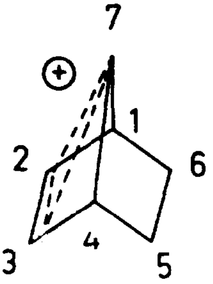
Tetrahedron Letters No. 52, pp 5357 - 5360, 1972. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF A NEW TRICYCLIC ISOMER OF HEXAMETHYLDEWARBENZENE

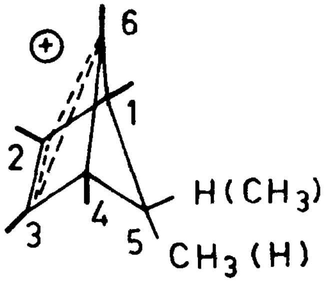
H. Hogeveen and P.W. Kwant
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

(Received in UK 8 November 1972; accepted for publication 30 November 1972)

In the 7-norbornenyl cation (1)[1] and in the 1,2,3,4,5,6-hexamethylbicyclo[2.1.1] hexenyl cations (2)[2], the positive charge is distributed over the bridge carbon atom and carbon atoms 2 and 3. This can be explained best by non-classical resonance delocalisation.



1

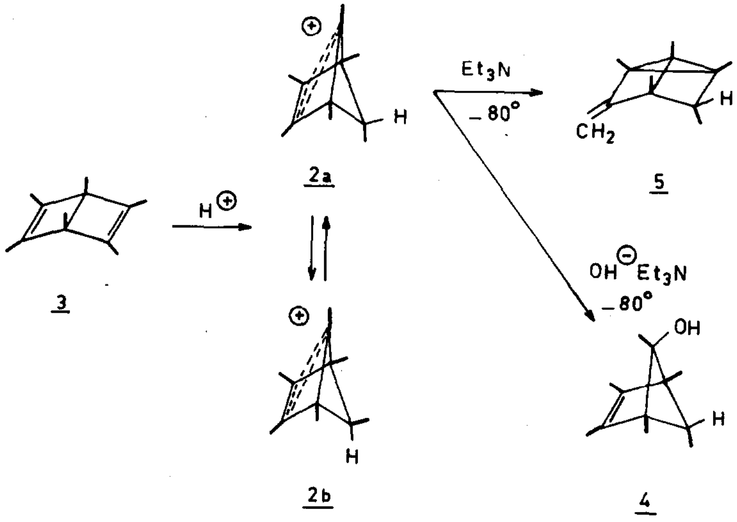


2

The three carbon atoms over which the charge is concentrated are all possible points of addition for an incoming nucleophile. Such an attack would lead to a tricyclic product in the case of reaction at carbon atoms 2 or 3 and to a bicyclic product were the reaction to take place at the bridge. Reactions of 7-norbornenyl and 7-norbornadienyl cations with the hydride donors sodium borohydride[3] or lithium aluminium hydride[4] give mixtures of bicyclic and tricyclic hydrocarbons. Reactions with other nucleophiles, e.g. hydroxide ion, yield bicyclic products only. Only bicyclic products have thus far been obtained from reaction of methoxide[5,6] and chloride ions[6] with 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations 2a and 2b. Very recently the formation of tricyclo[2.2.0.0^{2,6}]hexane has been reported[7] from the proposed reaction of a 5-bromobicyclo[2.1.1]hexenyl cation with $LiAlH_4$.

How will the ions 2a and 2b behave towards hydride transfer? All our attemps to obtain bicyclic or tricyclic hydrocarbons from these ions with $NaBH_4$ or Et_3SiH[8] or from the corresponding chlorides with $LiAlH_4$ (up to tenfold excess of hydride donor) failed because the decomposition of the reactants was faster than the hydride transfer in the temperature range studied (-80° to 0°). The same products were observed as in the reactions without addition of hydride donor.[6]

It was possible, however, to abstract a proton from the methyl group attached to the carbon atoms 2 or 3 of ions 2a, 2b. Treatment of the ions with triethylamine yielded the tricyclic compound, 1,2,4,5,6-pentamethyl-3-methylenetricyclo[2.2.0.0^{2,6}]hexane (5). The reaction with $OH^{\ominus}$ at the bridge carbon atom is much faster, however, than proton abstraction by triethylamine, yielding the bicyclic alcohol (4). From these observations it is concluded that the direction of attack on the ions 2a, 2b depends on the nucleophile.



A 3 : 1 equilibrium mixture of the ions 2a, 2b was prepared by dissolving hexamethyl-dewarbenzene (3) in methylene chloride (conc. about 0.5 mole/l) and introducing at -80° dry HCl (1.5 equiv.).[6] This ions mixture was treated at -80° with excess triethylamine (2 equiv.).

The mixture was poured into water and was washed with water until the smell of triethylamine had disappeared and was dried with anhydrous sodium sulfate. The solvent was evaporated leaving a yellow liquid, containing compounds 4 and 5. Repeating the experiment showed that the ratio of compounds 4 and 5 could be varied by changing the reaction time. When immediately after addition of triethylamine the mixture was poured into water and worked up, or when wet triethylamine was used, compound 4 was obtained as a yellow oil (80% yield, determined by NMR), which crystallised upon cooling: white crystals, mp. 61-63°. Structure 4 was assigned on the basis of the molecular weight: 180 (determined mass spectrometrically), the IR spectrum: a broad absorption at 3440 cm^{-1}, (OH) and the NMR spectrum in CCl_4: $\delta = 3.09$ (q, J=7 cps., 1H), 1.62 (s, $2CH_3$), 1.27 (s, 1H), 0.99 (s, $1CH_3$), 0.82 (s, $2CH_3$), 0.68 (d, J=7 cps., $1CH_3$). The chemical shift of the quartet and the doublet in the NMR spectrum indicate the *exo* position of the hydrogen atom.[5] This assignment was confirmed by the shift enhancement upon addition of $Eu(dpm)_3$[9], which will complex at the oxygen lone pair electrons.[10] The shift enhancement is about four times as large for the quartet as for the doublet. This is only consistent with the configuration in which the hydrogen is situated *exo*. Compound 4 was formed also (60% yield, determined by NMR) when a mixture of ions 2a, 2b was treated with excess KOH in ethanol at -80°.

With a longer reaction time the amount of compound 5 increased, showing that the reaction with triethylamine is much slower than with $OH^{\ominus}$ ion. When the reaction mixture was maintained at -80° for 3 hrs and was warmed slowly (over 3 hrs) to room temperature followed by work up, 85% of compound 5 was obtained and only 3% of compound 4. Compound 5 was purified by vacuum distillation, bp. 47.5-48.5° at 3.7 mm Hg. (80% yield in a preparative experiment). An analytically pure sample was obtained by preparative glc (SE-30 column, all temperatures below 200°). Structure 5 was assigned to the product on the basis of the following data: elemental analysis[11], the molecular weight: 162 (determined mass spectrometrically), IR spectrum: absorptions due to C-H and C-C and absorptions at 3070 cm^{-1} ($=CH_2$ stretching) 1655 cm^{-1} (C=C stretching) and 860 cm^{-1} ($=CH_2$ out of plane deformation) and the NMR spectrum in methylene chloride: $\delta = 4.56$ (d, J=0.8 cps., 1H), 4.54 (d, J=0.8 cps., 1H), 2.05 (q, J=7 cps., 1H), 1.32, 1.29, 1.03, 1.00 (s, each $1CH_3$) and 0.87 (d, J=7 cps., $1CH_3$). From these data it could not be concluded whether the position of the hydrogen is *endo* or *exo*, but the simultaneous formation of the *exo* alcohol 4 makes an *exo* position of the hydrogen more likely.

On hydrogenating compound 5 with Pd on C (5%) or Pt_2O as catalyst in hexane at room temperature and a hydrogen pressure of 2 atm., 1 equivalent hydrogen (± 0.1 equiv.) was consumed. A complex reaction mixture was obtained, indicating that the catalyst caused at least partial isomerisation. Hydrogenation with diimide[12] was not possible. When compound 5 was stirred for 4 hrs at room temperature with 50 fold excess potassium azodicarbonate, which was decomposed by addition of a 2 : 1 methanol-water mixture, starting material was recovered quantitatively. This is readily explained by the sensitivity of diimide reductions to steric approach control, which is well documented in the literature.[12]

On pyrolysis at 225° during half an hour, 5 was isomerised to its more stable isomer hexamethylbenzene (35%) and other yet unidentified products. Hexamethylbenzene was also obtained on treating compound 5 with transition metal catalysts at room temperature. Reaction of compound 5 with $AgClO_4$ (10 mol%) in dry benzene yielded hexamethylbenzene (75%) in one hr. $Rh_2(CO)_4Cl_2$ (10 mol%) in $CDCl_3$ yielded hexamethylbenzene (30%) and at least one yet unidentified compound with a terminal methylene group (40%).[13] In a subsequent much slower reaction the latter compound is transformed into hexamethylbenzene.

FOOTNOTES AND REFERENCES.

1. M. Brookhart, A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, 88, 3135 (1966);
   H.G. Richey, Jr. and R.K. Lustgarten, *ibid.*, 88, 3136 (1966).
2. H. Hogeveen and H.C. Volger, *Rec. Trav. Chim.*, 88, 353 (1969);
   H. Hogeveen and C.J. Gaasbeek, *ibid.*, 89, 395 (1970).
3. H.C. Brown and H.M. Bell, *J. Amer. Chem. Soc.*, 85, 2324 (1963);
   S. Winstein, A.H. Lewin and K.C. Pande, *ibid.*, 85, 2324 (1963).
4. P.R. Story, *ibid.*, 83, 3347 (1961).
5. L.A. Paquette, G.R. Krow, J.M. Bollinger and G.A. Olah, *ibid.*, 90, 7147 (1968).
6. H. Hogeveen and P.W. Kwant, *Tetrahedron Letters*, 3197 (1972).
7. R.J. Roth and T.J. Katz, *J. Amer. Chem. Soc.*, 94, 4770 (1972).
8. F.A. Carey and H.S. Tremper, *J. Org. Chem.*, 36, 758 (1971).
9. a. K.J. Eisentraut and R.E. Sievers, *J. Amer. Chem. Soc.*, 87, 5254 (1965);
   b. J.K.M. Sanders and D.H. Williams, *ibid.*, 93, 641 (1971).
10. P.V. Demarco, T.K. Elzey, R.B. Lewis and E. Wenkert, *ibid.*, 92, 5734 (1970).
11. When the analysis is not carried out immediately after preparation, the content of C and H is too low, presumably due to oxidation.
12. Reviews on the chemistry of diimide:
    C.E. Miller, *J. Chem. Educ.*, 42, 254 (1965);
    S. Hünig, H.R. Müller and W. Thier, *Angew. Chem. Int. Ed. Eng.*, 4, 271 (1965).
13. The same products are observed in about the same time using $Pd(C_6H_5CN)_2Cl_2$ (10 mole %) in $CDCl_3$ as catalyst.