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CONFIGURATIONAL ASSIGNMENT OF SEVERAL 1,4-SUBSTITUTED ADAMANTANES[1]

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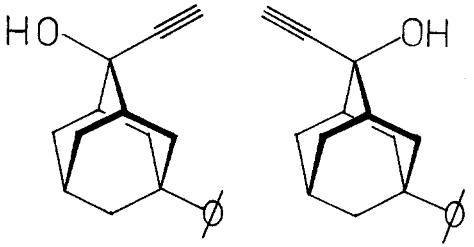
Summary: The configurations of several 1,4- (= 2,5-) disubstituted adamantanes have been determined by means of X-ray diffraction. Since these compounds have rigid skeletons and since there is almost no difference in stability or steric requirements between the geometric isomers, these epimers are expected to be very useful for stereochemical studies.

The beautifully regular shape of adamantane and the simple spatial relationships of the substituents make this molecule an ideal substrate with which to study stereochemical questions.[3] Thus, Schleyer[4] and Martin[5] demonstrated by means of appropriately 1,2-substituted adamantane derivatives that α-vinyl and -cyclopropyl substituted carbonium ions are greatly destabilized compared to the simple allylic and cyclopropylcarbinyl cations when the developing p orbital is effectively twisted by 90°.

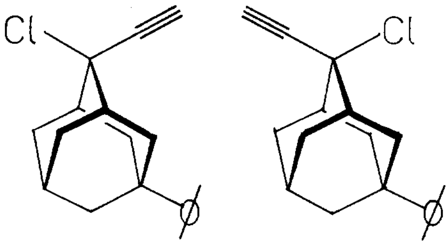
A potentially very useful type of substitution is that in which the substituents are carried by the 1- and 4- (or 2- and 5-) carbon atoms; this allows the study of stereochemistry at a saturated carbon via the use of geometric rather than optical isomerism. While this can also be done by means of simple monocyclic compounds, the rigidity of the tricyclic system and the large distance between the 1- and 4-carbons guarantee the virtual absence of conformational and steric effects. Unfortunately, few 1,4-disubstituted adamantanes are known,[6] and knowledge of configurations is virtually absent in these. An attempt has been made by Whiting to determine[7] the configurations of the epimeric 5-methyladamantan-2-ols by means of nmr analysis, but the interpretation of the small differences between the spectra proved to be difficult, and in fact, a reassignment was later required.[8]

In our pursuit of the mechanistic details of the base promoted solvolysis of tertiary propargyl halides[10] we have prepared the several derivatives I - III,



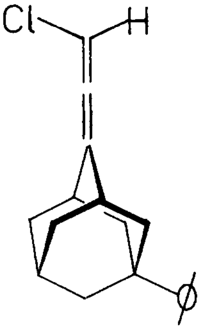
I

E Z



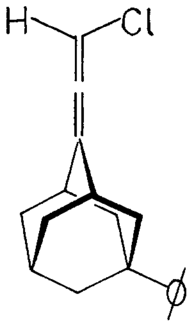
II

E Z



E

III



Z

and determined their configurations by means of X-ray diffraction. 5-Hydroxy-2-adamantanone was obtained by the treatment of adamantanone with nitric acid as described by Geluk.[6d] This was followed by treatment with thionyl chloride, then Friedel-Crafts reaction with benzene, and finally ethynylation to give I. The E,Z-mixture was separated by means of a succession of crystallizations and liquid chromatography. Treatment of the mixture of alcohols with Lucas reagent produced the chlorides II, which proved separable by a combination of crystallizations and high pressure liquid chromatography. Treatment of the pure isomers of I with thionyl chloride yielded the allenes III with retention of configuration. As we hoped, all six of these compounds are solids, and they are distinguished by either their melting points and/or by the small differences in chemical shift of the acetylenic and allenic protons.

The X-ray analyses were carried out with single crystals; the diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer with monochromatized Cu-Kα radiation. The computations were carried out on a PDP 11/45 and the Structure Determination Package.[11] Table I contains the principal data.

Table I

Crystallographic and Other Data for Compounds I-III.

Compound	I		II		III	
	E[b]	Z[c]	E	Z	E	Z[b]
M.p., °	97.5-98.5	89.0-89.5	92.5-93.0	91-92	64-65	101.5-102.5
Chem. shift[a]	7.47	7.47	7.31_5	7.30_0	4.14	4.17
Space group		$P2_12_12$	$P2_1/c$	$P2_12_12_1$	C2/c	
a, Å		20.74_3	7.22_9	6.78_7	26.67_2	
b, Å		13.28_6	14.30_5	10.06_6	6.93_3	
c, Å		10.24_2	15.30_8	21.12_3	23.94_7	
β		-----	113.5°	-----	137.2°	
R[d]		0.052	0.038	0.053	0.050	

(a) In τ units, of the acetylenic/allenic protons. (b) Suitable crystals could not be obtained in this case. (c) The asymmetric unit contains two molecules, both of the same configuration, with different orientations of the phenyl groups with respect to the adamantane skeleton. (d) Degree of refinement, assessed as $\Sigma(|OBS| - |CALC|)/\Sigma|OBS|$.

These epimeric pairs should permit many other stereochemical investigations beside the one planned in our laboratory (see above). The chemistry of the propargylic and allenic units is well-known and should enable organic chemists to convert them into many other functional groups. The crystallographic information is of interest as well; thus, in all of these compounds the ring angle at C_1 of the phenyl group is well below normal (116-117^o), suggesting that the six hydrogen atom halo above the C_1 atom interferes with the ortho hydrogen atoms. We hope to report these structural features and the chemical studies in future publications.

Acknowledgements

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References and Footnotes

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