

189. Nucleophilic Additions to Unactivated Carbon-Carbon Double Bonds. Base-Catalysed Ether Formation

Preliminary Communication

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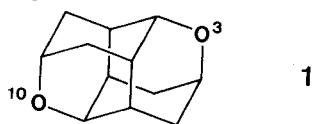
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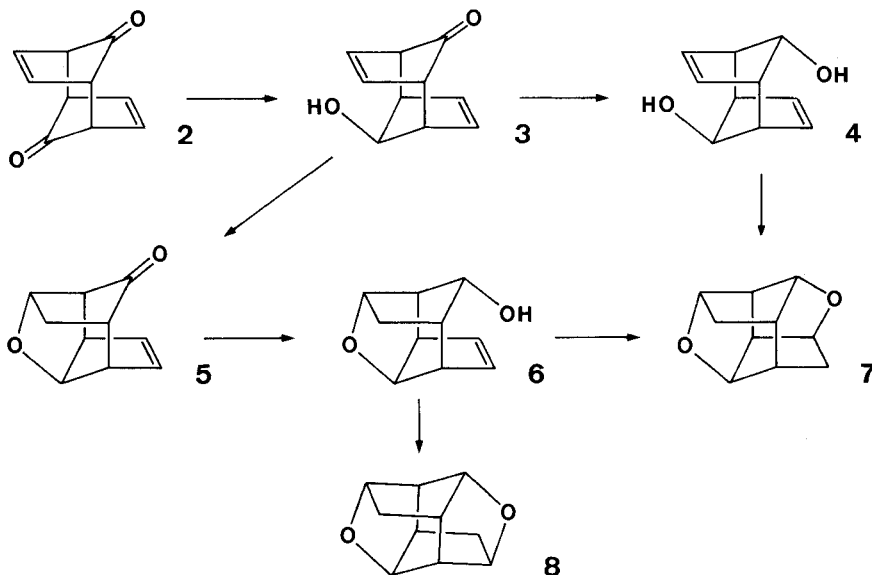
Summary

Several examples ($3 \rightarrow 5$, $4 \rightarrow 7$, $6 \rightarrow 7$, $9 \rightarrow 10$) of base-catalysed intramolecular ether formation involving nucleophilic attack on an unactivated carbon-carbon double bond are described.

In our synthetic approach to 3,10-dioxadamantane (**1**)¹⁾ we chose the known *anti*-cyclopentadienone dimer **2** [2] [3] as starting material. However, before at-

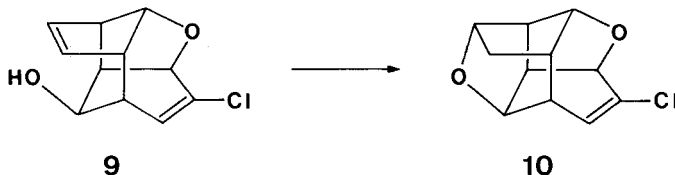


tempting to introduce the two additional carbon atoms, we focused our attention on ether formation from compounds structurally related to **2**. In our synthetic studies



¹⁾ See [1].

towards the isomeric diethers 7^2) and 8^2), the best results (almost quantitative yields) for cyclizations $3^2 \rightarrow 5^2$, $4^2 \rightarrow 7$, and $6^2 \rightarrow 7$ were obtained by reaction of the unsaturated alcohols **3**, **4** or **6**, respectively, in 2N aqueous NaOH/CH₃OH 1:1 either at room temperature for several days or at approximately 60° for several hours. Similarly compound 9^2) cyclized to 10^2).



These reactions must involve base-catalysed ether formation initiated by *nucleophilic attack on a carbon-carbon double bond, even though the latter bears no electron-attracting groups*³⁾. The matter is under further investigation.

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REFERENCES

- [1] W. Ammann, R. A. Pfund & C. Ganter, *Chimia* 31, 61 (1977).
- [2] E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta & K. Schaffner, *Helv.* 50, 297 (1967).
- [3] U. Klinsman, J. Gauthier, K. Schaffner, M. Pasternak & B. Fuchs, *Helv.* 55, 2643 (1972).

²⁾ Analytical and spectral data of all new compounds are in full agreement with the assigned structures. Compound **7** was prepared both as a racemate and optically active. The isomer **8** is achiral. The unsaturated alcohols were prepared as follows: NaBH₄-reduction in CH₃OH/H₂O at 0° yielded **3** from **2** (75 min), **4** from **3** (4 days), and **6** from **5** (5h); NaBH₄-reduction in CH₃OH/2N aqueous NaOH of the dichlorocarbene monoadduct of **2** gave **9**. Full experimental details will be given elsewhere.

³⁾ These results were first presented in a lecture at the University of Basel (December 13, 1974). Prof. C. A. Grob informed us then that he had also observed base-catalysed additions of this type



starting from **11** and **12**, however, only under more drastic conditions (15 h at 150° in a sealed tube in the presence of NaOEt, LiOEt or KOEt in ethanol); see C. A. Grob & H. Katayama, *Helv.* 60, 1890 (1977).