

ANIONIC OXYCOPE REARRANGEMENTS IN ACETYLENIC SPIRO SYSTEMS<sup>1</sup>

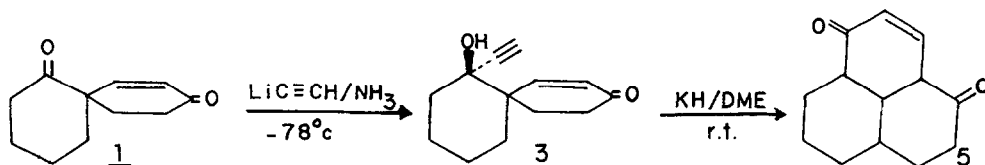
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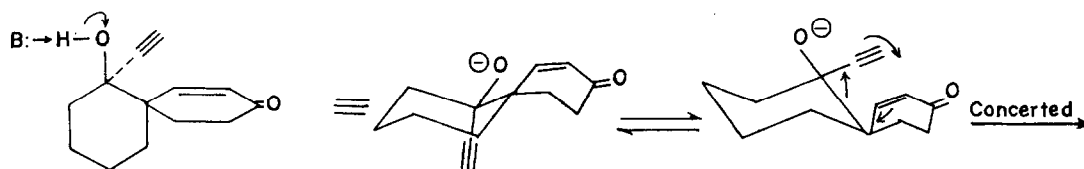
**Abstract** : The anionic oxy-Cope rearrangement of the acetylenic carbinol 3 furnishes the tricyclic diketone 5; substitution at the key position furnishes only the bicyclic 1,3-bridged dione 6.

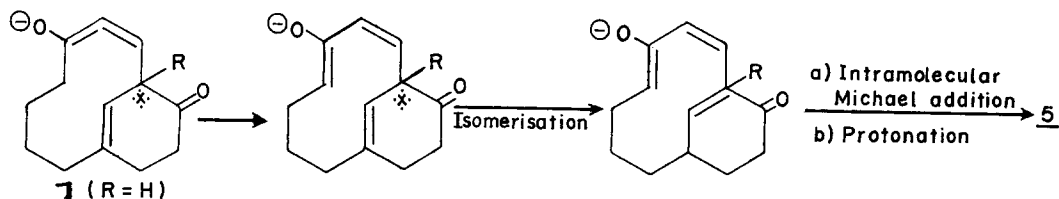
In oxy-Cope rearrangements of neutral substrates, the substitution of a C≡C for one of the olefinic moieties has been shown to accelerate such rearrangements<sup>2</sup>. It was of interest therefore to study the effect of such a substitution in anionic oxy-Cope rearrangements<sup>3</sup>. We report herein two anionic rearrangements of an acetylenic oxy-Cope moiety situated in a spiro system.

The spirodiones 1 and 2 were synthesized as per the reported procedures<sup>4,5</sup>. Addition of lithium acetylide in liquid ammonia at -78°C for 2 h to the spiro dione 1 followed by work up gave the ethynyl carbinol 3 as a colourless crystalline solid<sup>6</sup> (m.p. 124-125°C).



Treatment of the ethynyl carbinol 3 with potassium hydride in 1,2-dimethoxyethane at room temperature for 2 h afforded, after workup and purification, a colourless crystalline solid (m.p. 104-105°C) in 55% yield. Spectral data coupled with elemental analysis<sup>7</sup> favour structure 5 for the rearranged product. The formation of compound 5 can be rationalised as in scheme I.

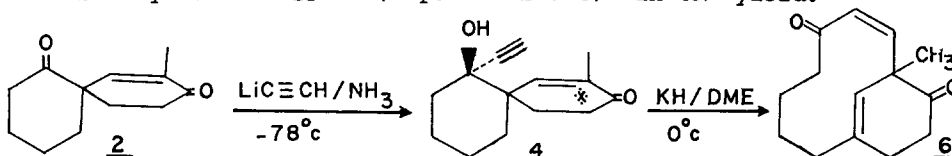




Scheme 1

In the above mechanism a flip of the cyclohexane ring to a more favourable diequatorial geometry is envisaged for the concerted reaction to occur followed by an isomerisation and a transannular Michael addition. It was of interest to study the rearrangement of compound 4 which contains a methyl group at a key atom (\*) involved in the isomerisation step in the above sequence.

Addition of lithium acetylide in liquid ammonia at  $-78^{\circ}\text{C}$  for 2 h to the spirodione 2 followed by workup gave the ethynyl carbinol 4 as a colourless crystalline solid (m.p.  $102-103^{\circ}\text{C}$ )<sup>7</sup> in 45% yield.



Treatment of the ethynyl carbinol 4 with potassium hydride in 1,2-dimethoxyethane at  $0^{\circ}\text{C}$  for 1 h afforded after workup and purification a viscous liquid in 67% yield. Spectral data coupled with elemental analysis<sup>7</sup> favour structure 6 for the rearranged product. Compound 6 is probably formed by a mechanism similar to the one pictured in Scheme 1; since isomerisation in species 7 (R=Me) is not possible the transannular Michael addition does not take place and the product is the product of protonation of species 7 (R = Me) itself viz the 1,3-bridged dione 6.

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**References :**

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7. All the new compounds had the expected analytical values and IR and PMR absorptions.

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