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A NEW METHOD FOR CYCLOPENTENONE ANNELATION VIA THE REARRANGEMENT OF BICYCLIC CYCLOPROPYL KETONES. SYNTHESES OF BICYCLO[4.3.0]-NON-6-EN-8-ONE AND BICYCLO[5.3.0]DEC-7-EN-9-ONE

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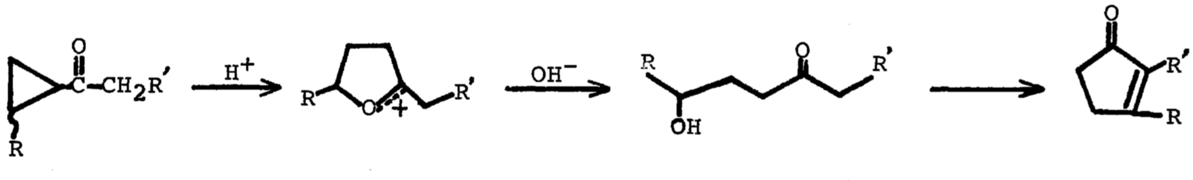
A new sequence for cyclopentenone annelation is described which involves the rearrangement of protonated bicyclic acetylcyclopropanes as a key step. Applications of the annelation procedure to cyclohexene and cycloheptene afforded the bicyclo[4.3.0]nonane and bicyclo[5.3.0]decane frameworks, respectively. Further elaboration of the bicyclodecane derivative provides a simple and efficient synthetic route to 2-substituted azulenes.

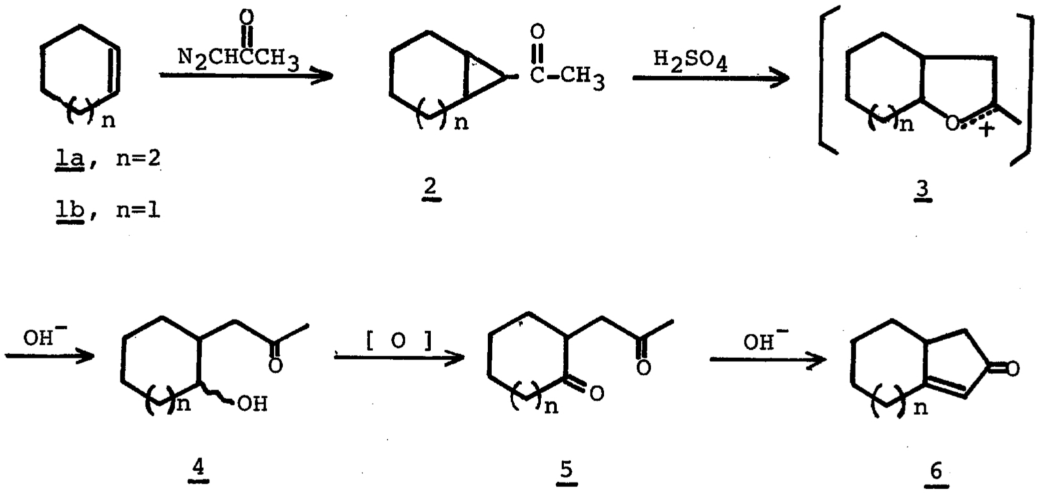
1,4-Dicarbonyl compounds are valuable intermediates for further elaboration to either furan or cyclopentenone systems, and a variety of synthetic routes to these compounds have been developed.[1)] In our continuing investigation of the synthetic utilization of cyclopropane rearrangements, we have recently reported[2)] a new synthetic route to 1,4-dicarbonyl compounds and cyclopentenones including dihydrojasmone which is based upon the utility of the rearrangement[3)] of protonated cyclopropyl ketones (eq 1).



(1)

We now wish to report an interesting application of the convenient reaction sequence to bicyclic cyclopropyl ketones providing a new method for cyclopentenone annelation, and to demonstrate the potential applicability of the annelation method to synthesis of 2-substituted azulene starting with cycloheptene. Scheme I outlines the reaction sequence for the new cyclopentenone annelation.

Scheme I



Bicyclic ketones 2a and 2b were prepared from the corresponding cycloalkene and diazoacetone following the literature procedures.[4)] The rearrangement of 2 into the respective oxolan-2-ylium ions (3) was carried out in 75% sulfuric acid at 75° for 1 hr; the nmr spectra of the resulting solutions confirmed the complete rearrangement [3a (n=2), δ6.70 (m, 1H) and 3.58 (s, 3H); 3b (n=1), δ6.57 (m, 1H) and 3.70 (s, 3H)]. Further treatments of the resulting solutions containing 3 with an aqueous solution of sodium bicarbonate followed by extractive work-up afforded γ-hydroxyketones 4 [4a (n=2), 93%; ir (film), 3430 (OH) and 1700 cm^{-1} (C=O, weak [5)]); nmr ($CDCl_3$), δ1.55[5)] (s, 3H); 4b (n=1), 80%; ir (film), 3400 (OH) and 1705 cm^{-1} (C=O, strong); nmr ($CDCl_3$), δ3.85 (m, 1H) and 2.21, 2.19[6)] (2s, 3H)].

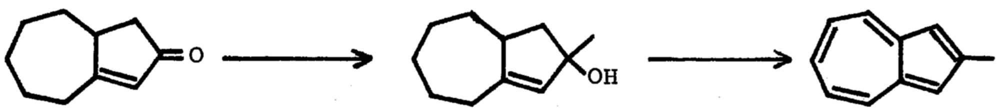
Jones' oxidation of 4 gave γ-diketones 5 [5a (n=2), 48%;[5)] ir (film), 1700 cm^{-1} (C=O); nmr (CCl_4), 2.10 (s, CH_3CO); 5b (n=1), 92%; ir (film), 1705 cm^{-1} (C=O); nmr (CCl_4), δ2.12 (s, CH_3CO)].

γ-Diketones 5 were further cyclized with 5% ethanolic potassium hydroxide to bicyclic cyclopentenones 6 [6a (n=2), 70%; ir (film), 1685 (C=O) and 1605 cm^{-1} (C=C); nmr (CCl_4), δ5.80 (m, ⪢H); 2.4-dinitrophenylhydrazone, mp 172-4° C (lit.[7)] 184-5°C); 6b (n=1), 60%; ir (film), 1700 (C=O) and 1620 cm^{-1} (C=C); nmr (CCl_4), δ 5.75 (s, ⪢H); 2.4-dinitrophenylhydrazone, mp 186-8°C (lit.[7)] 200°C)].

The structures of 5a and 6a were confirmed by comparisons of the ir and nmr spectra with those of authentic samples prepared by the method of Islam.[7)] The structures of 2[9)] and 5b[8)] were confirmed by comparisons of the ir and nmr data with the reported literature values.

As a consequence of the cyclopentenone annelation onto cycloheptene, hydroazulenone 6a is accessible as a starting material for the synthesis of 2-substituted azulenes. Thus, we have carried out a simple synthesis of 2-methylazulene 8. Scheme II outlines the sequence of reactions utilized.

Schem II



6a 7 8

Treatment of 6a with methyllithium in ether at 0°C followed by usual work-up10) afforded 7 quantitatively; ir (film), 3400 (OH) and 1640 cm^{-1} (C=C); nmr (CDCl$_3$), δ5.25 (m, $>\!\!=$-H). Dehydration and dehydrogenation of 7 were accomplished by heating with sulfur in triglyme at 200°C under nitrogen at reduced pressure for several minutes followed by column chromatography on alumina using pentane as the eluent, yielding 2-methylazulene 8 as a blue oil [40%; visible spectrum (pentane), λ_{max} 670, 646, 610, 590, and 560 nm]. The spectral data were essentially identical with the reported literature values.11)

Finally, it should be pointed out that the present cyclopentenone annelation sequence is of particular interest since only a limited number of methodology exists for cyclopentenone annelation,12),13) especially onto seven-membered ring systems. Furthermore, this approach offers significant features in comparison with the recently developed methods;12) the starting materials, bicyclic acetylcyclopropanes, are readily accessible and the procedure is operationally simple. Further study on the application of the cyclopentenone annelation procedure is in progress.

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References and Notes

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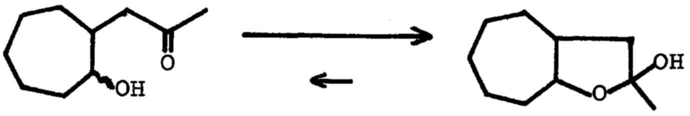
5) The ir and nmr spectra show that hydroxyketone 4a exists mainly in its hemiacetal form 4a'. The hemiacetal formation is at least partly responsible for the low yield of γ-diketone 5a.



4a 4a'

6) The two singlet peaks in the nmr spectrum of 4b may be due to two kinds of acetyl groups, suggesting the presence of the cis and trans isomers of 4b.

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11) M. Gordon, Chem. Rev., 50, 127 (1952); K. Hafner, Angew. Chem., 70, 419 (1958).

12) For recent cyclopentenone annelation procedures other than refs 7 and 8, see R. Noyori, K. Yodoyama, S. Makino, and Y. Hayakawa, J. Am. Chem. Soc., 94, 1772 (1972); P. A. Grieco and C. S. Pogonowski, J. Org. Chem., 39, 732 (1974); A. B. Smith, III, J. Chem. Soc., Chem. Commun., 1975, 274.

13) For recent cyclopentanone annelation methods, see ref. 9 and B. M. Trost and M. J. Bogdanowicz, J. Am. Chem. Soc., 95, 289, 5311 (1973). It is interresting to note that both the cyclopentanone annelation procedures are based on the utilization of the ring-opening rearrangements of cyclopropane rings.

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