## SHORT COMMUNICATIONS

# Photolysis of Sugar Tosylate. A New Procedure for the De-*O*-tosylation

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The authors wish here to report a new method for the photolytic de-*O*-tosylation of sugar tosylate.[1]

Sugar tosylates are extensively used as important intermediates in the synthesis of carbohydrate derivatives. De-*O*-tosylations have usually been performed by catalytic hydrogenolysis,[1] but the application of this reaction is somewhat limited by the fact that a side reaction of a considerable extent might occur simultaneously.

Very recently it has been found in our laboratory that a tosyl group of sugar derivatives can be readily removed by a photolysis without any side reaction.

When a sugar tosylate in methanol is irradiated by UV in the presence of an equimolecular amount of sodium methoxide at room temperature, a parent sugar derivative is regenerated in an excellent yield. Without any UV irradiation, the de-*O*-tosylation does not occur under the same reaction conditions. A typical method is as follows: a methanolic solution (250 ml) of methyl 6-*O*-tosyl-α-D-glucopyranoside[2] (1.0 g) containing sodium methoxide was irradiated with a 100-W high-pressure mercury lamp in a water-cooled quartz immersion well (*Ushio Denki Co.*) at 25—27°C for 5 hr, with a gentle bubbling-in of nitrogen. The progress of the reaction was examined by thin-layer chromatography (TLC). The irradiated mixture was filtered and evaporated *in vacuo* to afford a brown syrup, which was then purified by silica-gel column chromatography. Methyl α-D-glucopyranoside was recovered in a 90% yield; it was identified with an authentic sample by a mixed-melting-point determination and by a comparison of their infrared spectra.

Without any UV irradiation, the starting material was recovered quantitatively under the same conditions. By cutting off wavelengths under 3100 A in an UV irradiation with a Pyrex tube,[*1] the reaction was also retarded completely.

A similar procedure for 1,2:3,4-di-*O*-isopropylidene-6-*O*-tosyl-α-D-galactopyranose,[3] which has a primary tosyloxy group, gave quantitatively the syrupy 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose, which could be identified with an authentic specimen[3] by a comparison of their IR spectra and by TLC, and which could also be converted into the tosylate again. This tosylate was identified with the starting material by a comparison of their melting point and IR spectra.

The method described above has been successfully applied to a secondary tosyloxy group: from methyl 3-*O*-tosyl-β-D-glucopyranoside, which had been prepared by the selective de-*O*-acetylation of methyl 2,4,6-tri-*O*-acetyl-3-*O*-tosyl-β-D-glucopyranoside,[4] methyl α-D-glucopyranoside was obtained in a 80% yield, while from 1,2 : 5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucopyranose[5] 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucopyranose was regenerated in a quantitative yield.

The details of this work will be reported later.

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[1] R. S. Tipson, *Advances in Carbohydrate Chem.*, **8**, 107 (1953).

[2] F. Cramer, H. Otterbach and H. Springmann, *Ber.*, **92**, 384 (1959).

[*1] This tube (Corning 774) may be used for experiments at wavelengths longer than 3100A.

[3] K. Freudenberg and R. M. Hixon, *ibid.*, **56**, 2119 (1923).

[4] S. Peat and L. F. Wiggins, *J. Chem. Soc.*, **1938**, 1088.

[5] K. Freudenberg and O. Ivers, *Ber.*, **55**, 929 (1922).