and ammonium chloride in methanol solution.[3] This four-step procedure, which can be performed on large scale quantities, delivers exclusively **4** in

68% purified overall yield. The identity of **4** follows from its ^1H (e.g., a 6 H methyl singlet at δ 3.66) and ^{13}C NMR spectra (eight lines); the contrasting C_s nature of **3** is equally self-evident (methyl peaks at δ 3.70 and 3.63; 11 ^{13}C signals).

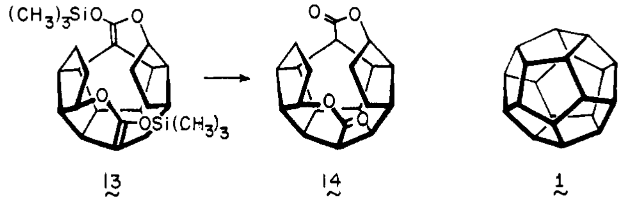
To achieve the bisspiroannulation of **4**, use was made of cyclopropyldiphenylsulfonium ylide.[4] This reaction generated a mixture of isomeric cyclobutanones (77%) highly enriched in the indicated endo,endo stereoisomer (**8**). This transformation merits particular attention since it achieves twofold addition of three carbon atoms to a preexisting C_{14} frame (the evanescent ester methyl groups are not included) and consequently delivers an axially symmetric product possessing the same carbon content as dodecahedrane. Since no additional carbon centers need be introduced, the problem is now reduced to one of functional group manipulation.

In this context, **8** was converted to dilactone **9** (100%) with 30% hydrogen peroxide solution. The latter could be conveniently transformed to bisenone **10** (65%) by treatment with phosphorus pentoxide in methanesulfonic acid (50 °C, 36 h).[5] Catalytic hydrogenation of **10** in ethyl acetate over standardized 10% palladium on charcoal gave saturated diketo diester **11** stereospecifically (100%): mp 213 °C dec; ir (KBr) ν 1730 cm^{-1}; ^{13}C NMR (ppm, $CDCl_3$) 217.25, 171.90, 62.32, 61.48, 57.01, 53.08, 51.86, 51.32, 43.22, 38.88, and 24.40. Thus, delivery of hydrogen operates exclusively from the sterically unencumbered convex surface, necessitating that the cyclopentanone units be projected to the inner regions of the developing sphere.



The highly folded nature of **11** is revealed by its chemical reactivity. Reduction with sodium borohydride in methanol at 0 °C, for example, effected further cyclization and formation of dilactone **12** (86%): mp 225-226.5 °C dec; ir (KBr) 1732 cm^{-1}. The relatively simple ^1H NMR spectrum ($CDCl_3$) exhibits multiplets at δ 4.91 (2 H), 3.13-2.47 (12 H), 2.36-2.03 (4 H), and 1.78-1.46 (2 H). The ^{13}C NMR spectrum ($CDCl_3$) contains only ten lines (172.13, 86.52, 59.61, 59.09, 54.80, 52.78, 45.83, 41.54, 37.44, and 23.86 ppm) as required for maintenance of a molecular C_2 axis. The presence of this symmetry element means that **12** (and similar molecules) can be viewed as an intermediate possessing but one functional group!

Various types of molecular models reveal the sphericality of **12** to be adequate to seriously limit the entry of solvent molecules into the cavity. As this phenomenon relates to synthetic design, it means that further manipulation of the system will require little attention to stereochemical control since presumably all reagents are hereafter relegated to convex attack. This feature is revealed by the reductive central bond cleavage in **12** which was brought about with sodium and trimethylsilyl chloride in refluxing toluene.[6] The resulting bistrimethylsilyl enol ester (**13**) was not purified, but hydrolyzed directly with methanol. Lactone **14** (mp 255-259.5 °C dec) was thereby produced (82%): ir (KBr) 1715 cm^{-1}; ^{13}C NMR (ppm, $CDCl_3$) 173.03, 84.06, 65.12, 51.47, 50.45, 46.94, 45.48, 41.27, 39.44, and 27.25.[7] Confirmation of the structural assignment to **14** and elaboration of its key molecular dimensions have been accomplished through x-ray crystal structure analysis.[8]



Elaboration of dodecahedrane (**1**) from triseco precursor **14** requires development of a dehydrative retro-Baeyer-Villiger sequence which will not trigger transannular reactions, and ultimate closure by threefold C-C bond formation. This and other approaches to **1** remain under active investigation.

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Preparation and Reactivity of Dithioether Dications $[R_2S^+-^+SR_2]$: a New Functional Group

Sir:

We wish to report the preparation and reactivity of dicationic dithioethers containing a sulfur-sulfur bond, $[R_2S^+-^+SR_2]$. These species are easily formed by a two-electron oxidation of mesocyclic dithioethers (1,5-dithiacyclooctane, DTCO, and 1,6-dithiacyclodecane, DTCD) with $NOBF_4$ or $NOPF_6$ in acetonitrile. The $R_2S^+-^+SR_2$ functional group has never been reported before, and preliminary studies of the chemistry of the $DTCO^{2+}$ dication have shown that these di-