Cyclic Ketals from 2-Hydroxymethylene-hexachloro-norborn-5-enes by Alkaline Dechlorination

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Hexachloro-norborn-5-ene-derivatives carrying a hydroxymethylene function in position 2 and / or 3 are easily monodechlorinated at the vinylic chlorines by nucleophilic attack either by a hydroxyl- or an alkoxyl-group.

The resulting mixed cyclic ketals – an O-CH_2-group forming a ring between position 2 and 6 or 3 and 5 of the bicyclo(2,2,1,)heptan – may open a pathway of metabolism of the hexachloro-norborn-5-ene-moiety of endosulfan metabolites.

Hexachloro-norborn-5-ene-derivatives lacking a hydroxymethylene-function in a suitable position undergo this monodechlorination at the vinylic chlorines in a sharply reduced rate if at all.

The degradation of the hexachloro-norbornene moiety is one of the already proved or to be expected slow steps of final metabolism in the environment of the widely used classes of cyclodiene-insecticides[1], -fungicides[1] and -flameretardants[2].

We have started to investigate chemical[3], photochemical[4] and microbial[5] ways of conversion of the hexachloro-norbornene moiety.

ADAMS and MACKENZIE[6] have reported stereoselective reductive dechlorination of aldrin, dieldrin, isodrin, endrin and related compounds by sodium methoxide in methanol-dimethyl sulphoxide at temperatures of about 125 °C. Preferably the anti-chlorine of the dichloromethylene bridge is substituted by hydrogen.

The reactivity of hexachloro-norbornadiene and -norbornenes to nucleophilic attack at the vinylic chlorines has been studied in detail by DAVIES and ROWLEY[7]. They suggested a mechanism whereby a carbanion is stabilized by interaction with the 2,3 -double bond and / or the 7 *anti*-chlorine, thus explaining the reduced reactivity of tetrachloro-norbornadiene and hexachloro-norbornene-derivatives. Hydrolysis experiments fully support this explanation[4].

The more surprising is the pronounced reactivity toward a nucleophilic attack of the vinylic chlorines of hexachloro-norbornene-derivatives carrying a hydroxymethylene group as substituent in position 2 and / or 3, known to be metabolites of cyclodiene insecticides endosulfane[8-10].

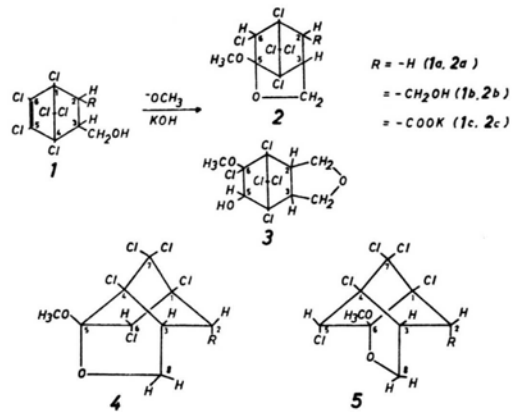
For such hexachloro-norbornene-derivatives methanolic potassium hydroxide (5% KOH in 96% methanol) leads to an easy loss of one chlorine per molecule[4] with the formation of a defined product in high yields. Dehydrochlorination is strongly inhibited by steric reasons and two structures for resulting pentachloro-derivatives have been advanced[4,11] (**2** and **3**).

From chemical and spectroscopic evidence we can show, that cyclic half ketal or mixed ketals (**2**), respectively, are the common feature of nucleophilic dechlorination of hexachloro-norbornene-derivatives carrying a hydroxymethylene substituent in position 2 and / or 3.

Structure **2** for the pentachloro-derivatives is supported by the fact, that compounds **1a** and **1c** easily undergo the dechlorination reaction, too, though there is no way of forming a derivative analog to **3**.

The NMR assignments[11] are nearly identical for the structures **2b** and **3**, but adding of a shift reagent can help to distinguish between both structures. In **2b** the hydroxyl-group is vicinal to a CH_2- in structure **3** vicinal to a CH-group. The results are, that the doublet at 4.7 ppm unquestionable to be assigned to the CH_2-groups at position 2 and 3 does shift upon adding tris(dipivalomethanato)-europium. This strongly supports structure **2b** over **3**.

According to molecular models both the cyclo-ketal **4** and **5** could be formed:



Double resonance studies of compound **2a** should clarify this question. We consider the five-membered cyclo-ketal more likely. The exo-position of the hydrogen at C_6 (**4**) can be concluded from the large long-distant coupling constant (2.7 Hz) with the hydrogen in position 2 (W arrangement)[12].

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Experimental

The compounds **2a** and **2b** have been synthezised according to the procedure given by GREVE and WIT[11]. The starting-compound (technical endosulfan, compound **1a**, respectively) was refluxed in methanolic potassium hydroxide (0.09 M KOH/l) for 1 hour.

2a: yield: 51%; m.p. 97–98 °C; MW: 326 (masspectrom.).

2b: yield: 69%; m.p. 147–148 °C; MW: 357 (masspectrom.).

The precursor **1a** has been synthezised by Diels-Alder reaction of hexachloro-cyclopentadiene with allyl alcohol[13]. Yield: 53%; m.p. 165–166 °C.

The NMR spectra were recorded on a Bruker KIS-II 90 MHz spectrometer in $CDCl_3$.

δ (ppm) (compound **2a**): H_2, – 2.40, H_2 – 2.59, H_3 – 2.75, H_8, – 3.84, H_8 – 4.30, H_6 – 4.65.

Conclusions

Nucleophilic dechlorination of the hexachloro-norbornene moiety at the double bond apparently only has a chance of becoming a major reaction pathway if a neighboured hydroxymethylene group can support this nucleophilic attack. The reported reaction is therefore by no means common to all hexachloro-norbornene-derivatives as the stability to alkaline conditions of chlorendic-acid, aldrin or dieldrin prove[4].

Whether this dechlorination reaction has any significance for the environmental degradation of metabolites of the cyclodien insecticide endosulfan, carrying hydroxymethylene groups and whether hydroxylation of the pentachloro-derivatives may lead to an opening of the bicyclo-heptane-ring is under investigation.

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