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SYNTHESIS OF SOME HIGHLY COMPRESSED NORBORNEN-7-ONES

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We report the synthesis of several 5,6-disubstituted norborn-2-en-7-ones whose highly compressed structures are reflected in a remarkable manner by certain features of their proton magnetic resonance (PMR) spectra, and by their facile thermal decarbonylations.[1]

Reaction of 1,2,3,4-tetrachloro-5, 5-dimethoxycyclopentadiene 2 with norbornadiene 1 gave the previously described[2] tetrachloroketal 3 which was dechlorinated[3] with sodium in t-butanol-tetrahydrofuran to give ketal 4[4] m.p. 47-48°. Hydrolysis with aqueous perchloric acid-tetrahydrofuran at 20° provided ketone 8, m.p. 70.5-71.5°. Hydrogenation of 3 over palladium on carbon gave 5, m.p. 95-96° which on dechlorination, followed by hydrolysis, yielded ketal 6, b.p. 105° (bath)/1mm and ketone 7, m.p. 44-45° (Chart 1). An analogous series of reactions (Chart 2) starting with benzonorbornadiene 9 gave tetrachloroketal 11, m.p. 140-140.5°, ketal 13, m.p. 109.5-110° and ketone 15, m.p. 92-4° (decomposition).

The stereochemistry of the above compounds follows from a consideration of their PMR spectra.[5] In the spectrum of the adduct derived from norbornadiene and 2 the resonance assigned to H_{4a} and H_{8a} is a singlet (width at half height = 1.8 Hz) at 7.51τ indicating the absence of significant coupling to H_5 and H_8 respectively. A coupling constant of approximately zero is observed between a bridgehead proton and an adjacent endo-proton in the norbornene series[6] and hence the tetrachloroketal can be formulated as either 3 or 17, the products of exo-addition to norbornadiene[7]. Structure 17 is eliminated since the resonance at 7.48τ due to H_{4a} and H_{8a} in the ketal obtained on dechlorination is a multiplet ($w_{\frac{1}{2}h}$=3.7 Hz). This shows that in the dechlorinated ketal H_{4a} and H_{8a} are exo to the dimethoxy-substituted norbornene system, and experience coupling with the new bridgehead protons H_4 and H_1 respectively. The dechlorinated ketal must therefore have structure 4 rather than structure 18, in which H_{4a} and H_{8a} are endo to both norbornene rings. Inspection of molecular models suggests that ketals 17 and 18 would be extremely strained due to steric interference of H_{9s} with the syn-methoxyl group, whereas in ketals 3 and 4 steric clash of H_{9s} with the etheno bridge is less severe. This difference in crowding would be reflected in the transition states for the Diels-Alder addition, and would be expected to favour the formation 3 over 17. Similar considerations establish the structure of the benzonorbornadiene adduct as 11.

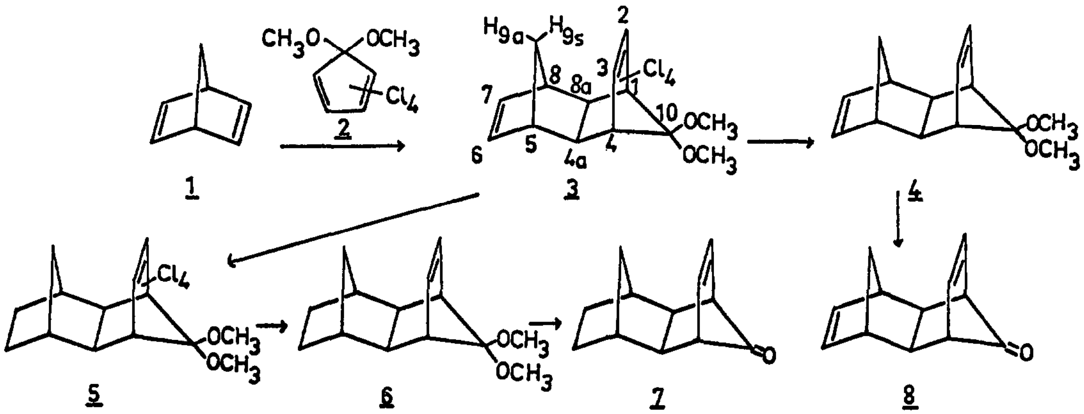


Chart 1

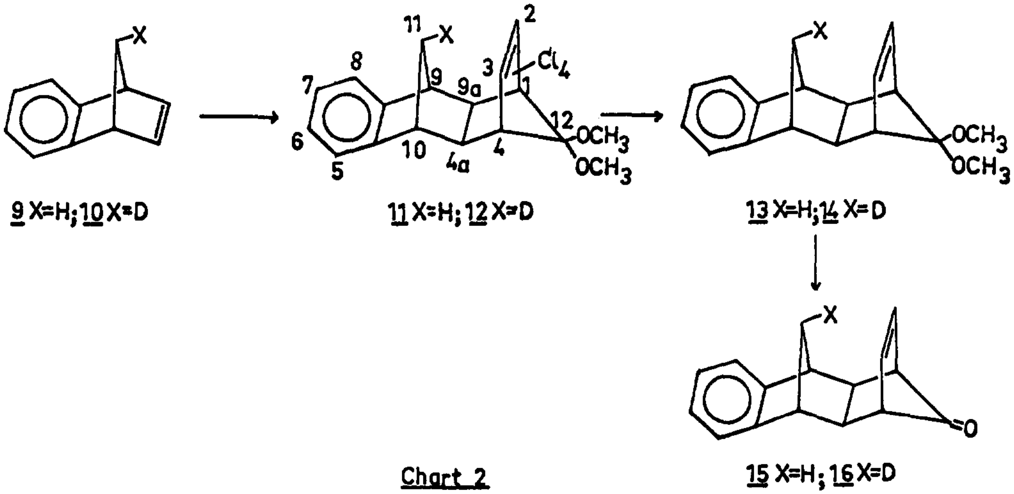
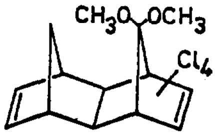


Chart 2



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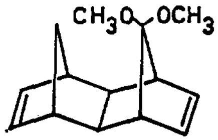

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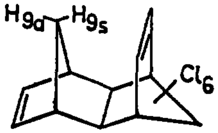

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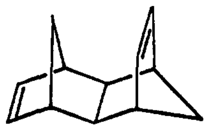

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The chemical shift difference of H_{9s} and H_{9a} in adducts 3 - 8 and of H_{11s}(X) and H_{11a} in adducts 11, 13 and 15 are shown in the Table. It can be seen that in the dechlorinated adducts, one proton of the bridging methylene group resonates at considerably lower field than the bridging protons in norbornane (8.79)[8], norbornene (*syn*-8.68, *anti*-8.73)[8] and benzonorbornene (*syn*-8.27, *anti*-8.52T)[8]. We propose that H_{9s}

in adducts 3 - 8 and $H_{11s}(X)$ in adducts 11,13 and 15 give rise to the lower field signal because they are sterically compressed against the π- cloud of the etheno bridge in each structure. Deshielding due to steric compression has been observed previously in other systems.[9]

Compound	Shift (τ)	Assignment	J(Hz)	$\Delta\nu$(Hz)	Compound	Shift (τ)	Assignment	J(Hz)	$\Delta\nu$(Hz)
3	8.44 8.77	H_{9s} H_{9a}	10	18	4	Ca 7.45* 9.11	H_{9s} H_{9a}	8.5	ca.100*
5	8.45 9.12	H_{9s} H_{9a}	11	40	7	ca 7.92* 9.26	H_{9s} H_{9a}	10	ca.80*
11	8.15 8.52	$H_{11s}(X)$ H_{11a}	11	22	8	7.56 9.06	H_{9s} H_{9a}	9.5	90
13	ca.7.15* 8.80	$H_{11s}(X)$ H_{11a}	10	ca.100*	15	7.34 8.79	$H_{11s}(X)$ H_{11a}	10	87

*overlap with other signals

Table. PMR data for AB quartets of bridging protons.
(60 MHz, carbon tetrachloride, TMS internal standard)

Our assignment is based on the PMR spectra of the adducts derived from benzonorbornadiene-7-anti-d_1 10[8]. Comparison of the spectra (see Figure) of ketone 15 and a 60:40 mixture of ketone 16 and 15 (prepared from a 60:40 mixture of 10 and 9[8]) shows a singlet at 8.79τ due to H_{11a} in 16 superimposed on the doublet due to H_{11a} in undeuterated ketone 15. Similarly in the spectra of 12 and 14 the higher field signal may also be assigned to H_{11a}, and the lower field doublet to H_{11s}. Analogous assignments for the norbornene derived adducts can safely be made (Table).

The finding that H_{9s} in the adducts in Chart 1 is deshielded due to steric compression necessitates a reversal of the assignments for the resonances of H_{9s} and H_{9a} in aldrin 19 and hydrocarbon 20 made by Marchand and Rose.[10] These authors assigned the upfield signal to H_{9s} and the downfield signal to H_{9a}. Steric deshielding is clearly also operating here.

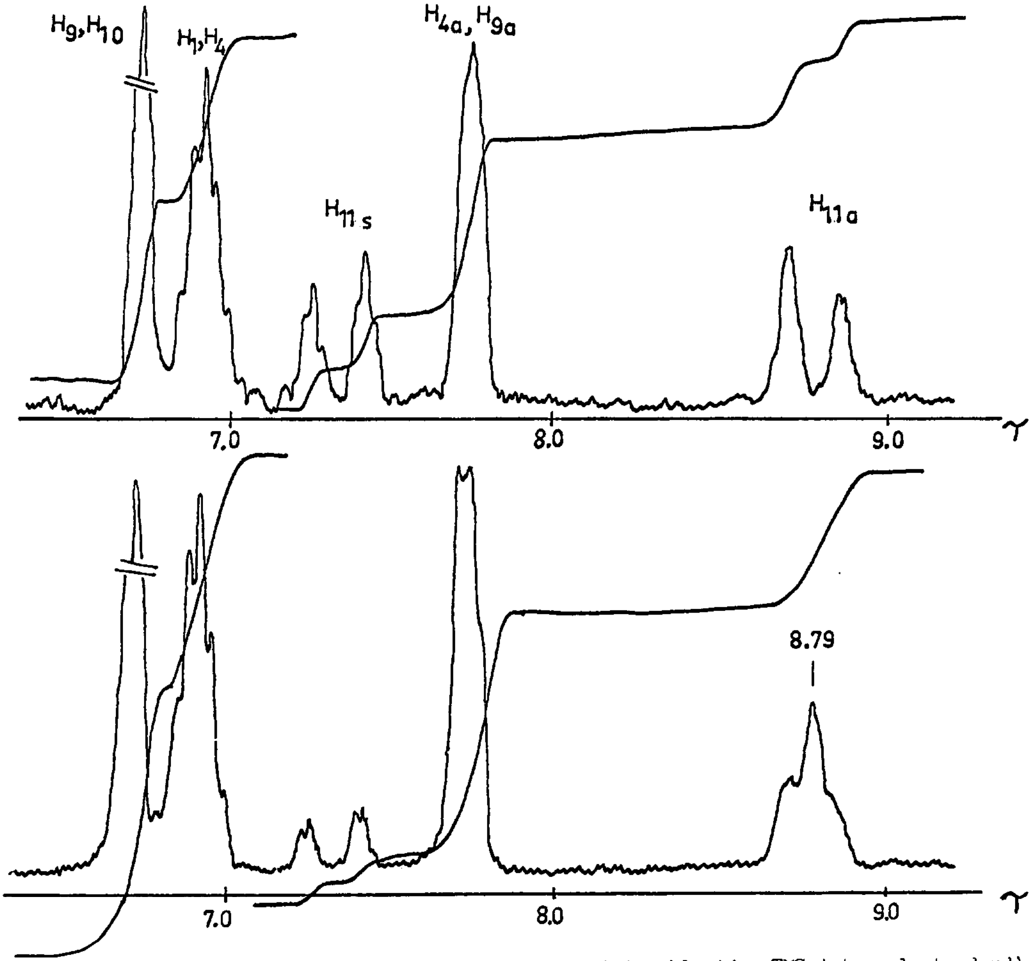

Figure. Upfield region of PMR spectra (60 MHz carbon tetrachloride, TMS internal standard) of ketone 15 (upper) and of 60:40 mixture of ketones 16 and 15 (lower).

REFERENCES AND FOOTNOTES

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