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An Anomalous Reaction of Dimethyloxosulfonium Methylide

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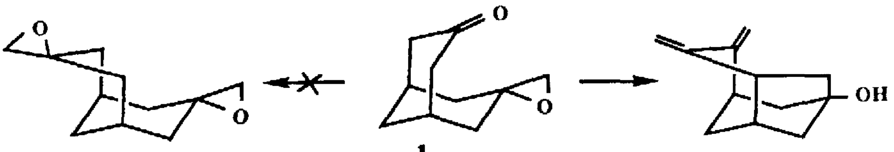
Abstract: On treatment with dimethyloxosulfonium methylide in the presence of sodium methylsulfinylmethide, 3-methylenebicyclo[3.3.1]nonane-7-one oxide undergoes an unusual transformation to 4,5-dimethylenetricyclo[4.3.1.0^{3,8}]decane-1-ol.

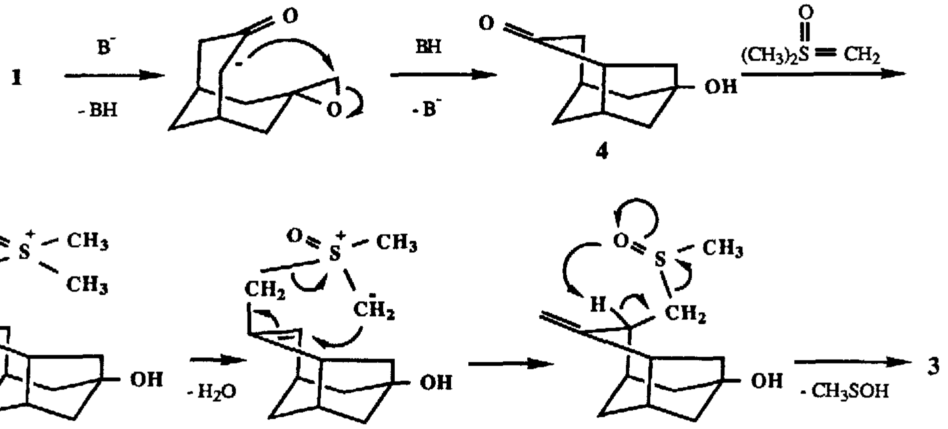
Dimethyloxosulfonium methylide is an extremely important reagent for preparing oxiranes^{1} or cyclopropanes.^{2} However, our attempt to obtain diepoxide **2** from 3-methylenebicyclo[3.3.1]nonane-7-one oxide **1** was unsuccessful. Instead of the desired product, an unsaturated alcohol was formed^{3a} to which the structure 4,5-dimethylenetricyclo[4.3.1.0^{3,8}]decane-1-ol **3** was assigned by analysis of spectroscopic data.



2 **1** **3**

A molecular weight of 176 was indicated from mass spectrometry, (m/Z 176, electron impact at 70 eV). The ^{13}C NMR spectrum showed the presence of 12 carbons (3 quarternary, 3 tertiary and 6 secondary) and suggested that the molecule had two carbon-carbon $C = CH_2$ double bonds (δ 32.83, 35.58, 38.25, 41.40, 45.32, 47.05, 47.42, 77.08, 106.39, 108.29, 149.93, 152.37). Sixteen protons were accounted for from the ^{1}H NMR data: four olefinic protons (δ 4.50, 1H, d, J = 2 Hz; 4.65, 1H, s; 4.85, 1H, d, J = 2 Hz; 5.07, 1H, s), a hydroxy proton (δ 3.57) and 11 protons of the protoadamantane nucleus. The ^{1}H NMR spectra in the presence of Eu(fod)$_3$ indicated that the olefinic protons were quite distant from the hydroxy group. IR spectra showed the absorption of a hydroxy group (3610 cm^{-1}) and C-C double bonds ($\nu_{C=C}$, 1638 and 1341 cm^{-1}, $\nu_{C\text{-}H}$, 3085 cm^{-1}). The UV spectrum showed a band for the absorption of conjugated double bonds (λ_{max} 237.6 nm, log ε 4.06, dioxane).

The first stage of the processes was proved to be a cyclization reaction. The anion, generated from oxide **1** by a strong base, yielded tricyclo[4.3.1.0^{3,8}]decane-1-ol-4-one^{3b} **4**, which was converted to the same diene **3** as was formed from oxide **1** under dimethyloxosulfonium methylide treatment, but in much lower yield.^{3c} The next stages may include dehydration, sigmatropic rearrangement and abstraction of methylsulfenic acid[4] to give 4,5-dimethylenetricyclo[4.3.1.0^{3,8}]decane-1-ol **3**.



Although some unusual rearrangements of sulfur ylides are known,[5] the above-mentioned transformation represents a reaction of a novel type.

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References and Notes

1. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., **84**, 867 (1962).
2. B. Loev, M. F. Kormendy and K. M. Snader, Chem. Ind., 1710 (1964).
3. (a) Typical procedure: Trimethyloxosulfonium iodide (0.863 g, 3.9 mmol) was added under argon to a stirred dispersion of NaH (0.80 g, 33.3 mmol) in 70 ml DMSO. After the addition was complete (5 - 10 min.) the mixture was stirred for 0.5 hr at 25° C, then solution of **1** (0.50 g, 3 mmol) in dry DMSO (20 ml) was added and the mixture was stirred for 20 min at 115 - 120° C. The reaction mixture was poured on to ice and extracted with chloroform. Usual work-up led to a crude product which was purified by chromatography on aluminium oxide (elution with diethyl ether - methanol, 19 : 1) to give 0.129 g (0.78 mmol, 26%) pure **3**.

   (b) 1-Hydroxyprotoadamantane-4-one **4** was obtained by treatment of **1** (0.5 g, 3 mmol) with sodium or potassium methylsulfinylmethide in DMSO (0.8 g, 33.3 mmol NaH - 20 ml DMSO or 1.0 g, 8.9 mmol t-BuOK - 20 ml DMSO) at 115 -120° C . Yield 29 - 47.6%.

   (c) When **4** had been used as a starting compound, diene **3** was isolated in 3 -5% yield.
4. C. A. Kingsbury and D. J. Cram, J. Am. Chem. Soc., **82**, 1810 (1960).
5. For reviews see: S. Braverman in "The chemistry of sulfones and sulfoxides". S. Patai, Z. Rappoport, Eds.; Wiley, New York, 1988; chapter 14. E. Block. Reactions of organosulfur compounds; Academic Press, New York, 1978. B. M. Trost, L. S. Mevin, Jr. Sulfur ylides; Academic Press, New York, 1975.

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