Highly Selective Oxidations of Diols by Silver Carbonate

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Summary The oxidation of α-, β-, and γ-di-secondary diols by silver carbonate on celite leads to hydroxy-ketones.

SILVER CARBONATE on celite has proved to be an efficient reagent for oxidizing primary or secondary alcohols to aldehydes or ketones, in high yields, and under very mild conditions.[1] The behaviour of diols such as butane-1,4-diol, pentane-1,5-diol, and hexane-1,6-diol is different; they give the corresponding γ-, δ-, and ϵ-lactones.[2]

We report on the results which have been obtained with other classes of diols. In general, a high selectivity has been observed, and only hydroxy-ketones were isolated, unless forcing conditions (larger excess of silver carbonate, reflux for many hours) were used.

Usually, oxidations are carried out in boiling benzene, with an excess of silver carbonate on celite† and the course of the reaction is followed by t.l.c. When the diol has disappeared, the solid is filtered off, carefully washed with benzene, and the solution evaporated. The nonvolatile material is purified either by chromatography on silica gel or by g.l.c.

Vicinal diols are not cleaved; they give α-hydroxy-ketones. For instance, cyclohexane-1,2-diol gives 2-hydroxycyclohexanone (45%, difficult to purify; the monomeric liquid dimerizes readily). 2,4-Dinitrophenylosazone: m.p. 224—226° dec., ν_{CO} (CCl_4) 1720 cm.$^{-1}$, dimer m.p. 156—158°.[4] A small quantity of cyclohexane-1,2-dione (40 mg., still impure, from 1·16 g. of starting diol) is also isolated [ν_{CO} (CCl_4) 1680 and 1660 cm.$^{-1}$; blue colour with $FeCl_3$–EtOH].

β-Glycols give β-hydroxy-ketones, usually in high yield. Thus, butane-1,3-diol, when heated for 2 hr. in benzene under reflux with 5 equiv. of silver carbonate on celite, gives 1-hydroxybutan-3-one in 80% yield. No significant amount of hydroxy-aldehyde could be detected. In the same way, commercially available pentane-2,4-diol (mixture of *threo* and *erythro*) is oxidized to 4-hydroxypentan-2-one (83%). The structures of these two compounds are proved by n.m.r.

Cyclohexane-1,3-diol leads to a mixture of cyclohexenone (24%) [ν_{CO} (CCl_4) 1690 cm.$^{-1}$; 2,4-dinitrophenylhydrazone m.p. 168—170°][5] and 3-hydroxycyclohexanone (58%) [ν_{CO} (CCl_4) 1722 cm.$^{-1}$] (These two ketones give the same 2,4-dinitrophenylhydrazone). The latter pure ketol with an excess of fresh silver carbonate does not give any diketone; dehydration of the hydroxy-ketone takes place much more rapidly than its oxidation.

When pentane-1,3,5-triol (1 mmole) is treated with 4·5 equiv. of silver carbonate–celite for 1 hr., a 43% yield of 1,5-dihydroxypentan-3-one is obtained. As expected, this compound is very unstable, and no crystalline derivative has been prepared so far. However, it can be isolated by chromatography on silica gel, and identified by i.r. [ν_{CO} ($CHCl_3$) 1710, ν_{CO} ($CHCl_3$) 1060 cm.$^{-1}$, primary OH] and n.m.r.

Hexane-2,5-diol (mixture of *threo* and *erythro*) affords a 68% yield of 5-hydroxyhexan-2-one [i.r. ν_{CO} (CCl_4) 1720 cm.$^{-1}$; semicarbazone m.p. 149—150°].[6]

Cyclohexane-1,4-diol is oxidized to 4-hydroxycyclohexanone (80%) [ν_{CO} (CCl_4) 1725 cm.$^{-1}$, 2,4-dinitrophenylhydrazone m.p. 151—152°[7] benzoate m.p. 61°[8] in 15 hr. with 4 equiv. of silver carbonate. Further treatment with a larger excess of oxidizing agent gives cyclohexane-1,4-dione [ν_{CO} (CCl_4) 1730 cm.$^{-1}$, m.p. 77—78°, dioxime m.p. 191—192°;[9] direct comparison with an authentic sample].

A few other diols have been investigated. As indicated previously[2] pentane-1,5-diol and hexane-1,6-diol give the corresponding δ- and ϵ-lactones. Heptane-1,7-diol and octane-1,8-diol, however, give 1-hydroxyheptanal and 1-hydroxyoctanal, respectively.

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† The preparation of the reagent has been described elsewhere;[1,3] 0·57 g. of silver carbonate on celite = 1 "equivalent" per millimole.

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