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On the Construction of Bicyclo [m.3.0] Bridged Alkenes: Thermal Rearrangement of Spirocyclic Vinylcyclopropanes[§]

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Abstract: A facile transformation of spirocyclic vinylcyclopropanes to titled bridged-alkenes is presented; this approach finds an application in the synthesis of natural product carbon framework of diverse nature such as that of precapnelladiene and muscone.

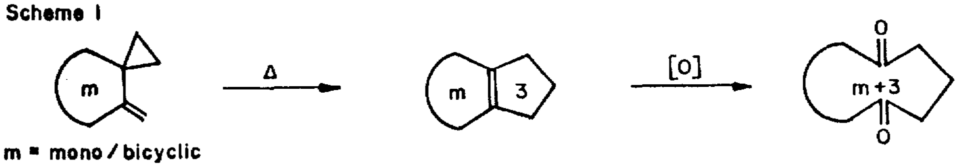
A large number of terpenoid natural products of carbon framework incorporating cyclopentane moiety fused to medium-sized rings have come to focus recently as synthetic targets.[1] This may be exemplified by precapnelladiene[2] [5-8] and the sesterterpene ophiobolin F[3] [5-8-5]. In this context, we perceived that devising a simple and efficient method to build a cyclopentane ring onto a given medium/large ring that would generate a class of bicyclo [m.3.0] bridged-alkenes, would be of immense synthetic value.

Our approach towards this objective primarily rests upon the well-known vinylcyclopropane-cyclopentene rearrangement, a versatile and widely-used cyclopentane annulation strategy.[4] Surprisingly, we find that the thermal transformation of spirocyclic vinylcyclopropanes has remained practically unexplored.[4,5] (Scheme-1).

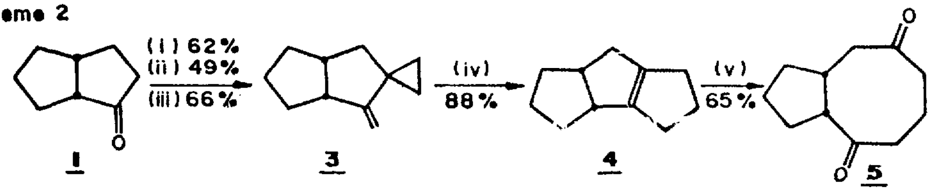
We wish to report herein our preliminary results from such a reaction that generated bicyclic and tricyclic bridged-alkenes and their oxidative scission to the corresponding medium and large-sized 1,5-diones, a class of potentially useful synthetic intermediates (Schemes 2 and 3).

The results arising from the substrates 1[6,7] and 2 are noteworthy and illustrate the efficacy of the approach. The first example provides a short and efficient synthesis of triquinane 4[7] and the bicyclic dione 5 in high yields. Interestingly, 5 constitutes a well-recognised entry point to the synthesis of precapnelladiene,[8] a biologically active sesquiterpenoid of marine origin. Especially, the facile transformation of 6 into 7 demonstrates the high degree of flexibility associated with the approach; that is, the highly mobile conformation of the C-12 carbocycle compared to that of the relatively rigid 3[9] does not deter the rearrangement. From the synthetic point of view, the suitability of the dione 8 as a key intermediate leading to muscone[10] is well recognised. It is significant to note that the transformations 3→5 and 6→8 represent three-carbon ring expansion process, an exercise of active current interest.[11] The generality of this approach and its potential in natural product synthesis, especially the framework of Taxol, a complex diterpene of current chemo-therapeutic interest, are being explored.

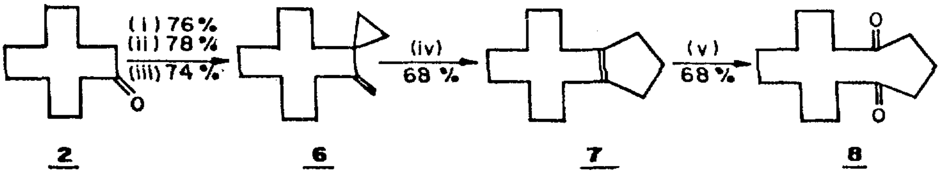
Scheme I



Scheme 2



Scheme 3



(i) Mannich / CH_3I ; (ii) $\overset{+}{-}\overset{|}{\underset{|}{S}}=O\ I^-$ / NaH ; (iii) Zn / $TiCl_4$ / CH_2Br_2 ; (iv) Δ, 500°
(v) $RuCl_3 - NaIO_4$, CCl_4 / MeCN / H_2O

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