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

Preliminary Communication

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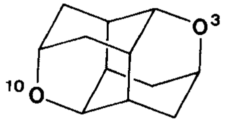
Summary

Several examples (**3**→**5**, **4**→**7**, **6**→**7**, **9**→**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-dioxadiamantane (**1**)1) we chose the known *anti*-cyclopentadienone dimer **2** [2] [3] as starting material. However, before attempting to introduce the two additional carbon atoms, we focused our attention on ether formation from compounds structurally related to **2**. In our synthetic studies



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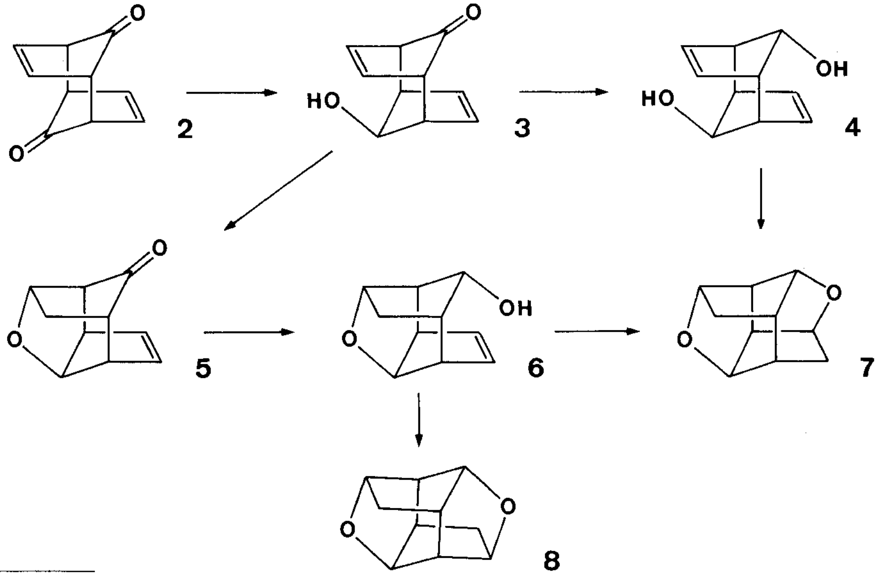

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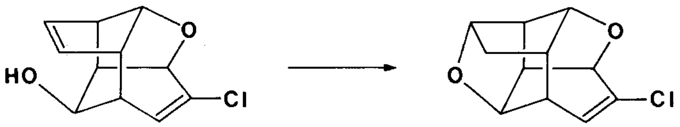
1) See [1].

towards the isomeric diethers **7**[2]) and **8**[2]), the best results (almost quantitative yields) for cyclizations **3**[2]) → **5**[2]), **4**[2]) → **7**, and **6**[2]) → **7** were obtained by reaction of the unsaturated alcohols **3**, **4** or **6**, respectively, in 2N aqueous $NaOH/CH_3OH$ 1:1 either at room temperature for several days or at approximately 60° for several hours. Similarly compound **9**[2]) cyclized to **10**[2]).



9 **10**

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).

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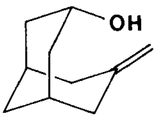
[2]) Analytical and spectral data of all new compounds are in full agreement with the assigned structures. Compound **7** was prepared both as a racemate and optically active. The isomer **8** is achiral. The unsaturated alcohols were prepared as follows: $NaBH_4$-reduction in CH_3OH/H_2O at 0° yielded **3** from **2** (75 min), **4** from **3** (4 days), and **6** from **5** (5h); $NaBH_4$-reduction in CH_3OH/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



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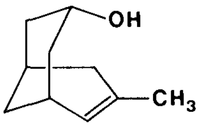

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starting from **11** and **12**, however, only under more drastic conditions (15 h at 150° in a sealed tube in the presence of NaOEt, LiOEt or KOEt in ethanol); see *C. A. Grob & H. Katayama,* Helv. *60,* 1890 (1977).