

FORMATION OF γ - AND δ -LACTONES BY ANODIC OXIDATION OF
SODIUM BISULFITE-ADDITION PRODUCTS OF CYCLOALKANONES

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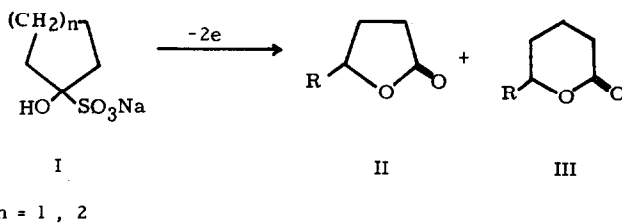
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Sodium bisulfite-addition products have been used for separation and purification of carbonyl compounds, because of their specific physical properties and ease of formation and decomposition. However, no synthetic use of them has been investigated except the use as intermediates of cyano-hydrin formation¹.

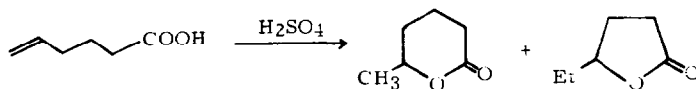
We describe here a simple preparation of γ - and δ -lactones by anodic oxidation of sodium bisulfite-addition products of cyclopentanone and cyclohexanone.



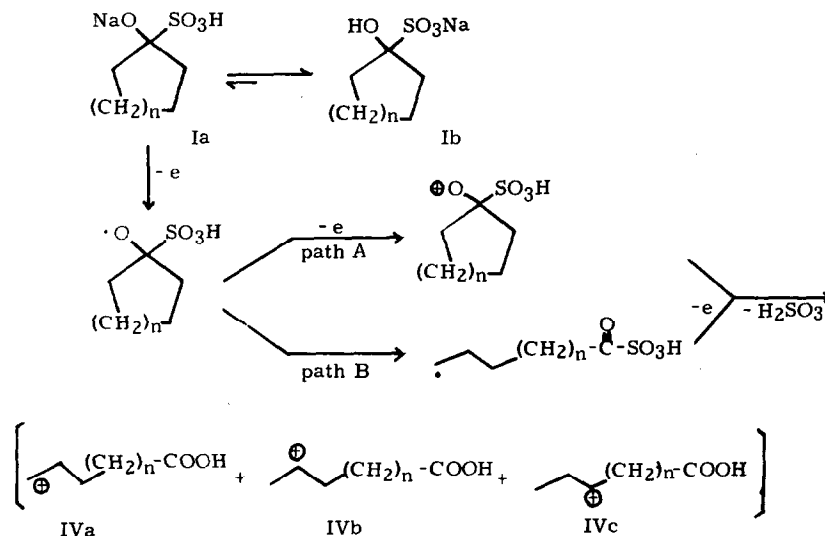
Illustrative is the anodic oxidation of sodium bisulfite-addition product of cyclohexanone. The anolyte contained an aqueous solution of the adduct (I, $n=2$, 20 g.) and the catholyte contained a dilute solution of sodium carbonate. Platinum anode and cathode (area ca. 12 cm^2) were used in a cell similar to one described by Allen². Electrolysis at 5 - 8 amps. was conducted at $30 - 40^\circ\text{C}$ for 5 - 9 hours. After the reaction, the electrolyte was extracted with a mixed solvent of ether and methylene chloride. An oily material was obtained after the removal of the solvent. Vacuum distillation afforded a fraction, b. p. $89 - 117^\circ\text{C} / 36 \text{ mmHg}$ in ca. 20% yield along with cyclohexanone. The fraction was confirmed to be a mixture of 4-hydroxyhexanoic acid lactone (II, $R=\text{Et}$) and 5-hydroxyhexanoic acid lactone (III, $R=\text{CH}_3$) in a ratio of about 3 to 2 by vapor phase chromatography (apiezon at 200°C), infrared and NMR spectroscopies and the comparison with authentic samples^{3, 4}.

From the aqueous solution, cyclohexanone was recovered. The electrolysis of the adduct (I, $n=1$) under a similar condition afforded γ -valerolactone⁵ (II, $R=\text{CH}_3$), b. p. $92 - 93^\circ\text{C}$, as a major product and a small amount of δ -valerolactone⁶ (V, $R=\text{H}$). The yields of II were 17 - 20%.

The formation and relative amounts of the lactones by the anodic oxidation of sodium bisulfite adducts are similar to the acid-catalysed reaction of 5-hexenoic acid⁴. Therefore, it seems reasonable to assume



that the electrolytic oxidation proceeds through carbonium ion or oxonium ion species as shown below.



The structure of the adduct is accepted to be Ib and an equilibrium between Ia and Ib is considered in solution⁷. The formation of the lactones and the low conversion can more easily be explained from the structure Ia and path B will be preferred to path A from the consideration of the oxidation potentials of carbon (11.26 V) and oxygen (13.64 V)⁸.

The relative stability of carbonium ion species IVa, IVb and IVc explains well the relative amounts of lactones. Furthermore, when the electrolysis of adduct (I, n-2) was carried out in methanol solution, methyl 5-methoxyhexanoate was isolated as a major product, which strongly supports the existence of carbonium ion IVb during the anodic oxidation.

References

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- 4) F. Dubois, Ann., 256, 134 (1890); R. P. Linstead and H. N. Rydon, J. Chem. Soc., 580 (1933).
- 5) Satisfactory elemental analysis was obtained for this lactone.
IR: 1775 cm^{-1} . NMR: 8.6 τ , 3H, doublet (>CH-CH_2); 5.4 τ , 1H, multiplet ($-\text{H}_2\text{C}-\overset{1}{\text{C}}\text{H}-\text{CH}_3$).
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