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A Convenient Preparation of Cyclohepta-2,4-dienone: Isomerisation of Protonated Cyclohepta-3,5-dienone to Protonated Cyclohepta-2,4-dienone

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Summary Protonated cyclohepta-3,5-dienone has been shown to isomerise cleanly to protonated cyclohepta-2,4-dienone in FSO_3H at $+10°$; quenching of the acid solution affords a convenient preparation of cyclohepta-2,4-dienone.

CYCLOHEPTA-2,4-DIENONE and its simple derivatives have, despite their seeming simplicity, proved to be difficult to prepare. The synthesis of (**1**) reported by van Tammelen and Hildahl,[1] although effective, is lengthy and not suitable for the preparation of large quantities. Since cyclohepta-

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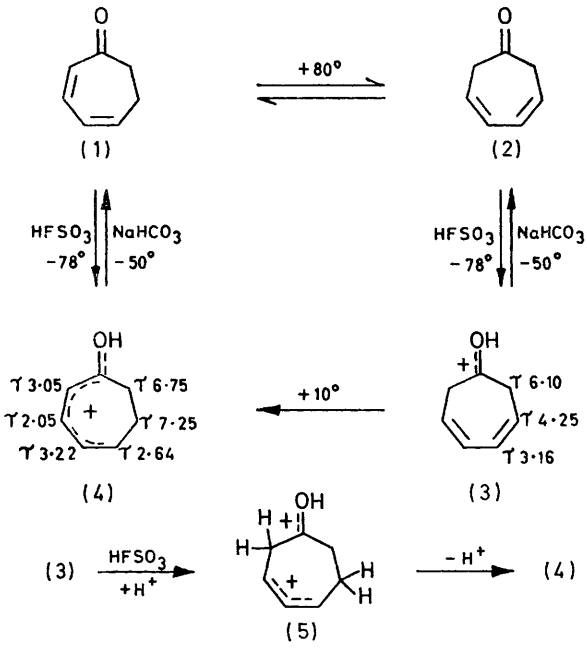
3,5-dienone (**2**) is well characterised, and readily available, we have investigated its possible isomerisations, in particular those giving (**1**).



Cyclohepta-3,5-dienone (**2**) was obtained by reduction of tropone[2] with sodium bis-(2-methoxyethoxyaluminium hydride) using the alkaline work up procedure described by Schuster *et al.*[3] Heating of (**2**) at 85° in CCl_4 gave, as previously reported,[4] an equilibrium mixture of (**1**) and (**2**) (**60**:**40**). Although separation of (**1**) and (**2**) was difficult owing to their ready thermal interconversion, small quantities of (**1**) could be obtained by preparative v.p.c. at low temperatures. The material so obtained had the same spectral properties as those previously described.[1,4]

Whereas (**1**) and (**2**) have comparable relative ground state energies, we find that there is a considerable difference in the relative energies of the two protonated forms (**3**) and (**4**). Thus solution of (**2**) in FSO_3H at −78° gave the hydroxy-cation (**3**). The n.m.r. spectrum of (**3**) is consistent with this structure and the ketone (**2**) can be recovered upon quenching the acid solution at low temperatures.† When the solution was warmed to +10°, (**3**) isomerised to a new hydroxy-cation which was identified as (**4**). The n.m.r. spectrum was consistent with this formulation and quenching of the solution at low temperatures gave (**1**) which was identical to authentic (**1**) in all respects. Protonation of (**1**) in FSO_3H at −78° generated (**4**) with the same spectral properties as the cation obtained by isomerisation of (**3**).

This rearrangement exhibits a marked dependence upon the acidity of the medium employed. Increasing the acidity of FSO_3H by the addition of SbF_5 caused a large acceleration in the rate of isomerisation which was proportional to the amount of SbF_5 added.[5] Moreover, when the isomerisation was carried out in $DFSO_3$, (**3**) was shown (n.m.r.) to have incorporated a deuterium atom at C(6) and not at C(2) or C(7). Taken together these observations strongly suggest that the diprotonated species (**5**) is an intermediate in this rearrangement. In weaker acids such as 98% H_2SO_4 a different mechanism is operative and additional products are formed.

As this isomerisation in FSO_3H proceeds until no (**3**) can be detected and as only one product (**4**) is formed, it provides the basis of a convenient preparation of (**1**). Typically (**2**) (750 mg) was dissolved in freshly distilled FSO_3H (5 ml) at −78°, warmed at +37° for 1 h, and quenched by addition to a suspension of $NaHCO_3$ in ether at −50°. Working up the heterogeneous ether mixture with water and distilling the product at 30° and 0·5 mm Hg leads to pure (**1**) (> 60% overall). This reaction can be extended to 2-alkyl substituted cyclohepta-3,5-dienones.

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† All chemical shifts are referred to CH_2Cl_2 taken as τ 4·70.

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