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ABNORMAL PINACOL REARRANGEMENTS

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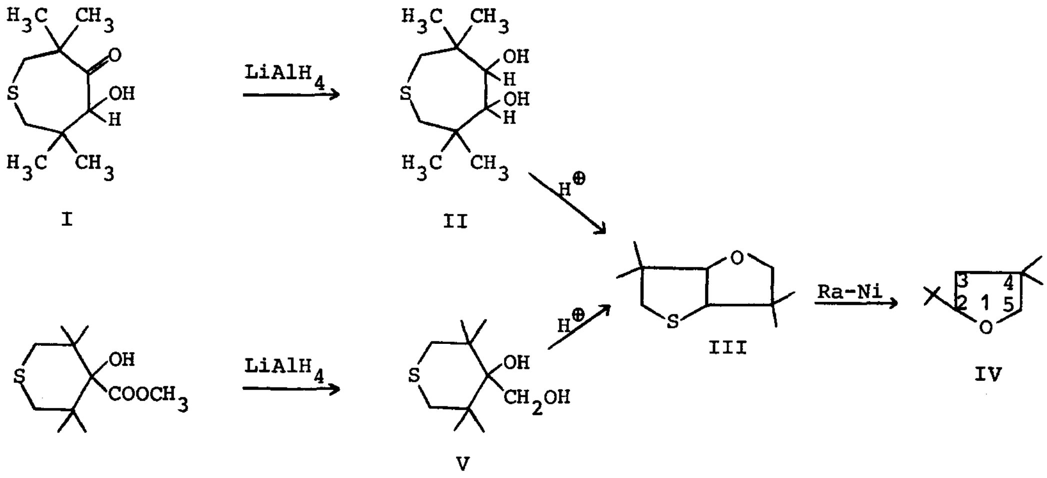
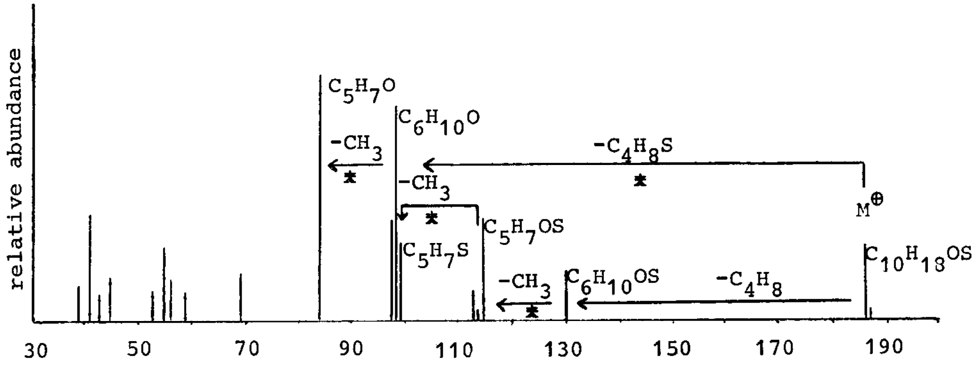
In our study of the reactions of the 3,3,6,6-tetramethyl-1-thiacycloheptane system (1,2) we prepared the diol II (3) by reduction of the hydroxy ketone I (2) with lithium aluminum hydride. Upon treatment of this diol with a few drops of concentrated sulfuric acid in boiling acetic acid the bicyclic compound III (Anal., calcd. ($C_{10}H_{18}OS$): C, 64.45; H, 9.74; S, 17.41; found: C, 64.5; H, 9.7; S, 17.1), b.p. 94 - 96°/13 mm, was isolated as the only product in a 66% yield.



The infrared spectrum of 3,3,6,6-tetramethyl-1-oxa-4-thia bicyclo[3,3,0]octane (III) shows no carbonyl or hydroxyl absorption, but an absorption at 1060 cm^{-1} indicating an ether linkage. The nmr spectrum (10% in carbon tetrachloride) shows six doublets with a total integration area of 6 protons at τ 5.93, 6.01 and 6.57, 6.62; 6.30, 6.43 and 6.57, 6.70; 7.13, 7.30 and 7.65, 7.82 and two singlets at τ 8.88 and 8.98 (integration area of 12 protons). The mass spectrum of compound III is given in Fig. 1 (4). In addition to a parent peak at 186 confirming the formula for III as $C_{10}H_{18}OS$, the fragmentation pattern shown in Fig. 1, is in accord with the assigned structure. The identity of the peaks is confirmed by exact mass measurement.

FIG. 1

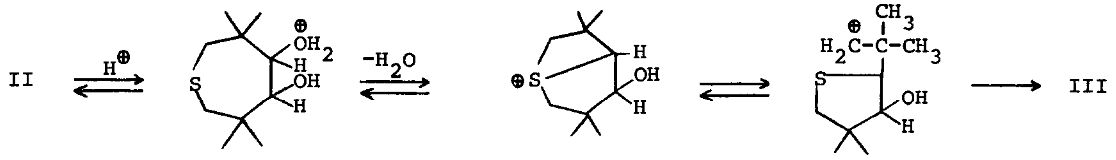


Support for the structure of III was obtained by its desulfurization. Treatment of III with Raney-Ni W 7 in alcohol furnished one product, b.p. 100-102°/110 mm, in 28% yield. In addition to its analysis as $C_{10}H_{20}O$ (calcd.: C, 76.87; H, 12.90; found: C, 76.7; H, 12.8), spectral evidence strongly indicated structure IV for this oil. The infrared spectrum of IV still shows the ether absorption at 1060 cm^{-1}. The nmr spectrum shows an ABX system at τ 6.27, 6.39, 6.42 and 6.54 (1 proton at C_2), a singlet at τ 6.63 (2 protons at C_5), an ABX system at τ 8.48, 8.63 and 8.64 (2 protons at C_3), a singlet at τ 8.93 (6 protons of two methyl groups at C_4) and a singlet at τ 9.15 (9 protons of the t-butyl group).

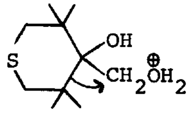
This abnormal pinacol rearrangement of diol II to yield as sole product III, was also found when diol V was treated under identical conditions. The identity of this latter product with the rearrangement product of II was established by nmr and infrared spectroscopy and by G.L.C.

Discussion.

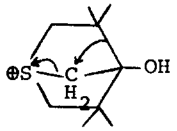
It is clear from structure III that one of the C-S bonds in diol II has been broken in this rearrangement. A transannular reaction involving the sulfur atom as conceptualized below formally explains the formation of III.



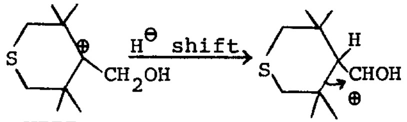
Although the formation of III from V cannot proceed by an identical path, a transannular reaction involving sulfur appears again an attractive possibility. It is necessary to assume a ring enlargement in this case. This ring enlargement can proceed in a concerted manner via the protonated primary hydroxyl group (ions VI and VII) or via the tertiary carbonium ion VIII.



VI



VII



VIII

Further work on these reactions is in progress.

References.

1. Ae. de Groot, J.A. Boerma, J. de Valk and Hans Wynberg, in preparation.

2. Ae. de Groot and Hans Wynberg, J. Org. Chem. 31, 3954 (1966).

3. Satisfactory elemental analytical data for this diol have been obtained.

4. We wish to thank Dr. C. Bokhoven of the Central Laboratory of the Dutch States Mines for his cooperation in the recording and the interpretation of this mass spectrum.