

1,2,5,6-TETRAMETHYL-3,4-DIMETHYLENETRICYCLO[3.1.0.0<sup>2,6</sup>]HEXANE

## SYNTHESIS AND REACTIONS WITH ACIDS

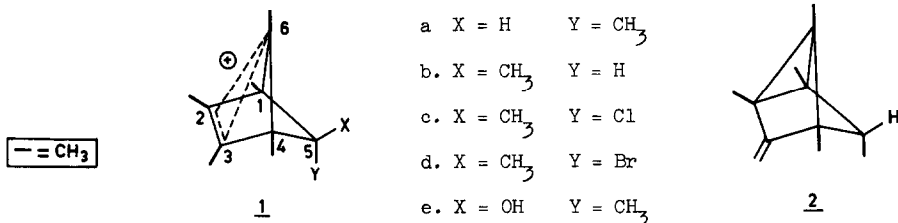
H. Hogeveen and P W. Kwant

Department of Organic Chemistry, The University

Zernikelaan, Groningen, The Netherlands.

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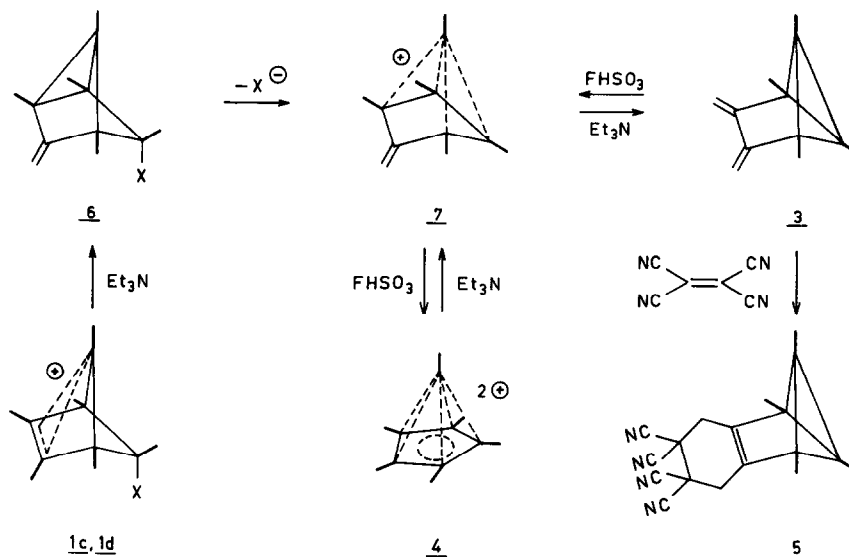
The positive charge in 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations 1 has been shown to be delocalised on C-2, C-3 and C-6. Proton abstraction by triethylamine occurred from the methyl groups attached to C-2 or C-3 of ion 1a, to yield 2, rather than from the methyl group at C-6, indicative of high positive charge at C-2 and C-3.<sup>1</sup> This agreed very well with the conclusion on charge distribution as deduced from the PMR and CMR data of the ions 1.<sup>2</sup> We wish to report here the synthesis of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0<sup>2,6</sup>]hexane, starting from monocationic ions 1c and 1d, and from dication 4.



Solutions of ions 1c and 1d were obtained from reaction of a solution of hexamethyldewabenzene in methylene chloride at -80° with one equivalent of dry chlorine gas<sup>3</sup> and bromine<sup>4</sup>, respectively. Excess triethylamine (3 eq.) was added at -80° and the mixture was maintained at this temperature for two hrs. during which time triethylammonium salt separated. After warming to room temperature (over two hrs) the reaction mixture was diluted with pentane and extracted with water until the smell of triethylamine disappeared. Drying the solution and evaporating the solvent yielded a crude product, which consisted of 70% 2 (detected by PMR). Separation of the crude product by preparative GLC (all temperatures below 150°) provided analytically pure 2 as a colourless liquid (60% yield), hexamethylbenzene (20% formed from pyrolysis of by-products) and a number of minor products

The assignment of the structure 3 rests on the following data elemental analysis, mass spectrum parent peak at  $m/e = 160$ , FMR ( $\text{CCl}_4$ ) = 5.00 (s, 2H) 4.53 (s, 2H) 1.42 (s, 6H) and 1.14 (s, 6H) CMR ( $\text{CH}_2\text{Cl}_2$ ) peaks at 157.5, 98.7, 47.1, 31.4, 10.0 and 6.0 ppm downfield from external TMS, IR absorptions at 3080 ( $=\text{CH}_2$  stretching), 1640 (C=C stretching) and  $865\text{ cm}^{-1}$  ( $=\text{CH}_2$  out of plane deformation), UV  $\lambda_{\text{max}}^{\text{ethanol}}$  204 ( $\log \epsilon = 3.95$ ) and 250 nm ( $\log \epsilon = 3.78$ )

Compound 3 underwent at room temperature in chloroform solution a quantitative Diels-Alder reaction with tetracyanoethylene, which was complete within one minute, yielding the white crystalline solid 5, which decomposed without melting at  $125^\circ$ , the products formed melted at  $230\text{--}232^\circ$ . The addition product 5 was characterized by the following data elemental analysis, mass spectrum, parent peak at  $m/e = 282$ , FMR ( $\text{CDCl}_3$ ) = 3.12 (s, 4H) 1.47 (s, 6H) and 1.16 (s, 6H), IR absorptions at 2260 ( $-\text{C}\equiv\text{N}$ ) and  $1665\text{ cm}^{-1}$  (w, C=C)

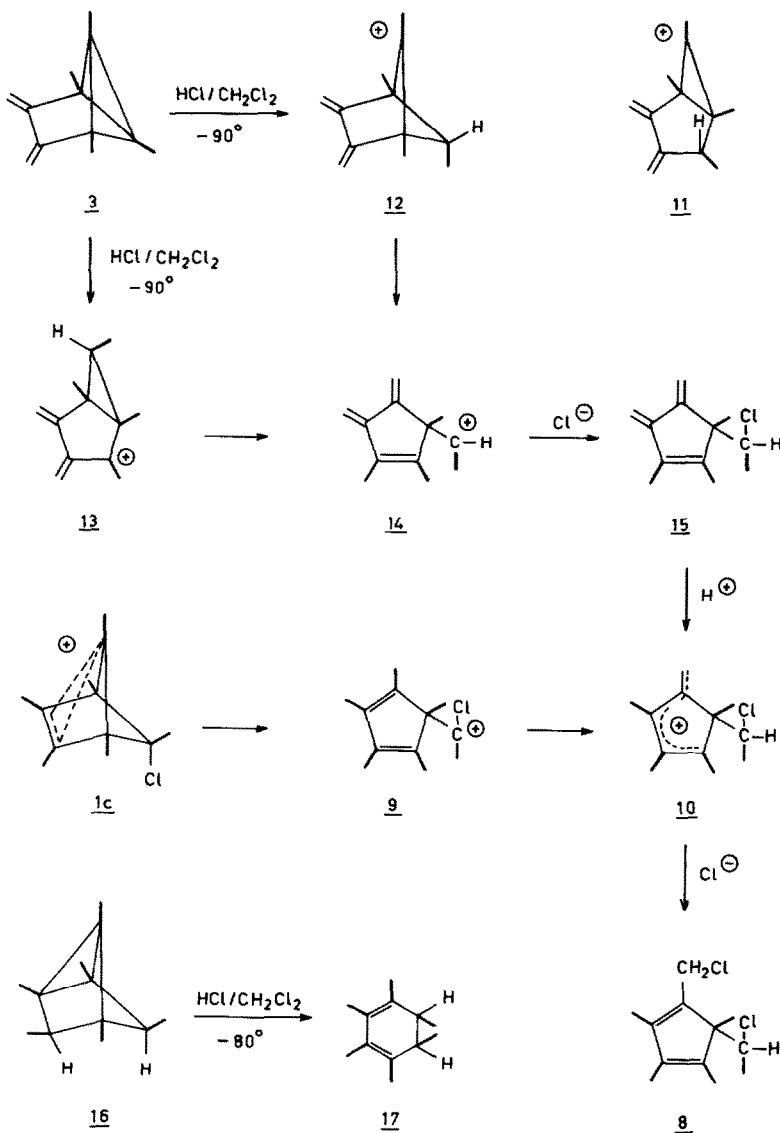


The mechanism of the reaction of 1c and 1d with triethylamine proposed here first involves proton abstraction from one of the methyl groups attached to C-2 or C-3<sup>1</sup>. The tricyclic compound 6 formed dissociates rapidly<sup>2</sup> to give ion 7. The positive charge in this ion should be concentrated chiefly on the carbon atoms allylic to the methylene group. Conjugated diene 3 arises on triethylamine induced removal of a proton from a methyl group attached to one of these carbon atoms.

Upon addition of  $\text{FHSO}_3$  to a solution of 3 in methylene chloride at  $-90^\circ$ , the dication 4<sup>5</sup> was observed. Mechanistically the formation of 4 can be viewed as two successive steps involving protonation of a methylene group. The first step gives ion 7, which in the second step takes up another proton to give 4. Pouring a solution of dication 4 in a solution of excess triethylamine in methylene chloride at  $-80^\circ$  gave rise to the reverse reaction and 3 was shown to be the major product (80% by

PMR and GLC). The reactions of dication 4 remain subject of further studies.

Addition of dry HCl to a methylene chloride solution of 3 at  $-90^{\circ}$  however, did not give rise to observable amounts of 4 or 7. The PMR spectrum of the reaction mixture at  $-90^{\circ}$  showed compound 8 to be formed, even when an excess of 3 was still present. The PMR spectrum of the reaction mixture remained unchanged upon warming to room temperature and 8 was isolated by evaporating the solvent. The assignment of the structure 8 depends on the following data mass spectrum parent peaks at  $m/e = 232, 234, 236$  (intensity ratio 9.6:1), PMR ( $\text{CH}_2\text{Cl}_2$ ): 4.27 (s, 2H) 4.15 (a,  $J=7$  cps, 1H) 1.88 (s, 6H)



1.80 (m, 3H) 1.13 (s, 3H) 1.10 (d, J=7 cps, 3H), IR 1. a absorption at  $1620\text{ cm}^{-1}$ , UV  $\lambda_{\text{max}}^{\text{pentane}}$  275 nm. The dichloride 8 is also formed by warming up a methylene chloride solution of 1c with chloride as counterion to room temperature in a reaction analogous to the known thermal reaction of 1d with bromide as counterion, which yields the corresponding dibromide, possessing similar spectra <sup>4</sup> The mechanism proposed for the reaction of 1d is thought to be equally valid for the reaction of 1c thereby implying 9 and 10 as intermediates.

It is difficult to rationalise the formation of compound 8 in the reaction of 3 with HCl by assuming protonation of a methylene group of 3 to be the first step. However assuming initial attack on a cyclopropane ring a reasonable mechanism can be drawn. According to Wiberg and Szeimies <sup>6</sup> the protonation of one of the cyclopropane rings is proposed to occur with retention of configuration. Due to symmetry only three intermediates are conceivable: 11, 12 and 13. Intermediate 11 is considered to be unlikely because it is energetically unfavourable and would open to a cyclohexenyl ion <sup>7</sup> Both intermediates 12 and 13 are possible although 13 is expected to be the most stable one; they are proposed to give the five membered ring compounds 14, 15 and 10 in subsequent steps. Finally intermediate 10, proposed to be an intermediate also in the thermal reaction of 1c, reacts with chloride anion to give product 8. The mechanism of this reaction shows a strong resemblance to that of the reaction of 2 with HCl in methylene chloride at  $-70^{\circ}$ . <sup>8</sup> In the latter case, attack on the cyclopropane ring by HCl is also favoured over attack at the methylene group; this is the exact reverse of the situation with  $\text{FHSO}_3$ , which adds preferentially to the methylene group. The high reactivity of the cyclopropane ring towards HCl in methylene chloride is illustrated further by the rapid quantitative reaction of 16 with HCl in methylene chloride at  $-80^{\circ}$  to give trans-hexamethylcyclohexadiene 17. The mechanism advanced for this reaction is analogous to that proposed for the  $\text{Ag}^{\oplus}$  catalysed reaction of 16 to 17 <sup>9</sup>, which involves also initial attack at the cyclopropane ring

The reaction of 3 with HCl and  $\text{FHSO}_3$  is another example of the difference of reactions of these acids with a compound containing a methylene group and a cyclopropane ring. These different reactions can be explained by assuming the attacking reagent in a cold mixture of HCl and methylene chloride to be a polar H-Cl molecule rather than a solvated proton. <sup>8</sup>

The chemistry of 3 is being actively investigated in this laboratory.

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