

Catalytic Reduction of Xanthone*

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On catalytic hydrogenation xanthone is reduced to a variety of products which include xanthene, various reduced xanthenes and also cleavage products (1,2). In xanthenes the central γ -pyrone ring is generally reduced first followed by the aromatic rings. We wish to report a hydrogenation procedure in which this sequence is reversed.

The hydrogenations were carried out at 100 atmospheres pressure in ethanol over a temperature range of 50 to 150°. The catalysts used were Raney nickel, Brown nickel and palladium on charcoal. Under these conditions, a new compound, $C_{13}H_{16}O_2$, was isolated from the crude reaction product. The yield of this compound was good when the hydrogenation was carried out below 80°, but decreased with increasing temperature and at temperatures greater than 100° the compound was not detected. Similar results were observed with all three catalysts.

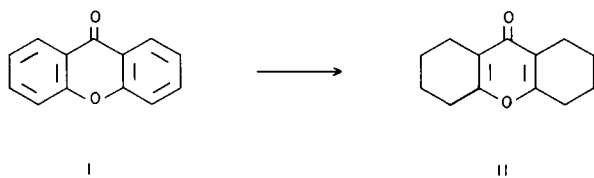
The U.V. spectrum showed an absorption at 257 $m\mu$, characteristic of a γ -pyrone ring. This was supported by the IR spectrum which showed absorptions due to an unsaturated carbonyl grouping (1660, 1615 cm^{-1}).

The lack of reactivity of this compound towards phenylhydrazine, hydroxylamine, bromine, and a negative reaction to the Baeyer test is characteristic of a γ -pyrone system.

The p.m.r. spectrum showed only two multiplets of equal intensity (1.7, 2.5 ppm) which were assigned to the α - and β -protons of a cyclohexene ring.

On the basis of spectral evidence and chemical tests it was concluded that the reduction product contained a γ -pyrone ring and partly reduced benzene rings and is represented by II.

The isolation of adipic acid on ozonolysis or permanganate oxidation was in full agreement with structure II.



The result of our work indicates that contrary to previous reports the pyrone ring of xanthone is relatively stable to hydrogenation. This is in keeping with the pseudo-aromatic nature of the γ -pyrone ring (3).

Under the reaction conditions used it would appear that a different hydrogenation mechanism is in operation from that commonly accepted for the reduction of xanthone (1,2).

EXPERIMENTAL

Octahydroxanthone (II).

Xanthone (10 g.) was dissolved in ethanol (200 ml.) and hydrogenated in an 0.5 l. autoclave at 80° and 100 atmospheres pressure for 24 hours. The crude product was purified by chromatography on a silica gel column (1 m x 2 cm). Elution was commenced with benzene, petroleum ether, ethyl acetate (2:2:1) followed by ethyl acetate to give octahydroxanthone. The product was recrystallized from pentane m.p. 132° (uncorrected); ν max (potassium bromide), 1660, 1615 cm^{-1} ; λ max (solvent ethanol) 214 (log ϵ 3.92), 257 $m\mu$ (log ϵ 4.1); proton resonance (deuteriochloroform), two multiplets of equal intensity at 1.7, 2.5 ppm.

Anal. Calcd. for $C_{13}H_{16}O$: C, 76.5; H, 7.88; O, 15.65. Found: C, 76.6; H, 7.88; O, 15.85.

Oxidation of II.

Octahydroxanthone (0.5 g.) was dissolved in acetone (100 ml.) and added to a solution of potassium permanganate (2 g.) in acetone (250 ml.) and sulfuric acid (1 ml.). The solution was allowed to stand overnight, and after filtering was diluted with water to less than 10% v/v acetone. The aqueous solution was extracted with ether (2 liters), the ethereal solution dried over sodium sulfate and evaporated to dryness. The residue (0.2 g.) was characterized as adipic acid.

Ozonolysis of II.

A solution of octahydroxanthone (0.3 g.) in carbon tetrachloride (50 ml.) was treated with ozone at room temperature for 2 hours. The solution was then washed with water, dried over sodium sulfate, and evaporated to dryness. The residue (0.1 g.) was characterized as adipic acid.

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