CHROMIC ACID OXIDATION OF CYCLOBUTANONES TO γ-LACTONES

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ABSTRACT

A mechanism for the novel Baeyer-Villiger type of oxidation by chromic acid of cyclobutanones to γ-lactones is presented. A 4-σ-bond coupling, noticed in the NMR *spectrum of a γ, γ-dimethyl-γ-butyrolactone system, is explained.*

1. INTRODUCTION

Recently Petterson *et al.*[1] discovered that hypochlorous acid converts cyclobutanone to γ-butyrolactone and reported the finding with the observation that this is very likely the first case of a Baeyer-Villiger reaction with a non-peroxidic reagent.

2. PRESENT FINDINGS

In the course of our work on the reactions of ethyl 2, 2-dimethyl-3-ketocyclobutyl acetate (Ib), we reported[2] that the cyclobutanol ester (Ia) or its corresponding keto ester (Ib) furnished on treatment with chromic acid under a variety of acidic conditions, an abnormal product, higher boiling than Ib, characterised as ethyl terpenylate (II). In this connection it was recorded (*loc cit.*): "To our knowledge this appears to be the first instance of a Baeyer-Villiger type of cleavage of a ketone to a lactone brought about by chromic acid under acidic conditions".

Later, in the course of our work on the optical rotatory dispersion and circular dichroism studies on some cyclobutanones derived from α-pinene,[3] we once again found that oxidation of 2,2,3-trimethylcyclobutanol (IIIa) with sodium dichromate-sulphuric acid furnished, besides the cyclobutanone (IIIb), a higher boiling product with an extra oxygen, the structure of which was established as β,γ,γ-trimethyl-γ-butyrolactone (IV).

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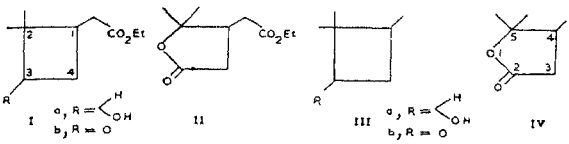
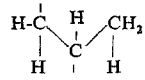


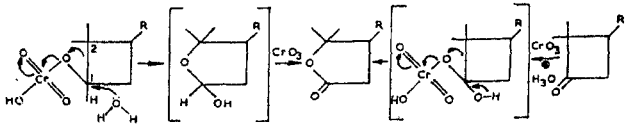
In the nuclear magnetic resonance spectrum (60 MHz, $\delta^{CCl_4}_{TMS}$) of the trimethyl-γ-lactone (IV) [$-O-\underset{\underline{CH_3}}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-$ 1.22 (3H, s), 1.37 (3H, s); $-\underset{CH_3}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underline{CH_3}$ 1.05 (3H, m); $-\underline{CH_2}-$ and $-\underset{|}{\overset{CH_3}{\overset{|}{C}}}-\underline{H}$ 2.0 to 2.67 (3H, b.m.)], the secondary methyl group at C-4 showed a novel multiple splitting feature. The multiplet (instead of the expected doublet) probably arises from the coupling of the secondary methyl protons with the C-4 methine and the C-3 methylene protons. A model of the γ-lactone (IV) revealed crowding of the secodary methyl with one of the *gem*-dimethyl groups, resulting in a restriction of rotation of the C-4 methyl. A 'M' arrangement



for one of the favoured conformations can lead to a 4 σ-bond coupling. In 2- and 11-keto steroids splitting of the C-18 and C-19 quaternary methyl groups has been explained on the basis of a similar 4 σ-bond coupling with the C-1 and C-12 methylene portons adjacent to the 2-and 11-keto functions.[4]

3. Mechanism of Lactone Formation

The following mechanism may be considered to explain the formation of the γ-lactones (II and IV) either directly from the cyclobutanol *via* the chromate ester and/or from the cyclobutanone formed initially by the normal chromic acid oxidation[5] of the cyclobutanol.



The essential feature of the mechanism is the migration of the C_1-C_2 bond to an electron deficient oxygen of the chromate ester, the migration being especially facilitated owing to the inherent strain in the 4-membered ring. The results of work on migration towards electron defficient hetero-atom centres in cyclobutane systems, currently under study in our laboratories, will be reported shortly.

REFERENCES

1. J. A. Horton, M. A. Laura S. M. Kalbag and R. C. Petterson .. *J. Org. Chem.*, 1969, **34**. 3366.
2. L. R. Subramanian and G. S. Krishna Rao .. *Tetraherdon*, 1967, **23**, 4167.
3. ——— .. .. *Can. J. Chem.*, 1969, **47**, 1147.
4. N. S. Bhacca and D. H. Williams .. *Application of NMR Spectroscopy to Organic Chemistry, Illustrations. from the Stercid, Field*, Holden-Day Inc , San Francisco, 1966, 115.
5. K. B. Wiberg .. *Oxidation in Organic Chemistry*, Academic Press, New York, 1966, 116.