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OXYGENATION OF ORGANIC COMPOUNDS
A NOVEL OXIDATIVE CLEAVAGE OF 1,2-GLYCOLS

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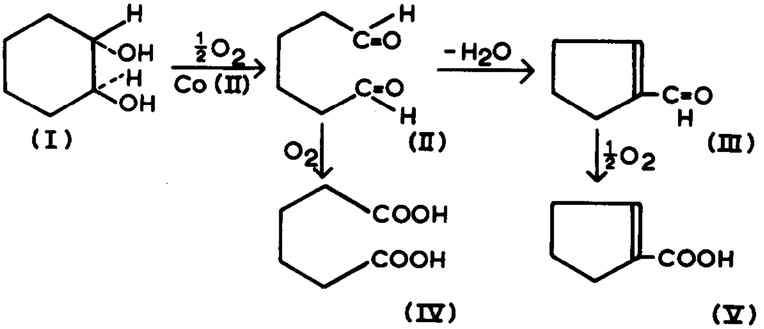
1,2-Glycols can be oxidized by several chemicals yielding aldehydes and ketones[1-5]. So far no catalytic, oxidative cleavage with the aid of oxygen of these diols is reported[(6)]. In the course of our investigations on specific catalytic oxidations of organic compounds, we found that cobalt(II)-salts are catalysts for the cleavage of 1,2-diols by molecular oxygen in an aprotic, polar solvent. The reaction takes place rapidly at 100°C when the mixture is vigorously shaken in an oxygen atmosphere and yields aldehydes in a good yield (60-80%). Good solvents are pyridine, 4-cyanopyridine, benzonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, anisole, chlorobenzene and thiacyclopentane-1,1-dioxide (Sulfolane), whereas water, primary alcohols, fatty acids and nitrobenzene proved to be unsuitable as solvents.

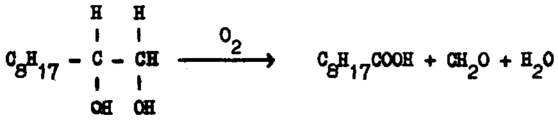
An interesting example is the cleavage of trans-1,2-dihydroxycyclohexane(I).



45 mmoles of (I), and 1 mmole of cobalt(II)acetate in 50 ml of benzonitrile were shaken in an oxygen atmosphere at 100°C. After 30 min. the oxygen uptake started and stopped after about 3 hours, during which time 350 ml (14 mmoles) of oxygen were taken up. The reaction mixture was analyzed on glycol, aldehyde and acid groups. 18.5 mmoles of glycol were oxidized, 12.8 meq. of aldehyde groups and 9.4 meq. of acid groups were formed. In the mixture adipic dialdehyde(II) and cyclopentene-aldehyde(III) (GLC, massspectrometry, 2,4-dinitrophenylhydrazone) were shown to be present. The acids formed were adipic acid and succinic acid. The oxygen consumption stops after oxydation of about 40% of the diol. Probably water formed during the reaction deactivates the catalyst. This was proved by adding water to the reaction mixture in the beginning, whereupon the oxygen uptake was lowered substantially in rate and quantity.

Besides the preparation of aldehydes, this method enables also the preparation of the corresponding acids, without prior isolation of the intermediate aldehydes. A typical procedure in this respect is the preparation of pelargonic acid from 1,2-dihydroxydecane.

45 Mmoles of 1,2-dihydroxy-n-decane and 1 mmole of cobalt(II)laurate were dissolved in 50 ml of benzonitrile and shaken with oxygen (1 atm.) at 100°C. After consumption of 19 mmoles of oxygen in a period of two hours the reaction stopped. The formaldehyde formed during this reaction was blown out of the mixture with pure oxygen and identified by its 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 165°C). Then again the reaction mixture was shaken in contact with oxygen and now 8 more mmoles of oxygen were taken up. Formaldehyde was blown out again a.s.o. Repeating this operation 5 times gave a total oxygen consumption of 46 mmoles. Based on this amount, the following reaction seems to take place:



$$C_8H_{17}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{CH}} \xrightarrow{O_2} C_8H_{17}COOH + CH_2O + H_2O$$

The reaction mixture contained 42 meq. acid and 8.6 meq. aldehyde. From the reaction mixture 5 g of pelargonic acid were isolated;

b_{18} = 150°C.

Equiv. weight, found: 160

calc.: 158,2.

Yield 70%.

REFERENCES

1. E.L. Jackson, *Organic Reactions* **II**, 341 (1946), J. Wiley and Sons Inc. New York, London.
2. R. Criegee, *Neuere Methoden der Präparativen organischen Chemie*, Band **I**, 21 (1963). Verlag Chemie, Weinheim/Bergstr.
3. R. Criegee, *Ann.* **507**, 159 (1933).
4. F.P. Greenspan and H.M. Woodburn, *J. Am. Chem. Soc.*, **76**, 6345 (1954).
5. Kunio Nakagawa, *Chem. Abstr.* **61**, 1789^c (1964).
6. Celanese Corporation of America. claims the cooxidation of 9,10-dihydroxystearic acid and oleic acid, with oxygen in propanol as a solvent, catalysed by cobalt(II)naphtenate. Brit. 809.452, Sept. 9, 1955; U.S. Appl. Sept. 10, 1954.