SYNTHESIS AND REACTIONS OF 1,2-CYCLOPROPANEDIOLS

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We recently reported the synthesis of cyclopropanediol derivatives via reduction of certain polyketones.[1] Publication of a similar report by Reusch and Priddy[2] prompts us at this time to communicate further details of our work on the preparation and reactions of this new class of compounds.

Reduction of I in the presence of acetic anhydride, either electrochemically or by a modification of the Clemmensen procedure, led to II in good yield.[1] A similar electrolysis of I in the presence of trimethylsilyl chloride produced the unstable bis trimethylsilyl derivative III (mp 52 - 55°; ir in CCl_4: 1740, 1080, 1055 cm^{-1}; nmr in CCl_4: 18H singlet at 0.20 δ, 6H singlets at 1.07 and 1.18 δ, 3H singlets at 0.97 and 1.05 δ) in high yield, as determined by gas chromatographic analysis of the crude reduction mixture. Addition of water to the electrolysate containing III produced the air-sensitive cyclopropanediol IV (mp 197 - 198°; ir in MeCN: 1735 and 3450 cm^{-1}; nmr in CD_3CN: 6H singlets at 1.05 and 1.20 δ, 3H singlets at 0.97 and 1.14 δ, OH at 3.2 δ), apparently identical to the diol obtained by Li-ammonia reduction of I.[2]

As part of our interest in the mechanism of the abnormal Clemmensen reduction,[3] we have studied the behavior of II and IV in acid media. Treatment of II with 2 M methanolic hydrochloric acid at reflux led to IV in 79% yield. During the early stages of this reaction we observed the formation of a second substance which slowly disappeared as the reaction proceeded. A trace of this material was also detected in the previously reported[1] rearrangement of II to VI by 9 M hydrochloric acid. On the basis of its spectroscopic properties (ir in CCl_4: 1755, 1710, 1600 cm^{-1}; nmr in CCl_4: 6H singlets at 1.08 and 1.25 δ, 3H singlets at 2.03 and 2.25 δ) and its formation from VI upon treatment with thionyl chloride in pyridine, we have assigned structure VII to this material.[4]

I

II   R = R' = Ac
III R = R' = (CH$_3$)$_3$Si
IV   R = R' = H
V   R = H, R' = Ac

VI

VII
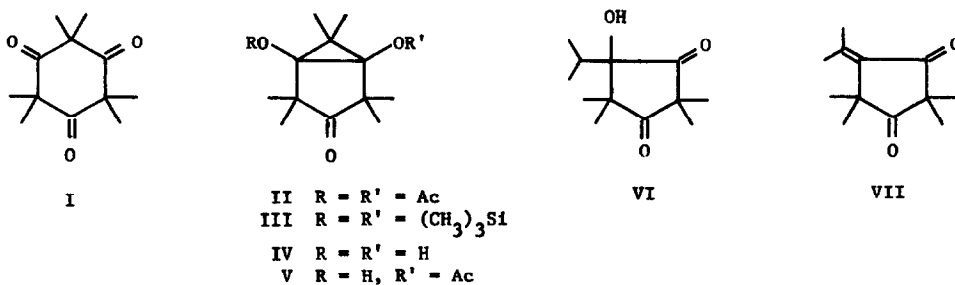
In contrast to the behavior of II, the diol IV, while unaffected by refluxing 2 M methanolic hydrochloric acid, was rearranged by refluxing 9 M hydrochloric acid cleanly to VI (78% isolated), with no trace of VII being detected. We interpret these experiments to mean that the enedione VII is formed in moderately strong acid only if one, or possibly both, of the cyclopropanediol hydroxyl groups are acylated. A reaction sequence which accounts for these results is that of Scheme 1. Solvolysis of diester II produces monoacetate V. Most of V is transformed further into diol IV, but a small fraction undergoes a concerted acid-catalyzed loss of acetic acid to form VII.[5] Under more vigorous conditions, diol IV then suffers an electrophilic ring-opening leading to ketol VI.

Scheme 1
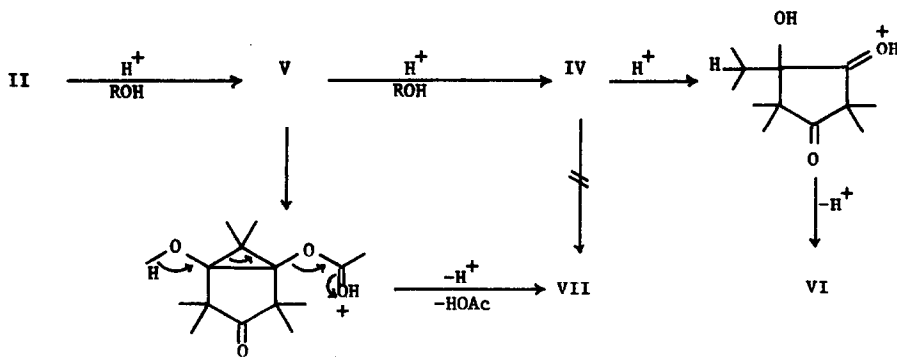
Two further comments concerning Scheme 1 may be made. First, the rearrangement of IV

to VI constitutes the first _direct_ proof of the correctness of the supposition[3,6] that cyclopro-

panediols formed by Clemmensen reduction of diketones rearrange predominantly, if not exclusively,

to ketols rather than to unsaturated ketones. Second, these experiments demonstrate that under

the appropriate conditions 1,2-cyclopropanediol derivatives undergo not only the electrophilic

attack on the ring typical of cyclopropanols[7] (_viz._ IV → VI), but also the concerted ionization-

ring opening reaction typical of cyclopropyl arenesulfonates[7] (_viz._ II → VII). It is thus

to be expected that even small changes in reaction conditions or in substituents will alter the

way in which these diol derivatives partition between the two reaction pathways.

Finally, we have sought evidence for the formation of a trishomocyclopropenyl cation[8] such

as VIII by examining the behavior of II in super acid media. In SO_2-SbF_5-FSO_3H solution at

-10° to -60°   II showed an nmr spectrum consistent with the presence of the triprotonated

species IX: δ(TMS capillary) 16.4 (s, 1H), 14.7 (s, 2H), 4.4 (s, 6H), 1.7 -2.2 (m, 18H).

Quenching of this solution led to 50% recovery of II, along with lesser amounts of I and VII.

No product was detected, such as V, which might reasonably have arisen from ion VIII. Warming

of super acid solutions of II to room temperature brought about rapid deacylation and oxidation

to trione I, obtained in 50% yield upon quenching with water. Although we cannot, on the basis

of the negative results of these crude experiments, rule out formation of the delocalized species

VIII or of a delocalized equivalent of IX, we suggest that, in view of the rather low driving

force associated with the formation of the trishomocyclopropenyl cation in systems not rigidly

locked in a chair conformation,[8] the severe interactions between axial groups in ions such as

VIII will prevent or strongly retard their formation. One might even question whether the classi-

cal ions equivalent to VIII can interconvert, the system presenting an interesting example of

steric inhibition of resonance.
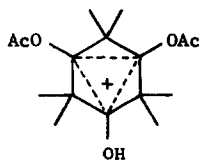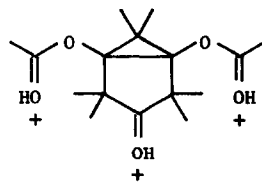
VIII   IX

Further studies of the synthesis and reactions of this new class of compounds are in progress.[9]

References

(1) T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCartney, and J. H. Williams, J. Am. Chem. Soc., 91, 2817 (1969).

(2) W. Reusch and D. B. Priddy, J. Am. Chem. Soc., 91, 3677 (1969). We thank Professor Reusch for sending us a copy of this communication prior to its publication, and we call attention to the accompanying communication giving further details of their work.

(3) T. J. Curphey and R. L. McCartney, J. Org. Chem., 34, 1964 (1969).

(4) Professor Reusch has informed us (personal communication) that he has observed formation of VII from the fluorosulfonic acid catalyzed rearrangement of IV.

(5) An alternative path for formation of VII would involve direct acid-catalyzed elimination of acetic anhydride from II. It is perhaps significant that the mass spectrum of II shows a major fragment at m/e 194 for loss of acetic anhydride, presumably leading also to VII and that a similar mechanism has been suggested (F. W. Breitbeil, D. T. Dennerlein, A. E. Fiebig, and R. E. Kuznicki, J. Org. Chem., 33, 3389 (1968)) to account for the thermolysis of 1,2-cyclopropanediol cyclic carbonates. Attempts to detect V as an intermediate have not been successful. However, even if VII is formed directly from II, the major conclusions of this communication remain unchanged.

(6) E. Wenkert and E. Kariv, Chem. Commun., 570 (1965); K. M. Baker and B. R. Davis, Chem. Ind. (London), 768 (1966).

(7) See C. H. DePuy, Accounts Chem. Res., 1, 33 (1968) for a summary and discussion.

(8) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, Tetrahedron, Suppl. No. 8, 621 (1966) and references therein; H. Tanida, T. Tsuji, and T. Irie, J. Am. Chem. Soc., 89, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, ibid., 89, 1954 (1967).

(9) Partial support from National Science Foundation Grant No. GP-8510 for the HA-100 nmr spectrometer used in this work is gratefully acknowledged.