ions, which must proceed *via* a transition state with a specific steric arrangement. Since the steric conditions for the transition state can be easily checked with the aid of molecular models, a mass-spectrometric identification of stereoisomers is possible in this way without the use of reference spectra.

It is known that a stereospecific 1,4-elimination of H_2O occurs in the molecular ions of cyclohexanol. Investigation of the mass spectra of stereoisomers of the cyclopentanediols, cyclohexanediols, and cycloheptanediols, and their dimethyl ethers also show stereochemical control for the elimination of HOR ($R = H, CH_3$) and CH_2O from the molecular ions if the substituents occupy the 1,3 or 1,4 positions. In the *trans* compounds the elimination of HOR dominates the fragmentation, whereas the elimination of CH_2O is characteristic of the *cis* compounds. The stereochemical control of the fragmentations also persists in *C*-methylated derivatives of 1,3-cyclohexanediol, with the exception of the 2-methyl and 2,2-dimethyl derivatives, in which fast ring cleavage of the molecular ions occurs.

Surprisingly, however, the expected steric effects cannot be detected in the mass spectra of the positional isomers and stereoisomers of the bicyclo[2.2.1]heptanediols and their dimethyl ethers. On the other hand, the expected effects are again observed in the mass spectra of decalindiols and of corresponding dimethyl ethers, so that mass-spectrometric identification of the stereoisomers is possible in this series of compounds. It is interesting to note that stereochemical control of the elimination reactions is also found for the 1,5-dimethoxydecalins if the methoxy groups can come close together in any conformation of the molecular ions.

Steric Effects in the Mass Spectra of Monocyclic and Bicyclic Diols and Their Derivatives

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The differences in the mass spectra of stereoisomeric compounds are partly due to elimination reactions of the molecular

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