Tetrahedron Letters, Vol.28, No.50, pp 6371-6372, 1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

EVIDENCE FOR A STEREOELECTRONIC EFFECT IN THE BAEYER-VILLIGER REACTION: INTRODUCING THE INTRAMOLECULAR REACTION

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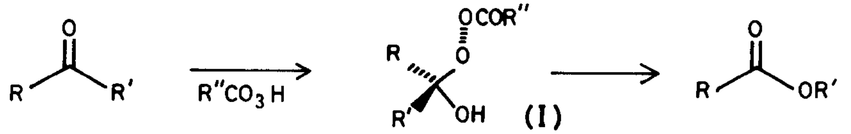
An intramolecular Baeyer-Villiger reaction has been effected involving a conformationally-fixed intermediate which breaks down with stereoelectronic control.

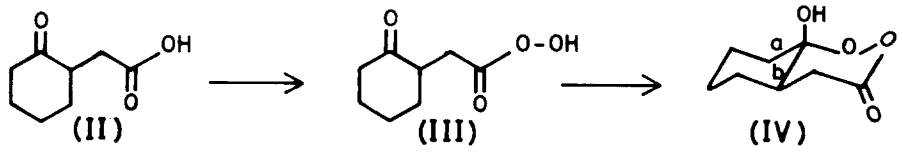
The Baeyer-Villiger reaction (eq. 1) takes place *via* an intermediate (I), the breakdown of which should be subject to a stereoelectronic effect. Accordingly, the migrating (R′) and leaving (OCOR″) groups in (I) would be expected to be anti-periplanar to each other in the transition state. Although such a stereoelectronic effect has been suspected to exist[2], the available evidence for it is not conclusive. We report here firm evidence for a concerted, stereoelectronically-controlled, mechanism.

The key idea of our strategy is a novel, intramolecular, Baeyer-Villiger reaction (eq. 2). Break-down of cyclic intermediate (IV) could take place by cleavage of either bond \`a′ (stereoelectronic control) or bond \`b′ (no stereoelectronic control). It is interesting to note that, classically, cleavage of bond \`b′ would be expected, as a tertiary group is known generally to migrate in preference to a secondary group.

When 2-oxocyclohexaneacetic acid (II) was treated with H_2O_2 in acetic acid at 70°C for 3h, diacid-acetate (VI) was isolated[3] (62%) as a viscous liquid, apparently formed *via* the corresponding lactone (V). There was no trace of either lactone (VIII) or its possible ring-opened products (IX) and (X), as seen by NMR. Hydrolysis of (VI) with KOH/MeOH yielded (VII) in 73%, m.p. 110-112°C.



(1)

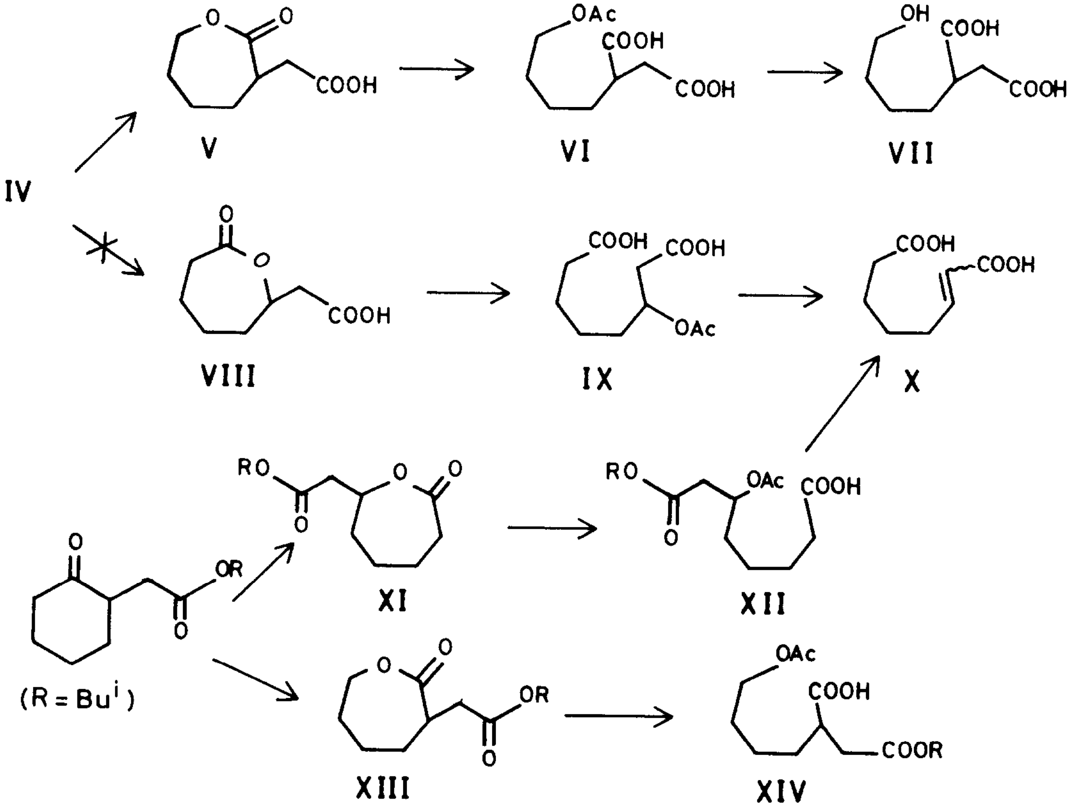


(2)

Further, when the 2-butyl ester of (II) was treated with H_2O_2 in acetic acid at 70° for 3h, there was obtained (81%) a mixture of ester-acid-acetates (XII) (XIV), presumably formed via lactones (XI) and (XIII) respectively, in an approximate ratio of 1:2 (NMR). After hydrolysis of the mixture with KOH/MeOH, unsaturated diacid (X) could be isolated by fractional crystallisation (30%).

The above observations are best explained by assuming that (II) undergoes, exclusively, an intramolecular Baeyer-Villiger reaction via (III) and (IV), and that rearrangement of (IV) is subject to a very strong stereoelectronic effect. Hence, unusually, a secondary centre migrates rather than a tertiary centre. Further, the 2-butyl ester of (II) can only undergo an intermolecular Baeyer-Villiger reaction; hence, migration of the tertiary centre also takes place.

References and Notes: (1) CSIR Junior Research Fellow. (2) P. Deslongchamps, Stereoelectronic Effects in Organic Chemistry, Pergamon, Oxford, 1983, p. 313; R. Noyori, H. Kobayashi, and T. Sato, Tetrahedron Lett., 2573 (1980); G. R. Krow Tetrahedron, 37, 2697 (1981). (3) All compounds have been characterised by spectral means (IR, NMR, MS) also by elemental analysis where relevant.



(Received in UK 13 October 1987)