

## 154. Reaction of Bicyclo[3.2.1]octenols with Thionyl Chloride

Preliminary Paper<sup>1)</sup>

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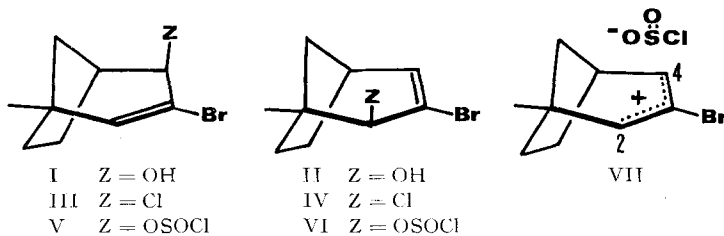
(3. VI. 71)

*Summary.* The allylic 1-methyl-3-bromobicyclo[3.2.1]octenyl *exo*-2 and *exo*-4 alcohols were treated with thionyl chloride in ether or pentane solution at 0°. In each case, a 50/50 mixture of *exo* allylic chlorides was obtained. No evidence for a predominant  $S_Ni'$  reaction was detected; reported cases of such  $S_Ni'$  processes using these conditions should therefore be treated with reserve.

$S_Ni'$  processes are not common. Expected cases should be provided by the rearrangement of the chlorosulfite esters of those allylic alcohols which possess rigid or semi-rigid skeletons. Complete allylic rearrangement has been reported in the reaction of 4 $\beta$ -hydroxycholest-5-ene, 6 $\beta$ -hydroxycholest-4-ene and the isomeric 5-methyl-2-cyclohexenols on treatment with thionyl chloride [1]. It was thought that the same stereochemical course would obtain on carrying out the same reaction with the stereochemically similar bicyclo[3.2.1]octenols (I and II). However, the results proved otherwise.

*Exo*-4-hydroxy-3-bromo-1-methyl-bicyclo[3.2.1]oct-2-ene (I) and *exo*-2-hydroxy-3-bromo-1-methyl-bicyclo[3.2.1]oct-3-ene (II) were separately added to react with pure, acid-free thionyl chloride in excess dry ether at 0°. After five minutes the ether was removed *in vacuo* and the residual oil was examined immediately at 0° by <sup>1</sup>H-NMR spectroscopy. In both cases, 50:50 mixtures of the *exo*-allylic chlorides III and IV were formed. There was no indication whatsoever that predominant allylic rearrangement had occurred under these conditions which were hitherto thought to be essential for the occurrence of an  $S_Ni'$  mechanism [2]. The residual alcohols were found to be unrearranged and the chlorides themselves (III and IV) did not undergo interconversion under the reaction conditions or during the time of the experiment. No *endo* chlorides were detected. The same stereochemical results were obtained when pentane was used as solvent.

By separating the mixtures on chromatoplates, it was found that conversion of octenols to chlorides was about 35% in ether solution and about 20% in pentane solution.



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The results can be reasonably explained in terms of the intermediate formation of the isomeric chlorosulfite esters V and VI which then undergo dissociation to the common intimate ion pair VII. Subsequent loss of sulfur dioxide from the chlorosulfite anion generates chloride ion which then attacks randomly the *exo*-allylic positions C-2 and C-4 to give the *exo*-allylic chlorides III and IV. Diversion from the expected  $S_Ni'$  process is probably due to the exceptional stability of the rigid bicyclo-[3.2.1]octenyl cation.

It has been suggested that although the  $S_Ni'$  process is often depicted as a cyclic transition state [3], the formation and collapse of highly oriented ion pairs [2] could produce the same stereochemical result. It can now be concluded that in a symmetrical allylic intimate ion pair, such selective orientation does not exist, or at least is difficult to attain. Indeed, in these cases any net allylic rearrangement of the reactant should be just a reflection of the relative rates of attack at the alternative allylic termini by the gegenion. Accordingly, a prerequisite for the occurrence of an  $S_Ni'$  reaction appears to be a low stability of the related allylic cation.

Experiments are under way to re-investigate several long-standing claims for classic  $S_Ni'$  processes by means of our NMR. spectroscopic method.

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### 155. Note on the rôle of cyanides and polyphosphates in the formation of peptides in aqueous solutions of amino acids, at room temperature, as a possible prebiotic process

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*Résumé.* Les cyanures et les polyphosphates jouent un rôle important dans l'évolution chimique. Des solutions aqueuses d'acides aminés additionnées de trimétaphosphate et de cyanure, amenées à pH 11,5–12 par  $\text{NH}_3$  et maintenues à ce pH 4 jours à température ordinaire, contiennent les dipeptides correspondants, formés avec des rendements à peu près doubles de ceux obtenus en présence du seul trimétaphosphate. En présence uniquement de cyanure, il ne se forme pas de peptides. Dans ces mêmes conditions, une solution de cyanure ne fournit ni acides aminés ni peptides. Pour la formation abiotique de peptides à partir d'amino-acides, le système polyphosphate-cyanure est donc plus efficace que chacun de ses composants individuellement.

Hydrocyanic acid, HCN, formed by electric discharge in mixtures simulating supposed primitive atmospheres, e.g.  $\text{CH}_4 + \text{NH}_3 + \text{H}_2\text{O}$ , is known to be a precursor