

NMR STUDIES OF 7-CIS- β -IONOL AND RELATED COMPOUNDS.

RING-CHAIN CONFORMATIONAL PREFERENCE

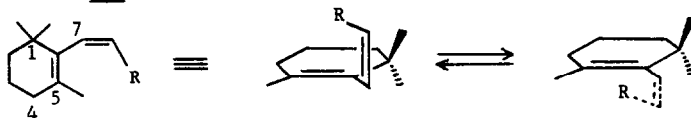
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(Received in USA 8 May 1972; received in UK for publication 14 August 1972)

The 7-cis-isomers of carotenoids are known to be highly sterically hindered. To relieve steric crowding, olefinic linkages in the ring and side-chain are not expected to be planar. The photochemistry of related compounds recently reported by us are consistent with this expectation.² We now wish to report nmr studies on some of the newly synthesized hindered 7-cis model carotenoids giving direct evidence to this special ring-chain conformational preference.

Compounds I-II were prepared by the method of selective sensitization² and III by reaction of methyl Grignard with cis- β -ionone.^{2,3} The pmr spectra of these compounds at various tempera-

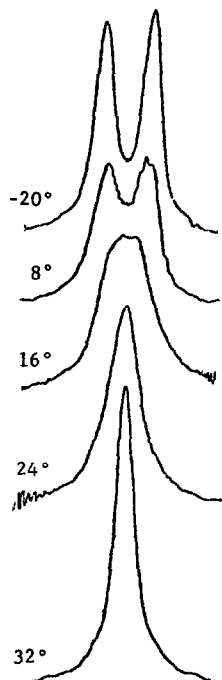


I: R = CH₂OH, II: R = CH(CH₃)OH, III: R = C(CH₃)₂OH

tures were recorded. The patterns of variation are consistent with systems of two-site conformational equilibration as shown. For I and III, rotational barriers have been determined by line-shape analyses of the temperature dependent 1,1-dimethyl resonances. For I, at ambient temperature a singlet δ (0.9 ppm) is observed and at temperatures below -40°C broadening occurs with eventual separation into two singlets ($\Delta = 10$ Hz). For III, broadening occurs around 30°C. Results of the latter compound are partially shown. A computer program similar to that reported⁴ was used for generation of equivalent theoretical spectra providing the exchange rate constants. Activation energies of equilibration are found to be 7 and 15 kcal/mole for I and III respectively.

Compound II represents a more complicated system. In its high temperature spectrum the geminal methyl resonances appear as two singlets² probably due to the C₉ asymmetric carbon ($\Delta\delta$ being field invariant). The low temperature spectra are therefore much more complex. Complete analyses of spectra are still in progress. However, its coalescence temperature (-32°C)

expectedly falls in between those (-60°, 20°) of compounds I and III.



Recently, by extended HMO calculations, the rotational barrier of the much less hindered trans- β -ionone was obtained (13 kcal/mole).⁵ In view of our results with more hindered cis-compounds, their method appears to have over-estimated the barrier. In fact, experimentally we have not detected any splitting of the geminal methyl signals in β -ionone (to -130°C) thus in agreement with a lower barrier.

Through decoupling experiments we have also determined the long range coupling constants between H₇ and the two sets of ring allylic hydrogens, H₄ and H₅'s: $J_{4,7} = 1.3$ Hz; $J_{5,7} = 2.4$ Hz. When analyzed in a way similar to that reported for 7-trans-carotenoids⁵ we obtained a ring-chain dihedral angle of 40-53° for III, a value perhaps somewhat lower than expected when the photochemistry of such compound is taken into consideration. We note, however, that long-range coupling constants appear to underestimate the dihedral angles when compared to results obtained by other methods.⁵ Structural determination by x-ray diffraction of related compounds is therefore planned.⁶

References

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6. HA-100 nmr spectra were taken by Mr. J. Loo. The work was partially supported by the Sloan Foundation and NSF.