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## Stereospecific Acid-Catalyzed Rearrangement of 1,6-Dimethylpentacyclo[6.4.0.0$^{2,7}$.0$^{3,10}$.0$^{6,9}$]dodecane-5,12-dione to a Bisnordiadamantane

*Sir:*

On treatment with trifluoroacetic acid at room temperature, pentacyclo[6.4.0.0$^{2,7}$.0$^{3,10}$.0$^{6,9}$]dodecane-5,12-diones having a methyl group at C-2 (**1**), synthesized photochemically from Diels-Alder dimers (**2**) of cyclohexa-2,4-dienones, reverted easily to **2** in high yield.[1] Stabilization of a carbonium ion at C-2 by a methyl group was assumed to be the most important requirement for this acid-catalyzed reversion.[1b]

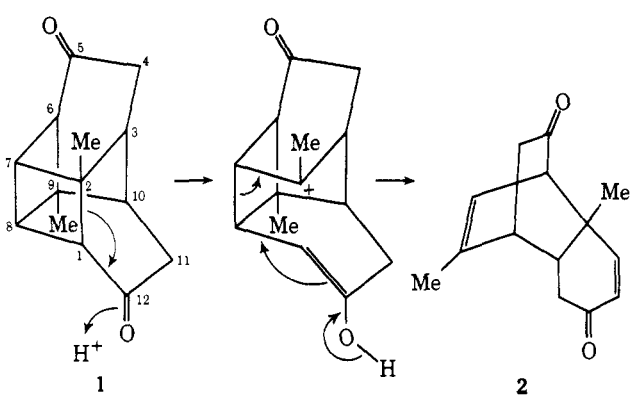
A cage compound, with a methyl group at C-1, on acid treatment would be expected to release most of the strain of the bicyclo[2.2.0]hexane system in a different way as shown here by the stereospecific rearrangement of the representative **3**.

When **3** was heated under reflux in trifluoroacetic acid for 15 min, or in benzene with *p*-TsOH for 45 min, the isomeric rearrangement product **4** was isolated in almost quantitative yield: mp 182–184°, from *n*-hexane; $\nu^{Nujol}$ 1735 cm$^{-1}$; *m/e* 272 (M$^+$); $^1$H nmr $\delta^{CDCl_3}$ 0.84 (s, 6 H), 0.96 (s, 6 H), 0.96 (s, 6 H), 1.03 (s, 6 H), 2.38 (m, 4 H), 2.48 (m, 2 H); $^{13}$C nmr $\delta^{CDCl_3}$ 11.6 ($CH_3$), 20.6 ($CH_3$), 26.8 ($CH_3$), 48.4 (C), 52.2 (CH), 53.8 (CH), 57.2 (C), 57.5 (CH).

Protonation of one of the carbonyl groups in **3** causes the formation of the methyl-stabilized carbonium cation at C-1 through rearrangement of either bond a or b, followed by another set of *twofold Wagner–Meerwein rearrangements* to yield a less strained cage compound, such as **4**, **5**, or **6**. A few precedents of such rearrangements have been reported in simpler cases, propellanones[2] and spiranone.[3] Both **4** and **5** have a twofold axis of symmetry whereas **6** has not. Since $^1$H and $^{13}$C NMR spectra clearly indicate that the product is symmetric, **6** is excluded. Although it is impossible to distinguish between **4** and **5** by the usual spectral data, there is a marked difference in their dipole moments: estimated value for **4** ca. 4.0 D; and for **5** ca. 0.0 D. The observed value (ca. 4.2 D) shows that **4** is the correct structure, a conslusion which is confirmed by Roentgen-ray analysis.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 6.818 (4) Å, $b$ = 12.586 (5) Å, $c$ = 17.966 (8) Å, and $\beta$ = 106.8 (1)°. There is one molecule per asymmetric unit corresponding to a calculated crystal density of 1.22 g/cm$^3$. The structure was solved by the symbolic addition procedure for centrosymmetric crystals[4] and refined by full-matrix least-squares methods[5] to an $R$ factor of 5.8%. The stereodrawing[6] in Figure 1 which was constructed with the experimentally determined atomic coordinates displays the results of the X-ray analysis. Within experimental error, the molecule has twofold rotation symmetry.[7] So far cedrone[8] seems to be the only other representative of the interesting bisnordiadamantane type.

The most important reason for the favored rearrangement of bond a must lie in the stability difference between the rearranged cations **3a** and **3b** both of which arise by conversion of the strained four, six, six-membered ring system in **3** (thick line) to the more stable five,five,six system with release of strain energy. Inspection of models clearly indicates that the six-membered cationic structures, **3a** and **3b** (shaded parts), are quite different, though the strain in the remainder of the molecules may be the same. The six-membered ring in **3a** is present in a normal chair conforma-



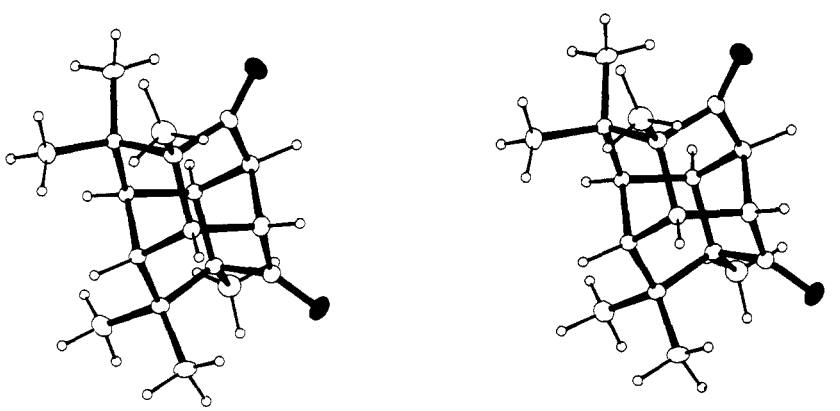
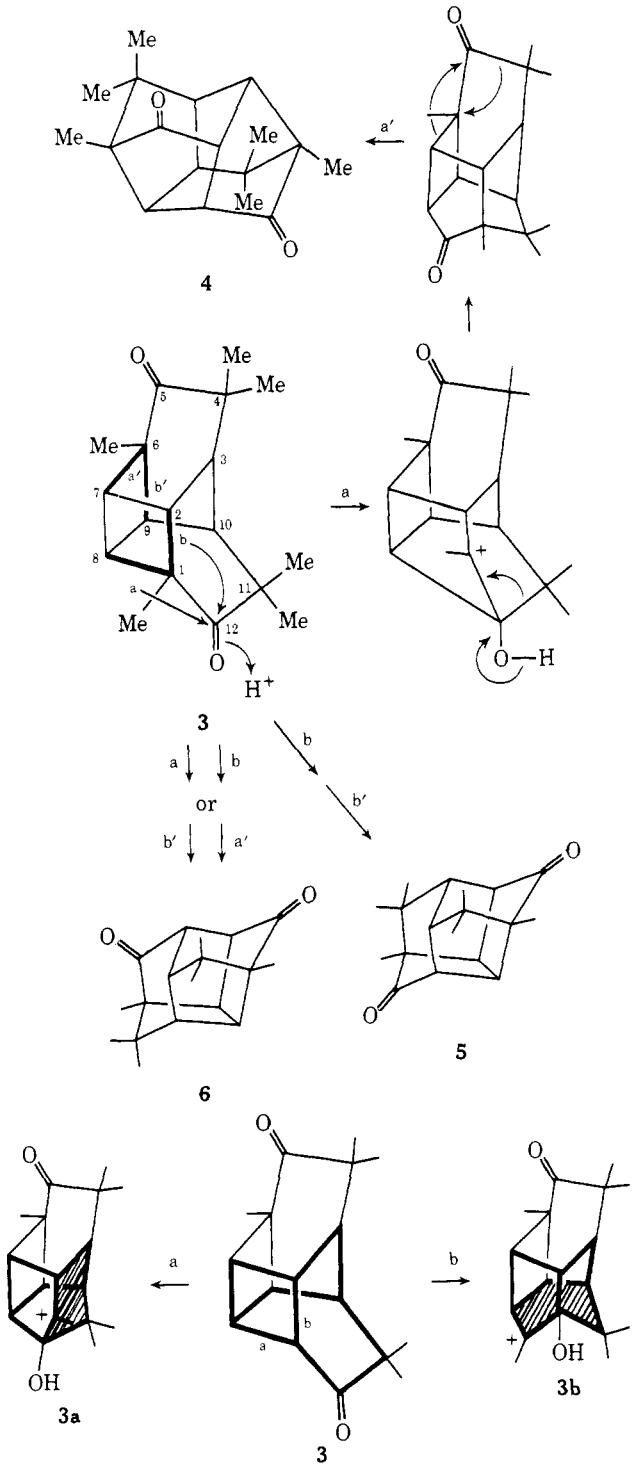



**Figure 1.** Stereodrawing of compound **4** executed with the experimentally determined coordinates from a crystal structure analysis. The shaded ellipses represent oxygen atoms.



tion, whereas in **3b** the chair conformation is strongly distorted by a directly fused four-membered ring, destabilizing the structure of **3b.**

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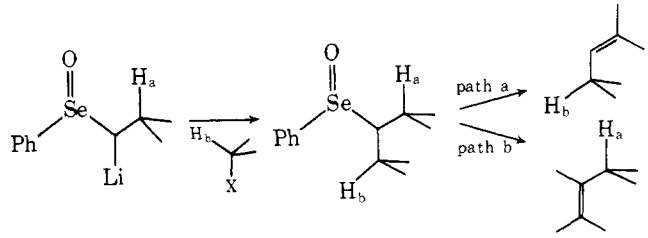
## Organoselenium Chemistry. α-Lithio Selenoxides and Selenides. Preparation and Further Transformation to Olefins, Dienes, and Allylic Alcohols

*Sir:*

Functionalized organolithium reagents have assumed an important role in synthetic organic chemistry. We report here the preparation and some reactions of several selenium stabilized organolithium reagents,[1] and synthetic applications based on the facile syn elimination of the selenoxide function.[2-4] The reaction products of selenium stabilized organolithium compounds with electrophiles could in general undergo selenoxide elimination in two directions.[5] Elimination away from the newly formed C-C bond (path a) results in an overall transformation synthetically equivalent to the operation of a vinyl anion; whereas, elimination across the new C-C bond (path b) results in a coupling of halides to form an olefin (alkyl selenides are usually prepared by nucleophilic displacements of halides or sulfonates by PhSe-Na). To be synthetically useful, reactions of this type must have one pathway predominant, either because one elimination is blocked (no $H_a$ or $H_b$) or by the operation of factors favoring one pathway over the other. We have found systems in which the exclusive operation of either path a or path b can be achieved.



Methyl phenyl and benzyl phenyl[7] selenoxides cannot undergo selenoxide elimination, and so preparation and handling pose no special problems. They are rapidly deprotonated at −78° by lithium diisopropylamide (LDA) giving the anions **1** and **2.** Longer chain alkyl selenoxides having β-hydrogens must be handled below 0° to avoid the elimination reaction. We have developed procedures for the low temperature in situ oxidation of phenyl alkyl selenides (by ozonization in ether at −78°,[8] or reaction with *m*-chloroperbenzoic acid in THF at −10° [9]), and for deprotonation