CHEMISTRY LETTERS, pp. 1297-1298, 1976. Published by the Chemical Society of Japan

DMSO OXIDATION OF CYCLOPROPYLMETHANOLS WITH REARRANGEMENTS. A THREE CARBON CHAIN EXTENTION OF ALDEHYDES TO α,β-UNSATURATED ALDEHYDES

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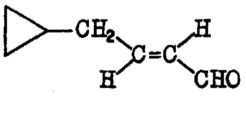
A rearrangement of cyclopropylmethanols in hot DMSO followed by in situ oxidation and double bond isomerization gave conjugated enals. The transformation was performed in a single operation. Utilization of cyclopropylmagnesium bromide provides a new route for the three carbon chain extention of aldehydes.

During the course of an investigation of the dehydration of cyclopropylmethanol derivatives in hot dimethyl sulfoxide (DMSO), it was realized that the major product isolated in some cases was a conjugated enal. For example, heating of dicyclopropylmethanol in DMSO at 165-170°C for 13 min in the presence of a trace amount of boron trifluoride etherate (0.4% by weight) gave *trans*-4-cyclopropylbut-2-enal (1, isolated in 39% yield as a 97% pure liquid, bp 74-75°C/ 21 Torr; semicarbazone, mp 183-184°C)[1] and 4-cyclopropylbut-3-enol (2, 5%).[2]



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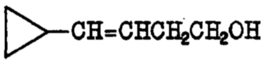

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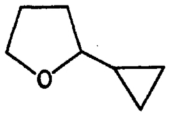

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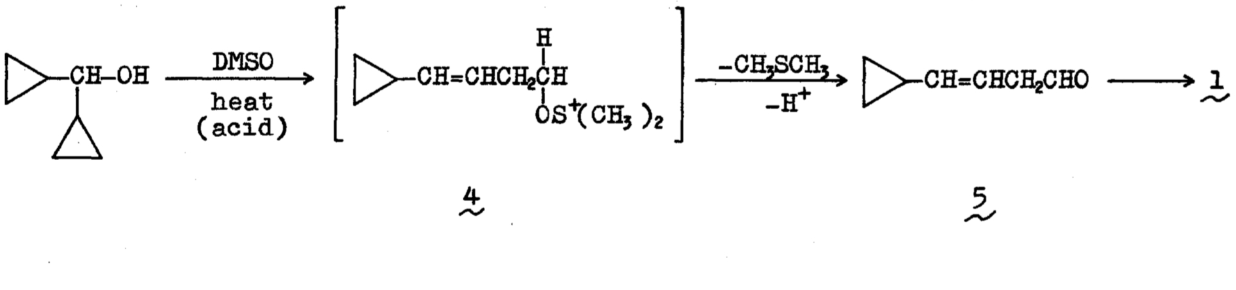
The reaction will most probably involve a cyclopropane cleaved sulfonium ion 4. The ring cleaved alcohol 2 is not an intermediate of the reaction, because a treatment of 2 under similar conditions (DMSO, BF_3 etherate, 170°C for 5 hr) yielded a furan derivative 3 (59%) instead of 1, and there was no indication for the production of 1 during the treatment. The elimination of dimethyl sulfide from 4 together with a loss of an α-proton is a well-known process in the DMSO oxidation,[3] and the resulting aldehyde 5 isomerizes to 1 under the reaction conditions.



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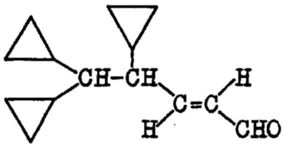
A similar treatment of 1,1,2,2-tetracyclopropylethanol[4] (DMSO, BF_3 etherate, 170°C for 30 min) yielded a conjugated enal 6 (41%; 2,4-dinitrophenylhydrazone, mp 137-138°C),[1] a furan 7 (10%), and an unidentified product (ca. 15%). On the other hand, certain tertiary carbinols, such as 1-cyclopropylcyclopentanol and 1-cyclopropylcyclohexanol, underwent dehydration predominantly and corresponding olefins were obtained in 37-58% yields.



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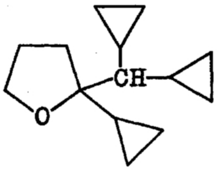

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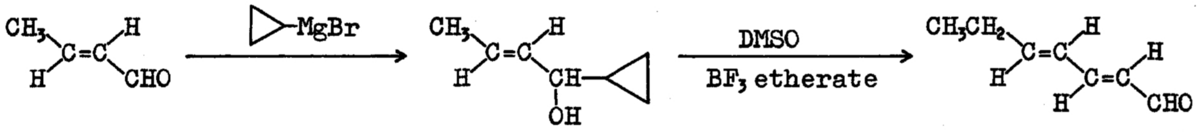
Since secondary cyclopropylcarbinols can be prepared from aldehydes and cyclopropylmagnesium bromide and transformed into α,β-unsaturated aldehydes, a sequence of the reactions can be a new and convenient way of extending a chain of the aldehydes in a three carbon unit. This was realized in a following example. A treatment of 1-cyclopropylbut-2-enol, which was prepared from crotonaldehyde, produced fully conjugated <u>trans</u>,<u>trans</u>-hept-2,4-dienal in 25% yield.[1]



Although the yields are moderate, a rather short step synthesis of <u>trans</u>-α,β-unsaturated aldehydes is a major advantage of the present transformation.

Acknowledgement. The authors are grateful for a Grant-in-Aid for Scientific Research from the Ministry of Education which supported the present work.

References and Notes

1) Satisfactory elemental analysis and spectroscopic data were obtained. For example, the enal 1 exhibited the following spectroscopic characteristics: IR (liquid film) 3095, 3015, 2900, 2820, 2740, 1695, 1020, 980 cm^{-1}; NMR (CCl_4) δ 9.40 (d, J=7.7 Hz, 1 H), 6.79 (d of t, J=15 and 5.6 Hz, 1 H), 6.07 (d of d of t, J=15, 7.7, and 1.7 Hz, 1 H), 2.21 (d of d of d, J=6, 5.6, and 1.7 Hz, 2 H), 0.65-1.03 (m, 1 H), -0.05-0.65 (m, 4 H); UV (ethanol) λ_{max} 218 nm (ε 19,000).

2) Comparisons were made with an authentic sample.

3) W. W. Epstein and F. W. Sweat, Chem. Rev., 67, 247 (1967); R. F. Butterworth and S. Hanessian, Synthesis, 1971, 70.

4) A. Nierth, H. M. Ensslin, and M. Hanack, Justus Liebigs Ann. Chem., 733, 187 (1970).

(Received October 5, 1976)