

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

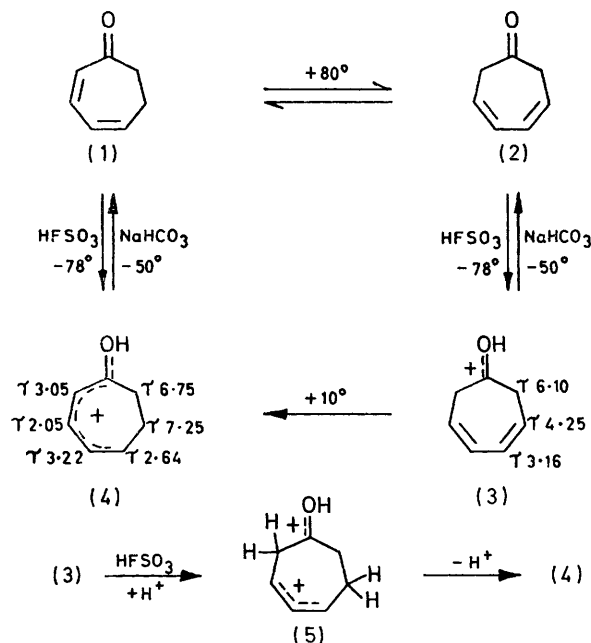
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Summary Protonated cyclohepta-3,5-dienone has been shown to isomerise cleanly to protonated cyclohepta-2,4-dienone in FSO_3H at $+10^\circ$; quenching of the acid solution affords a convenient preparation of cyclohepta-2,4-dienone.

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-

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 tropone² 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

† All chemical shifts are referred to CH_2Cl_2 taken as τ 4.70.

¹ E. E. van Tammelen and G. T. Hildahl, *J. Amer. Chem. Soc.*, 1956, **78**, 4405.

² P. Radlick, *J. Org. Chem.*, 1963, **29**, 960.

³ D. I. Schuster, B. R. Skolnick, and F. T. H. Lee, *J. Amer. Chem. Soc.*, 1968, **90**, 1300.

⁴ A. P. ter Borg and H. Kloosterziel, *Rec. Trav. chim.*, 1963, **82**, 1189.

⁵ R. J. Gillespie and T. E. Peel, *Adv. Phys. Org. Chem.*, 1971, **9**, in the press.

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 $+10^\circ$, (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 $+37^\circ$ 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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