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EFFECT OF ALKYL SUBSTITUENTS ON CYCLOBUTYL-CYCLOPROPYLCARBINYL TYPE REARRANGEMENT OF 2-OXABICYCLO[4.2.0]OCTAN-3-ONES

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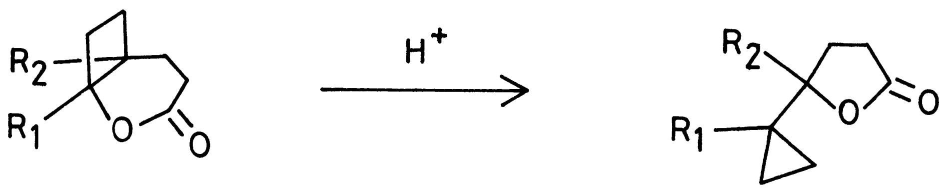
Cyclobutyl-cyclopropylcarbinyl type rearrangement of 2-oxabicyclo[4.2.0]octan-3-ones and remarkable effect of alkyl substituents at the bridgehead positions on this rearrangement are described.

While much attention has recently been shown on cyclobutyl-cyclopropylcarbinyl type rearrangement of constrained polycyclic lactones such as cage like compounds,[1] none is known for simple bicyclic or tricyclic system. We wish to report here the first example of this rearrangement of some simple 2-oxabicyclo[4.2.0]octan-3-ones having alkyl substituents at the bridgehead positions which facilitate the rearrangement.

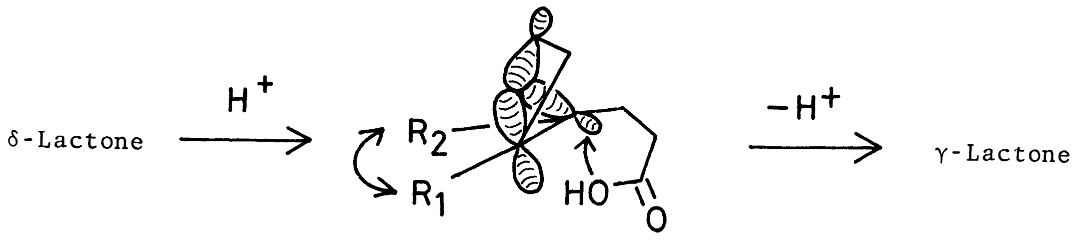
δ-Lactones (1)-(9)[2] were prepared by the Baeyer-Villiger oxidation (*m*-CPBA/$CHCl_3$ or H_2O_2/AcOH) of the corresponding ketones in good yields.[3] When unsubstituted or monomethyl substituted δ-lactones 1-3 were treated with acid (AcOH, reflux, 48h or *p*-TsOH/benzene, reflux, 48h), starting δ-lactones were recovered unchanged. On the other hand, dimethyl substituted δ-lactone 4 and ethyl methyl substituted one 5 gave the corresponding γ-lactones (10)[2] and (11)[2] in nearly quantitative yields under similar conditions (conversion; 20-40%).



1 $R_1=R_2=H$; 2 $R_1=CH_3$, $R_2=H$
3 $R_1=H$, $R_2=CH_3$; 4 $R_1=R_2=CH_3$
5 $R_1=C_2H_5$, $R_2=CH_3$

10 $R_1=R_2=CH_3$
11 $R_1=C_2H_5$, $R_2=CH_3$

It has been well known that the puckered geometry of cyclobutyl cation is favorable for cyclobutyl-cyclopropylcarbinyl rearrangement owing to overlap of ring orbitals.[4] Inspection of molecular models indicates clearly that, because of steric interaction between 1,2-dialkyl substituents, cyclobutane ring in cation intermediate (13) derived from dialkyl substituted lactones 4 and 5 are forced to have much puckered conformation compared to those derived from unsubstituted and monoalkyl substituted derivatives 1-3. Accordingly, it is reasonable that the present remarkable substituent effect may be attributed to steric effect which reinforces the puckered geometry of cyclobutane ring in cation 13.



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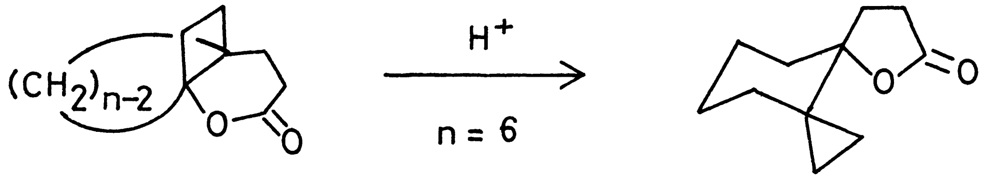
In order to develop the above concept further, the reactivity of tricyclic δ-lactones 6-9 toward the rearrangement was examined. Of four lactones 6-9, only the cyclobutane ring in a cation intermediate of 7 is expected to have puckered geometry owing to the requirement of the cyclohexane ring fused to the bridgehead positions to adopt chair conformation. As expected, 7 afforded the corresponding γ-lactone (12)^2 quantitatively (conversion; 90%) when treated with acid, whereas δ-lactones 6, 8, and 9 remained unchanged under similar conditions.



6 n=5; 7 n=6

8 n=7; 9 n=8

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References and Notes

(1) (a) G.Büchi and I.M.Goldman, J.Am.Chem.Soc., 79, 4741 (1957). (B) K.Hirao, H.Miura, H.Hoshino, and O.Yonemitsu, Tetrahedron Lett., 3895 (1976). (c) G.Mehta, V.Singh, and H.Duddeck, ibid., 1223 (1978). (d) Y.Yamashita, K.Sato, and T.Mukai, 37th Annual Meeting of the Chemical Society of Japan, Yokohama, April 1-4, 1978 (Abstracts of Papers, Vol 2, p 633).

(2) All new compounds gave satisfactory spectroscopic data and elemental analyses.

(3) In the case of 4, 5, and 7, trace of 10 and 11, and 10% of 12 were also obtained, besides the respective δ-lactones. These may be derived from initially formed δ-lactones by the rearrangement.

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