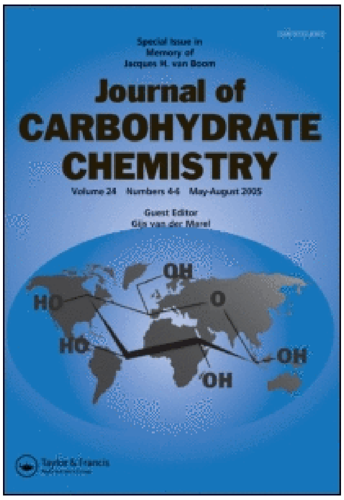

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Photochemical Reactions of Methanesulfonates. A New Deprotection Reaction

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COMMUNICATION

PHOTOCHEMICAL REACTIONS OF METHANESULFONATES. A NEW DEPROTECTION REACTION

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Although esters of methanesulfonic acid and p-toluenesulfonic acid have similar reactivity in substitution reactions, their photochemical behavior is quite different. p-Toluenesulfonates experience photochemical desulfonation in the presence of amines, a reaction which regenerates the parent alcohols (eq 1) in good to excellent yields and thus allows the p-tolylsulfonyl group to become an effective photoremovable protecting group.[1-4] In contrast, photolysis of methanesulfonates is not regarded as a viable method for group deprotection since deprotection is accompanied by reduction (eq 2).[5]

A significant difference in the reaction conditions for methanesulfonate photolyses, when compared to those of p-toluenesulfonates, is tne reaction solvent. Successful

$$\mathrm{ROTs} \xrightarrow[\mathrm{MeOH} \atop \mathrm{Et_3N}]{h\nu} \mathrm{ROH} \quad \text{(eq.1)}$$

$$\left[\mathrm{CH_3SO_2OR}\right]^{\overset{\ominus}{\cdot}}$$

1

$$\mathrm{ROMs} \xrightarrow[\mathrm{HMPA}]{h\nu} \mathrm{ROH} + \mathrm{RH} \qquad \text{(eq.2)} \qquad \left[\mathrm{CH_3C_6H_4SO_2OR}\right]^{\overset{\cdot}{\ominus}}$$

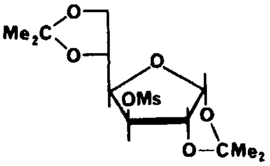
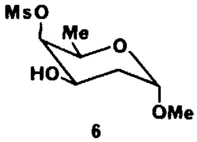
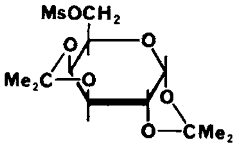
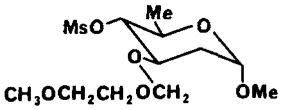
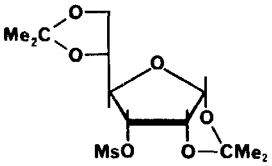
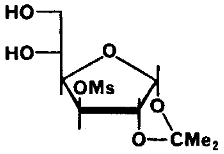
2

irradiation conditions for methanesulfonates involve photolysis in HMPA (hexamethylphosphoric triamide).[5,6] (p-Toluenesulfonates typically are irradiated in methanol.) The reason for selecting HMPA as a solvent is that it provides a pathway for sulfonate activation. Methanesulfonates absorb uv light only at short wavelengths (λ_{max} = 205 nm)[6] while HMPA is capable of much longer-wavelength light absorption (e.g., light from a typical, low-pressure, mercury-vapor lamp); consequently, the photolysis of methanesulfonates in HMPA begins with excitation of the solvent and is thought then to involve electron transfer from excited HMPA to the methanesulfonate to generate the radical anion **1**.[5] Since HMPA also is known to promote reduction reactions,[7] it is not surprising that a mixture of products is formed when this solvent is used; furthermore, it is reasonable to project that methylsulfonyl deprotection, without accompanying reduction, might occur in a solvent that does not promote the reduction reaction. Deprotection that avoids reduction would allow the methylsulfonyl group to become a candidate for a new photolabile protecting group.

Selecting a more typical irradiation solvent (e.g., methanol, ethanol, or ethyl ether) for methanesulfonates is a simple matter; however, formulating a new method for productive absorption of the incident radiation is a more difficult process. (Direct irradiation of methanesulfonates causes no reaction.)[6,8] A potential method for initiating reaction is suggested in the work of Jortner and coworkers,[9] who have shown that photolysis of iodide, bromide, or chloride ions causes electron ejection into solution. (This reaction is of particular interest in the case of iodide ion

TABLE I

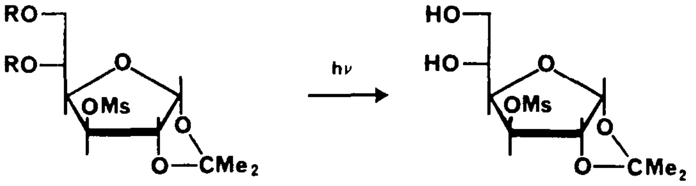
$$\mathrm{ROMs} \xrightarrow[\substack{\mathrm{MeOH} \\ \mathrm{NaHCO_3}}]{\substack{h\nu \\ \mathrm{KI}}} \mathrm{ROH}$$

METHANESULFONATE	PERCENT YIELD	METHANESULFONATE	PERCENT YIELD
 3	90	 6	74
 4	64	 7	70
 5	61	 8	60

since relatively long-wavelength uv light (254 nm) is absorbed.) If an ejected electron is captured by a methylsulfonyl protected compound, the radical anion produced (**1**) would be analogous to that (**2**) generated by p-toluenesulfonate photolysis.[10] A deprotection reaction similar to that observed for p-toluenesulfonates (i.e., no photoreduction) could be expected.

Irradiation of each of the methanesulfonates **3-8** (1.5 mmol) in methanol (250 mL) in the presence of potassium

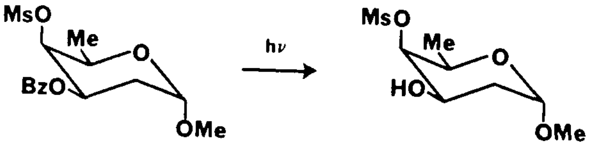
TABLE II



9 R = Ac 85 %

10 R = Ts 100 %

11 R = Bzl 60 %



12

98 %

iodide (4.0 mmol) and sodium bicarbonate (16 mmol) for 40 h gave the corresponding deprotected sugars in the yields shown in Table I.[11] Photolysis of methanesulfonates in the presence of iodide ion provides the desired method for deprotection without reduction; therefore, the methylsulfonyl group now can be considered to be a photoremovable protecting group. Compounds **3-8**, however, have no chromophore other than the methylsulfonyl group; consequently, to determine the situations in which this deprotection reaction will be useful, it is necessary to ascertain the photochemical behavior of methanesulfonates containing other protecting groups.

Photolysis of the methanesulfonates **9-12** (compounds which contain the acetyl, benzyl, p-tolylsulfonyl, and benzoyl groups) caused exclusive non-methylsulfonyl deprotection (Table II).[12] (None of these deprotection reactions occurred when **9-12** were subjected to the reaction conditions in the absence of light.) The reactions shown in Table II place a limitation on the situations in which methylsulfonyl protection can be removed without affecting other protecting groups. It appears that compounds with unsaturated (C=C or C=O) protecting groups will experience loss of these groups prior to methylsulfonyl deprotection. One consequence of these findings is that a pathway now is established for selective reaction of sulfonate esters; thus, irradiation of **10** first removes the p-tolylsulfonyl groups to form **8** and then further photolysis of **8** eliminates methylsulfonyl protection. An attractive method for conducting selective sulfonate deprotection is to remove the p-tolylsulfonyl groups by irradiation in the presence of triethylamine (conditions in which methylsulfonyl groups are unreactive) and then complete the deprotection by irradiation of the methanesulfonate in the presence of potassium iodide.

We currently are investigating the reactions of compounds **11** and **12** to determine the mechanism for loss of the benzoyl and benzyl groups. Based upon studies in non-carbohydrate systems,[12,13] it appears reasonable to propose that radical anions are involved in these reactions. We are interested not only in determining how these reactions take place but also in evaluating whether photochemical deprotection of these groups may have useful synthetic application.

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8. We were unable to observed any reaction of compound **3** upon irradiation with a Hanovia unfiltered, medium-pressure mercury lamp.

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11. Irradiations were conducted in a quartz reaction vessel using a Rayonet apparatus equipped with 16 Rayonet RPR-2537 A lamps. All new compounds reported in this paper have spectroscopic data consistent with the structures proposed. Satisfactory elemental analyses were obtained for all new compounds.

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