The Role of Sulphur Trioxide in the Rearrangement of Protonated Hexamethylcyclohexadienones

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Summary SO_3 reacts with hexamethylcyclohexadienones in strong acid media and changes the relative stabilities of the isomers.

THE rearrangement of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone (I) in fuming sulphuric acid has been used by Hart to prepare the symmetrical 2,3,4,4,5,6-hexamethylcyclohexa-2,5-dienone (II). Koptyug[2] has reported that the same rearrangement occurs in chlorosulphuric and sulphuric acids.

In strong acids, as far as can be detected by n.m.r., both of the dienones (I) and (II) are completely protonated to

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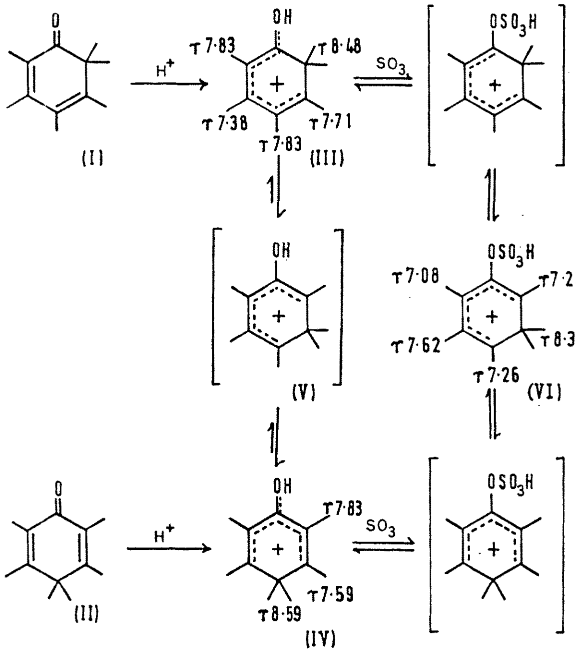
† Chemical shifts of the cations are all referred to internal methylene chloride taken as τ 4·70.

give the corresponding hydroxybenzenonium cations, (III) and (IV), the n.m.r. spectra† of which are given below. By using deuterium labelled compounds, Koptyug[2b] has shown that hydroxy-cation (V) is a transient intermediate in this rearrangement.



The rate of the rearrangement of the protonated unsymmetrical dienone (III) to the symmetrical dienone (IV) was determined by following the reaction by n.m.r. Provided electrophiles are absent I have found that the rate of this rearrangement is constant. Thus, at 61° the rate constant for this clean first-order process is $1{\cdot}10 \times 10^{-3}$ sec.$^{-1}$ ($\Delta F^{\ddagger} = 24{\cdot}1$ kcal./mole) in 85% and 95% *v/v* H_2SO_4 and $HFSO_3$ containing a small amount of anhydrous HF.

When the reaction was carried out in FSO_3H which had been fractionally distilled but not treated with HF it was found that there was a very large increase in the rate of rearrangement. The reaction which was no longer a simple first-order process, proceeded some 10^7 times faster than that described above at 61°. It was necessary to cool the solution to −40° before the rearrangement occurred with a comparable rate to that previously measured. The n.m.r. spectra of the protonated dienone (III) and product protonated dienone (IV) were identical to those seen in the solution which underwent the slow rearrangement at 61°.

It is clear that this very large increase in rate of rearrangement cannot be due to acid strength, as no change is seen in going from 85 to 95% H_2SO_4 and to $HFSO_3$ containing HF. The variable factor in these solutions is the presence of SO_3.[3] FSO_3H is contaminated by SO_3 which cannot be removed by fractional distillation. It is very effectively removed, however, by the addition of HF.[3] Another way of removing it is to add water[4] to the acid, and when this was done the reaction again proceeded at high temperatures. The addition of more, freshly-distilled SO_3 resulted in further increase in the rate of rearrangement. The same behaviour was observed in sulphuric acid systems, the rate of rearrangement being very much faster in fuming sulphuric acid.

While the n.m.r. spectra of the starting protonated dienone (III) and product protonated dienone (IV) in FSO_3H containing SO_3 were identical to those in acids not containing SO_3, during the course of the rearrangement of (III) into (IV) an intermediate was observed. Increase of the concentration of SO_3 increased the relative concentration of this intermediate until, in 20% SO_3 in $HFSO_3$ at −50°, only the spectrum of the intermediate could be detected. This intermediate was in equilibrium with the protonated symmetrical dienone (IV) and could be formed by the addition of SO_3 to a FSO_3H solution of (IV).

The n.m.r. spectrum of this intermediate, with chemical shifts typical of a polymethylbenzenonium cation with a full positive charge on the ring,[5] would suggest that it is the sulphate ester (VI). This is confirmed in that identical spectra were obtained from 2,4,6,6-tetramethyl-3,5-diperdeuteriomethylcyclohexa-2,4-dienone[6] and 2,4,4,6-tetramethyl-3,5-diperdeuteriomethylcyclohexa-2,5-dienone[1a] in FSO_3H containing SO_3. The same intermediate (VI), now as a zwitterion, was formed by reaction of either of the dienones (I) or (II) with anhydrous SO_3 in SO_2. It is interesting to note that no difference in the rate of methyl group migration in the heptamethylbenzenonium cation[7] could be detected in either 95% H_2SO_4 or 20% SO_3 in $HFSO_3$.

The differing order of stabilities of the three isomers of the hexamethylcyclohexadienones, when reacted with various electrophiles,‡ can best be understood in terms of a pentadienyl cation which can rearrange so as to put its substituents in their energetically most favoured positions.[5,8] The rates of methyl migration between the various isomers presumably reflect their relative thermodynamic stabilities.

I thank the National Research Council of Canada for financial support.

(*Received, June 5th,* 1969; *Com.* 789.)

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‡ Other strong electrophiles behave in a similar manner as SO_3.

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