

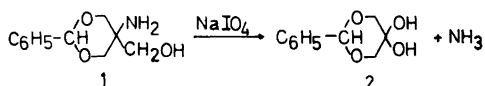
The Preparation of 5-Oxo-2-phenyl-1,3-dioxane

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On repeating the preparation of the synthetically useful benzal-derivative of 1,3-dihydroxyacetone the 5-oxophenyl-1,3-dioxane 2 by NaIO_4 -cleavage¹ of 5-hydroxymethyl-5-amino-2-phenyl-1,3-dioxane 1 according to Marei and Raphael² we encountered difficulties and obtained varying yields of impure 2.

On studying the reaction we found that the pH of the solution increased to 9.5 during the NaIO_4 -oxidation due to the liberated NH_3 . Since 2 seemed to be alkali-labile, we added an equivalent amount of KH_2PO_4 to the solution of 1 to neutralize the NH_3 and then obtained 2 in more than 90% yield. Control of the pH might be important in similar oxidations of 1,2-aminoalcohols with NaIO_4 liberating NH_3 or amines.



5-Oxo-2-phenyl-1,3-dioxane (2). The aminoalcohol 1 (105 g; 0.5 mol) was dissolved at 30 °C in H_2O (250 ml) and methanol (250 ml) and cooled to 5 °C with stirring. After adding solid KH_2PO_4 (68 g; 0.5 mol) a solution of NaIO_4 (107 g; 0.5 mol) in H_2O (1 l, dissolved at 30 °C) was added dropwise during 45 min maintaining a temperature of +10 °C – 15 °C inside the flask, whereupon a colorless precipitate formed. After warming to room temperature during 1 h the partly crystalline mixture was extracted with ethyl acetate (4 × 750 ml) and the extracts dried with Na_2SO_4 (300 g). Concentrating the extracts to 500 ml gave a first crop (70.0 g) of colorless crystalline hydrate 2, m.p. 84–85 °C. On concentrating the mother liquors to 100 ml and finally to 30 ml while adding each time about 0.5 ml of water, two further crops of slightly yellowish hydrate 2 (23.3 g), m.p. 78–80 °C were obtained. Combined yield of 2 92.3 g = 95%.

Crude yellowish hydrate 2 (50 g) can be readily recrystallized from ethyl acetate (250 ml) – water (5 ml) to give after cooling to –18 °C and washing with ice-cold ethyl acetate colorless 2 (43.8 g); m.p. 85–86 °C.

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