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[3.3.1]-PROPELLANE-2,8-DIONE

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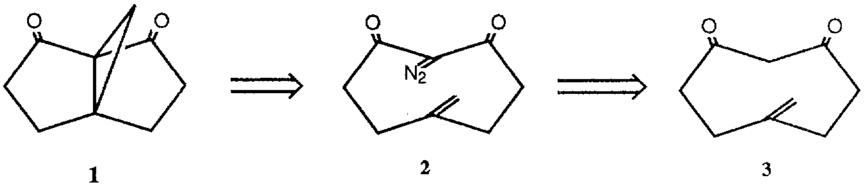
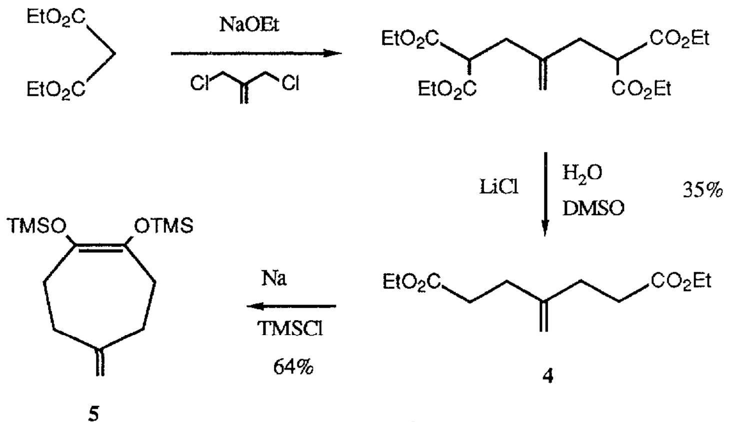
Summary: The title compound was prepared by transannular addition of a carbene to an exocyclic double bond. Rhodium acetate catalyzed decomposition of 2-diazo-6-methylene-1,3-cyclooctanedione gave **1** quantitatively.

We wish to report the first synthesis of the title compound, **1**, and a new approach to propellanes which we believe will have broad applications to other systems as well. We were intrigued by the idea of approaching this system from a monocyclic precursor using a transannular ring closure, as shown in Scheme 1. The necessary precursor, 6-methylenecyclooctane-1,3-dione (**3**), should in principle be readily available by acyloin condensation followed by ring expansion of the appropriate diester, a method Pirrung has used with great success to make the parent cyclooctanedione.[2] We are pleased to report that this approach has worked exactly as planned.



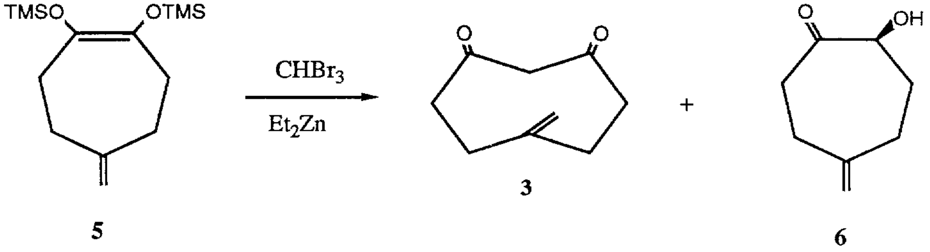
Scheme 1

To prepare the desired diester **4** (Scheme 2), 2-chloromethyl-3-chloropropene was treated with diethyl malonate anion and the resulting tetraester was decarboethoxylated using the method of Krapcho.[3] In this way, **4** was obtained in 35% yield after only one attempt.[4] Acyloin cyclization of this material in the presence of trimethylsilyl chloride occurred in 64% yield to give **5**.



Scheme 2

It then remained to be seen whether the exocyclic double bond would interfere with the ring expansion reaction . To avoid problems, limiting amounts of bromoform and diethyl zinc were used in the first attempt, but the undesired acyloin **6**, the result of hydrolysis of **5**, accompanied the desired cyclooctanedione **3** and was extremely difficult to separate from it (Scheme 3). The use of an excess of each reagent completely eliminated **6** and gave **3** quite cleanly in 50% yield. This product proved sufficient to complete the synthesis, so the reaction conditions have not been optimized. It is clear, though, that the more substituted double bond of **5** reacts first, so conditions for higher yields in this step will likely be found.



Scheme 3

It now remained to diazotize the alpha position and attempt the ring closure. Diazo transfer from tosyl azide[5] successfully inserted the diazo group in 50% yield.[4] The 300 MHz NMR spectrum of this key intermediate (**2**) showed two clean triplets and a singlet. Addition to **2** of a few crystals of rhodium acetate[6] caused immediate evolution of a gas and a gradual, quantitative conversion, over the course of an hour, to **1**, which has a far more complex NMR spectrum due to the loss of symmetry. Propellane **1** was identified by its proton and carbon NMR spectra, IR spectrum and mass spectrum. It forms beautiful crystals from benzene, mp 158-60°, and has survived several months in an open flask and a week in a steaming hot moving van with no noticeable decomposition.

We are continuing our investigations into this and related cyclizations in order to improve the yields and to investigate the applicability of transannular ring closures both to other propellanes[7] and to simple bicyclics also.[8]

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