Tetrahedron Letters No. 2, pp 155 - 158, 1974. Pergamon Press. Printed in Great Britain.

A SYNTHESIS OF TETRACYCLO [5.3.1.$1^{2,6}0^{4,9}$] DODECANE (ICEANE)

David P.G. Hamon* and Garry F. Taylor

Department of Organic Chemistry, University of Adelaide, Adelaide, S.A. 5000, Australia.

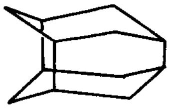
(Received in UK 8 October 1974; accepted for publication 5 December 1974)

In 1965 Fieser coined the name iceane for the hypothetical hydrocarbon 1.[1] This highly symmetrical molecule (D_{3h}) possesses five six-membered rings of which, because of the rigidity imposed by the carbon skeleton, two exist in chair configurations and three in non twist boat configurations. Although the model is free of skeletal strain, presumably the molecule has within it severe non-bonded interactions. It was expected therefore that iceane would possess unusual structural parameters and chemical properties as well as presenting a synthetic challenge. This communication outlines a route by which iceane has been synthesized.[2]

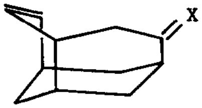
The olefinic ketone[3] 2 was converted ($Ph_3P{=}CH_2$, ether) to the diolefin 3 (mp 132-135°) (86%) whereupon selective hydroboration (disiamyl borane, THF; H_2O_2, NaOH) gave the olefinic alcohol 4 (mp 127-129°) (55%) ν_{max} 3350 cm^{-1}; nmr (CCl_4) δ6.1 and 5.6 (m, vinylic),[4] 3.7 (m, diastereotopic hydroxymethyl), 2.65 (s, hydroxyl) and 2.8-0.6 (methylene envelope). The configuration of the hydroxymethyl group in compound 4 (predicted to be as shown), was essential to the synthetic route and was established before proceeding. Oxymercuration[5] of the olefinic alcohol 4 gave a compound (mp 165-167°) isomeric with the starting material (mass spec) but showing no hydroxyl absorption (ir). The nmr spectrum showed no vinylic protons but resonances for three protons on carbon atoms bearing oxygen. From these data this new isomer could be only compound 5 or 6 either of which could have arisen only if the hydroxymethyl group in compound 4 had the configuration depicted.

It was intended to convert the compound 4 into a halo-epoxide, via the chloro-olefin 7, with the hope of effecting an intramolecular alkylation reaction.[6] However on refluxing 4 with Ph_3P in CCl_4, the reaction took an unexpected course. A mixture of two compounds was obtained (55%) each of which was shown to be isomeric with the expected compound 7 (glc-mass spec). The nmr spectrum of the mixture showed no vinylic protons but two resonances at δ4.82 and 4.00 consistent with protons on a carbon bearing chlorine. Both these compounds must therefore contain an extra ring. Assuming that there was no extensive rearrangement, it seemed likely that substitution had occurred, with double bond participation to give either both epimers of compound 8, or of compound 9 or a mixture of one of each.[7] A small amount of each chloro isomer was obtained by preparative glc; compound A (first eluted), (mp 215-217°), nmr δ4.00; compound B, (mp 272-274°), nmr δ4.82. Each chloride was reduced separately with tri-n-butylstannane and both appeared to give the same crystalline compound which was at least isomeric (mass spec) with iceane. The mixture of chloro compounds was reduced to yield a crystalline product, which did not melt but sublimed at 318° (sealed tube of small volume) and which was shown to be tetracyclo $[5.3.1.1^{2,6}0^{4,9}]$ dodecane 1 by the following data. The analytical data and mass spectrum were consistent with the molecular formula $C_{12}H_{18}$. The pmr spectrum (90 MHz) showed an AM pattern centred at δ0.94 and 1.90 ($J = 12$ Hz). This is consistent with the resonances due to the axial and equatorial protons respectively[8] of each methylene group. This difference in chemical shift is probably enhanced by van der Waals deshielding of the equatorial protons due to their position in the rings having a boat configuration. Each of these resonances is broadened by further minimal coupling to the bridgehead protons which absorb as a broad peak at δ2.18. The integration for each of the three regions was the same. The $^{13}C-\{{}^1H\}$ nmr spectrum showed only two resonances at δ28.70 and 31.72 (relative to TMS) integrating[9] for nearly equal areas. All of these nmr data are consistent with the six fold inversion axis in iceane. Furthermore X-ray data[10] revealed that the molecule must possess a minimum of three-fold symmetry.

Acknowledgements: G.F. Taylor acknowledges the receipt of a Commonwealth Postgraduate Scholarship. The authors are indebted to Dr. M.R. Snow, Dept. of Physical and Inorganic Chemistry, University of Adelaide, for the X-ray data and its interpretation.

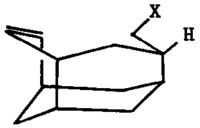


1



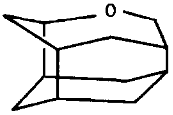
2 X = O

3 X = CH_2

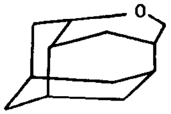


4 X = OH

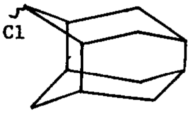
7 X = Cl



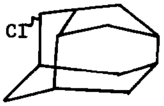
5



6



8



9

References

1. L.F. Fieser, J.Chem.Ed., 42, 408 (1965).
2. The synthesis of this compound was initially reported at the Royal Australian Chemical Institute Conference, Phillip Island, Victoria in February 1974. After the preparation of this manuscript an alternative synthesis of iceane appeared. C.A. Cupas and L. Hodakowski, J.Amer.Chem.Soc., 96, 4668 (1974).
3. The preparation of this compound will be reported elsewhere (manuscript in preparation)

4. Each multiplet was a doublet of doublets i.e. an AB-pattern further split by the neighboring protons.
5. H.C. Brown and Min-Hon Rei, J.Amer.Chem.Soc., 91, 5646, (1969).
6. R.R. Sauers, R.A. Parent and S.B. Damle, J.Amer.Chem.Soc., 88, 2257 (1966).
7. Models indicate that the carbon of the hydroxymethyl group can be positioned over the centre of the double bond with no obvious preference for either end.
8. Axial protons normally absorb at higher field than equatorial protons; see e.g. N.S. Bhacca and D.H. Williams, Applications of N.M.R. Spectroscopy in Organic Chemistry. Holden-Day, Inc., San Francisco 1964, p. 47.
9. Sufficient pulse spacing was employed to allow adequate time for the relaxation process.
10. Hexagonal crystals (from MeOH), cell constants a = 6.60 (1), c = 11.87 (1) A°, ρ = 1.04 g/cc giving FW = 210.5 (Z = 4), space groups $P6_3$ or $P6_{3/m}$ in which iceane must occupy positions of at least threefold symmetry.