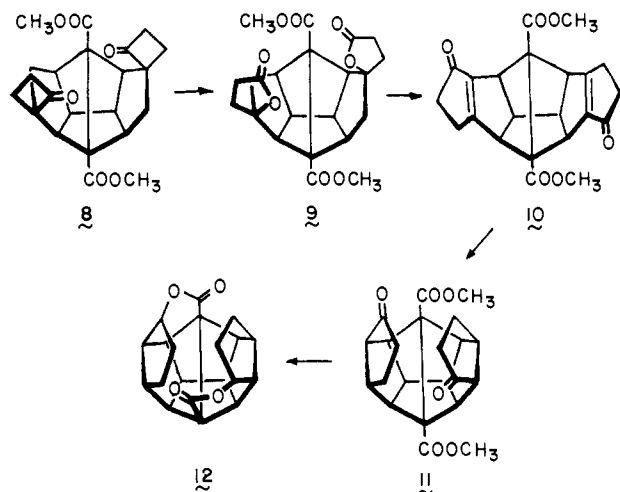


68% purified overall yield. The identity of **4** follows from its ^1H (e.g., a 6 H methyl singlet at δ 3.66) and ^{13}C NMR spectra (eight lines); the contrasting C_s nature of **3** is equally self-evident (methyl peaks at δ 3.70 and 3.63; 11 ^{13}C signals).

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.

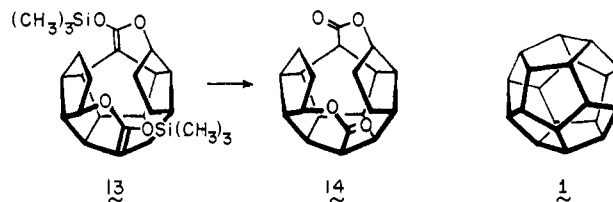
In this context, **8** was converted to dilactone **9** (100%) with 30% hydrogen peroxide solution. The latter could be conveniently transformed to bisenone **10** (65%) by treatment with phosphorus pentoxide in methanesulfonic acid (50 °C, 36 h).⁵ Catalytic hydrogenation of **10** in ethyl acetate over 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 sphericity 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 bis-

trimethylsilyl 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 [$\text{R}_2\text{S}^+-\text{SR}_2$]: a New Functional Group

Sir:

We wish to report the preparation and reactivity of dicationic dithioethers containing a sulfur–sulfur bond, [$\text{R}_2\text{S}^+-\text{SR}_2$]. 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 $\text{R}_2\text{S}^+-\text{SR}_2$ functional group has never been reported before, and preliminary studies of the chemistry of the DTCO^{2+} dication have shown that these di-

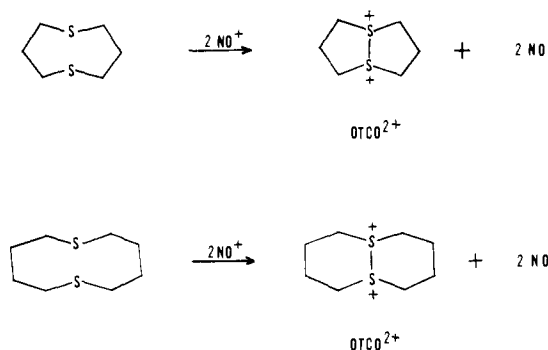


Figure 1. The reaction of DTCO and DTCD with NO^+

cationic species behave either as electrophiles or as two-electron oxidizing agents.

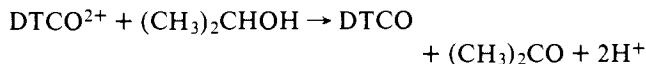
Although these dications are formed by the oxidation of dithioethers, they may also be viewed as dialkylated disulfides. However, disulfides have never been dialkylated. Only monoalkylation is achieved¹ by treatment of disulfides with the reactive alkylating agent, $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$. Therefore an oxidative coupling of two dithioether groups may provide the only route to this class of compounds.

The DTCO^{2+} dication is prepared by adding a solution of 1 mol of DTCO in acetonitrile ($\sim 10^{-1}$ M) to 2 mol of solid NOBF_4 on a vacuum line. As the NOBF_4 reacts, the solution turns yellow (the color of the cation radical, $\text{DTCO}^{\cdot+}$) and NO is evolved.² However, after all the NOBF_4 has reacted the solution becomes colorless and exhibits no ESR signal. The evolved NO was measured and corresponds to >95% of the theoretical amount expected for a two-electron oxidation. The color and ESR spectrum of the $\text{DTCO}^{\cdot+}$ cation radical can be regenerated by adding 1 mol of DTCO to the solution containing DTCO^{2+} .



Fractional crystallization of the solution of DTCO^{2+} gives a colorless solid having the correct chemical analysis for $\text{DTCO}(\text{BF}_4)_2$ but exhibiting no ESR signal. The ^{13}C NMR spectrum of the dication in CD_3CN shows two peaks 53 and 35 ppm at a ratio of two to one. The ^1H NMR is also consistent with a compound having two different methylene groups but the splitting pattern is extremely complicated and could not be resolved. The DTCO^{2+} ion exhibits λ_{max} at 233 nm in acetonitrile with an extinction coefficient of 7×10^3 .

The DTCO^{2+} dication reacts either as an electrophile or as an oxidizing agent depending on the added reagent. When solid $\text{DTCO}(\text{BF}_4)_2$ is treated with a saturated aqueous solution of sodium bicarbonate, 1,5-dithiacyclooctane monosulfide is formed in 80% yield. Conversely, when DTCO^{2+} is treated with isopropyl alcohol in acetonitrile, acetone is observed as the oxidation product in 50% yield. Likewise treatment of the dication with I^- gives I_2 .



The ten-membered ring dithioether, DTCD, also reacts with NOBF_4 in CH_3CN to give the dication, DTCD^{2+} (λ_{max} 232 nm, ϵ 4×10^3 .) However, with DTCD the dication is formed without the intermediate cation radical being observed. Even when equimolar amounts of DTCD and DTCD^{2+} are mixed, no ESR signal is observed, and it appears that no reaction has taken place.

Solid $\text{DTCD}(\text{BF}_4)_2$ gives the correct elemental analysis and exhibits ^1H and ^{13}C NMR spectra in CD_3CN which are consistent with the proposed DTCD^{2+} dication.

Another example of a dication with an $\text{S}^{+}-\text{S}^+$ bond is found in the S_8^{2+} ion formed by oxidizing S_8 with AsF_5 .³ The crystal

structure analysis of $\text{S}_8(\text{AsF}_6)_2$ shows that the eight-membered ring is fused in a cis manner to give the [3.3.0]bicyclic system.⁴ At the present time the manner of ring fusion in DTCO^{2+} and DTCD^{2+} has not been determined. However, the S_8^{2+} unit should be viewed as the parent of this class of compounds with the DTCO^{2+} ion having all the nonbridging sulfurs in the eight-membered ring replaced by methylene groups.

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4-Homoadamanten-4-yl Triflate. Ring Contraction and Ion Pair Return in Trifluoroethanol

Sir:

Carbenium ions from saturated adamantane and homoadamantane precursors do not undergo nondegenerate 1,2-hydride shifts,¹ presumably because of molecular rigidity and orthogonality between the vacant carbon orbital and an adjacent C-H bond.²

Pursuant to enticing this hydride shift we wish to report that the unsaturated homoadamantane Ia,³ in which the C_4 substituent orbital is held in-plane with the tertiary C_3 -H bond, solvolyzes at 100 °C to give ring contracted primary triflate IVa.⁴ Products Ib and III, the latter resulting from a 3,4-in-plane hydride shift, were not detected.⁵ Solvents used were neat trifluoroethanol (TFE) and 90% TFE in water, both buffered with pyridine, and neat pyridine. Even in the aqueous system the yield of IVa was minimally 95% and no 4-homoadamantanone was detected. At 150 °C in buffered TFE or in pyridine the initial formation of IVa was followed by slow⁶ conversion of IVa to IVb.⁷ There was no indication (VPC) that ring expansion of IVa to Ib occurred.

There is neither literature precedent for secondary to primary vinyl carbenium ion rearrangement,⁸ for complete lack of formation of ketone hydrolysis product in aqueous solvents, nor for complete capture of the "leaving" triflate group by the "cation"⁹ intermediates. Our observation of these phenomena upon solvolysis of Ia deserves comment.

Internal return and $\text{S}_{\text{N}}1$ character are known factors in vinyl substrate solvolyses.⁹ In TFE, a solvent most capable of separating ion pairs, solvent, *but not internal ion*, captured products usually predominate. The fact that the triflate group from Ia is retained in this medium, neat or aqueous, is unexpected and points to the formation of either: (1) an intimate ion pair intermediate of bent vinyl cation IIa that undergoes ring contraction^{6,8} to generate a linear (stabilized¹⁰) but primary destabilized⁸) vinyl cation which neutralizes itself by internal return; or (2) a bridged¹¹ intermediate IIb in which the triflate group is transferred from the C_4 to C_5 carbon as C_6 starts to bond to C_4 . Note that the geometry of Ia places the C_5 - C_6 bond *in-plane and vicinally trans*¹² to the "leaving" triflate. Either reaction path speculated above would benefit by the shielding of the side of C_4 opposite the departing group