

DISTORTED GEOMETRIES ABOUT BRIDGEHEAD CARBONS (1)

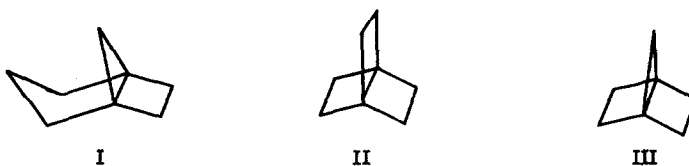
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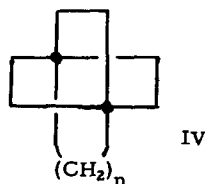
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Among polycyclic compounds, one unique structural type has not received significant attention by organic chemists. These are compounds in which all atoms joined to the bridgehead atoms lie in one hemisphere (i. e. in one plane or on one side of a plane passing through the bridgehead atoms). Two subclasses may be recognized. The first contains a central bridge and has an "inverted" tetrahedral geometry. Possible examples include the following (2):



The other group lacks the central bond, but has the four atoms lying in or near a plane below the bridgehead atoms. An example might be

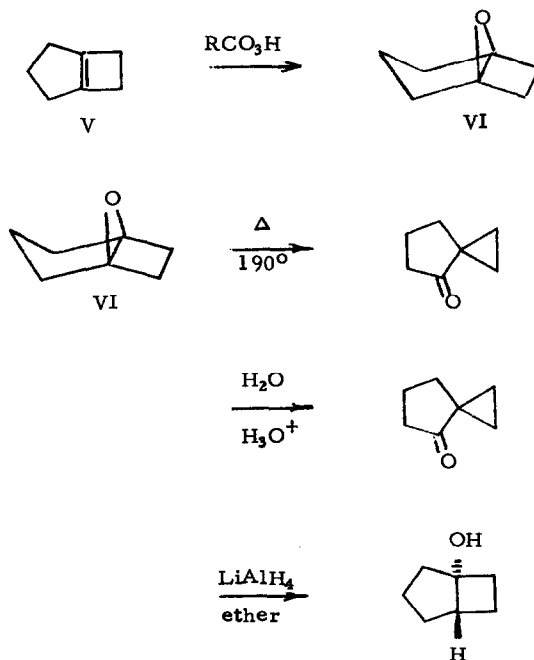


Here the bonding at the bridgehead atoms might approach a square planar configuration when n becomes small. It is clear that compounds of the types discussed above are of interest with regard to the hybridization at carbon.

We should like to report that compounds related to I are readily prepared from

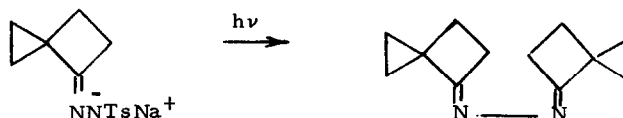
bicyclo[3.2.0]heptene-1 (V) (3). The reaction of V with *m*-chloroperbenzoic acid gave oxatricyclo[3.2.1.0^{1,5}]octane (VI) in good yield (4). The nmr spectrum of VI had complex absorption between 7.72-8.52 τ with a prominent multiplet of four peaks between 8.04-8.12 τ . The latter is also found in the spectrum of 9-oxatricyclo[4.2.1.0^{1,6}]nonane (VII). The mass spectrum of VI had a parent peak at $m/e = 110$. The mode of formation, the absence of vinyl nmr bands, the similarity of the spectrum with that of VII, and the mass spectral data all are in agreement with the assigned structure.

VI was quite stable thermally, and at 190^o it had a half life of 4 hrs in the liquid phase. The reaction product was spiro[2.4]heptanone-4. It reacted very rapidly with dilute acid to give spiro[2.4]heptanone-4. The reaction with lithium aluminum hydride in ether proceeded very slowly, and in 12 days gave 41% of trans-bicyclo[3.2.0]heptanol-1.



It is clear that compounds of the first subclass may possess reasonable stability. The detailed study of the properties of derivatives of I is in progress.

The preparation of the corresponding derivatives of III by the method described above has not, as yet, been successful. Whereas the photolysis of the sodium salt of spiro[2.4]-heptanone-4 tosylhydrazone gives bicyclo[3.2.0]heptene-1 in good yield,³ the corresponding reaction of spiro[2.3]hexanone-4 tosylhydrazone gives an azine:



References

1. This investigation was supported by the U.S. Army Research Office, Durham.
2. Compounds of this general type with larger rings have of course been known for some time (cf. J. J. Bloomfield and J. R. S. Irelan, Tetrahedron Letters, 2971 (1966); J. Altman, E. Babad, J. Itzhaki and D. Ginsburg, Tetrahedron, Suppl. 8, 279 (1966)). P. E. Eaton has indicated (Abst. 155th Meeting, American Chemical Society, San Francisco, 1968, p P1) that he is attempting the syntheses of derivatives of II.
3. W. Kirmse and K. H. Pook, Angew. Chem. Int. Ed., 5, 594 (1966).
4. All compounds gave satisfactory elemental analyses and had nmr spectra which were in agreement with the assigned structure.