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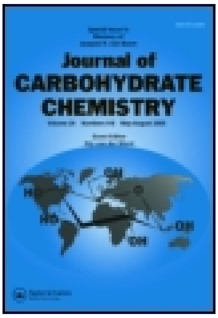

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Shaoming Duan [a], Roger W. Binkley [a] & Edith R. Binkley [b]
[a] Department of Chemistry, Cleveland State University, Cleveland, Ohio, 44115
[b] Center for Carbohydrate Study, Oberlin, Ohio, 44074

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PHOTOCHEMICAL REACTIONS OF IMIDAZOLE-1-SULFONATES (IMIDAZYLATES)

Shaoming Duan,* Edith R. Binkley,[#] and Roger W. Binkley*

*Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115
[#]Center for Carbohydrate Study, Oberlin, Ohio 44074

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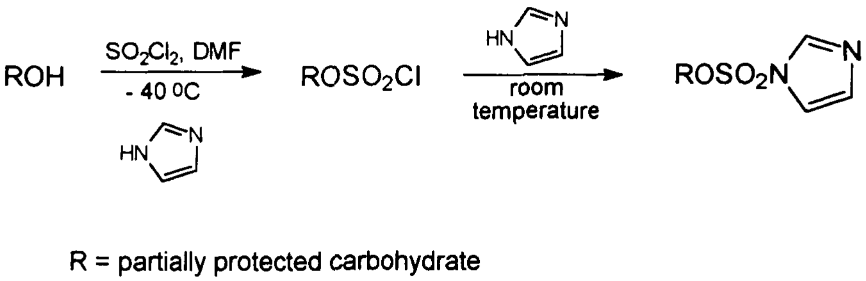
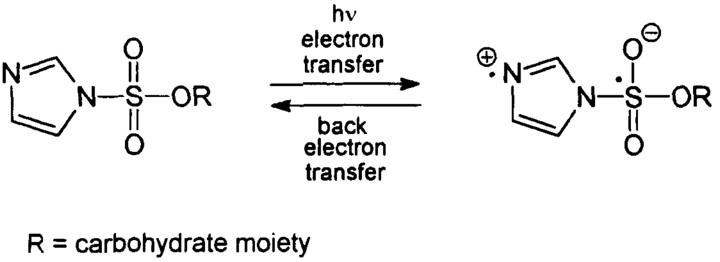
ABSTRACT

Imidazylates **1-3** were irradiated in methanol in the presence and in the absence of the electron donor triethylamine. In each case photochemical deprotection occurred in excellent yield to form the partially protected sugar from which the imidazylate was synthesized. Reactions in the presence of triethylamine required much shorter irradiation times.

INTRODUCTION

In 1981 Hanessian and Vatèle described several simple procedures for conversion of partially protected carbohydrates into imidazole-1-sulfonates (imidazylates).[1] (A typical synthesis is shown in Scheme 1.) Imidazylates were of interest because they were expected to be more reactive than tosylates in S_N2 substitution reactions. This expectation was fulfilled when these compounds were found not only to be much more reactive than tosylates but, in fact, comparable in reactivity to trifluoromethanesulfonates (triflates). Since their discovery imidazylates have become valuable synthetic intermediates that have been transformed into deoxyhalogeno[1,2] and azidodeoxy[1,3-5] sugars and used in inversion of configuration at chiral centers.[6]



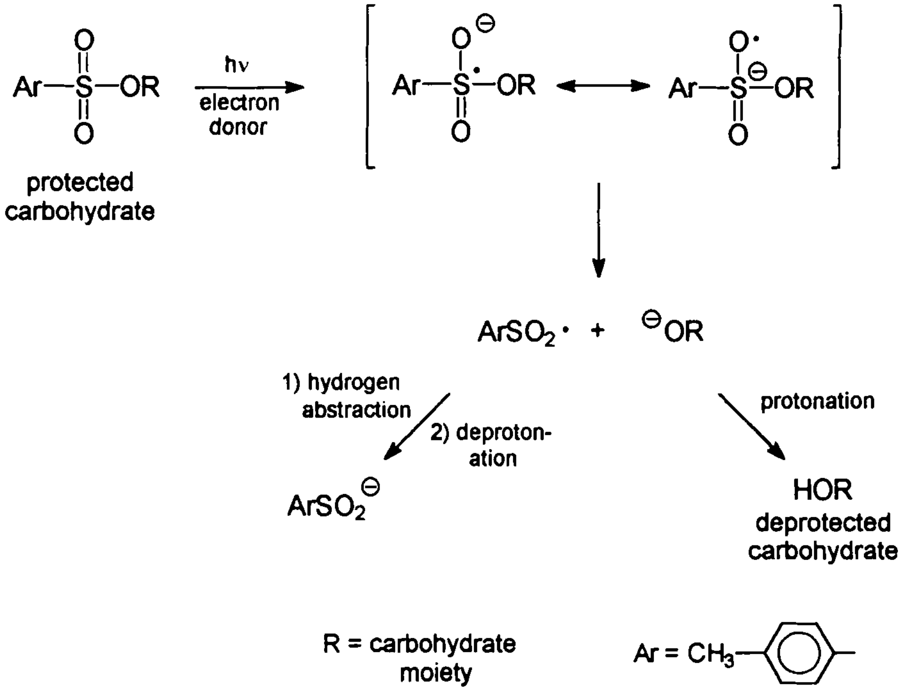


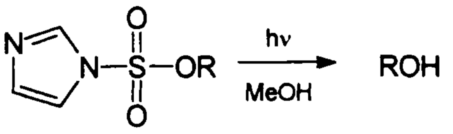
(1)

Scheme 1

Recently Vatèle and Hanessian published a detailed account of their studies of imidazylates.[7] In this paper they summarized the advantages of S_N2 displacement reactions involving these compounds by noting that imidazylates: a) may be easily prepared in several ways, b) are readily displaced by a variety of nucleophiles, and c) generally are stable enough to be stored for significant periods of time without decomposition. Our recent studies on sulfonate photochemistry make it possible to add one other feature to this list. In order to do so, however, it is useful first to discuss briefly some photochemistry of *p*-toluenesulfonates.

Photolysis of a carbohydrate *p*-toluenesulfonate in the presence of an electron donor, such as triethylamine, produces the corresponding radical anion. The radical anion fragments to give the *p*-tolylsulfonyl radical and an alkoxide ion (Scheme 2).[8,9] This photochemical reaction can be viewed as part of a protection-deprotection sequence in which hydroxyl groups are protected as esters of *p*-toluenesulfonic acid and, after appropriate synthetic steps, the ester protecting group is removed by UV radiation.[10,11] Since a critical part of this photochemical process is the transfer of an electron from an amine to an excited tosylate, photo-





(2)

R = carbohydrate moiety

Scheme 2

chemical deprotection could be particularly effective for imidazylates because the electron donor and electron acceptor potentially are part of the same molecule (eq 1).

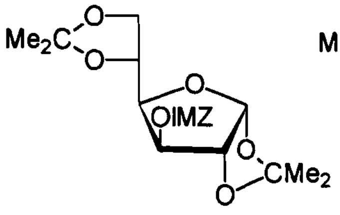
Irradiation of imidazylates **1-3** did generate in excellent yields the alcohols from which these compounds were synthesized, but the reactions required irradiation times that were as long or longer than reaction of the corresponding tosylates (eq 2, Table 1); consequently, these reactions provided no indication of increased reactivity due to internal electron transfer.

Table 1. Yields for Products from Irradiation of Imidazylates **1-3**

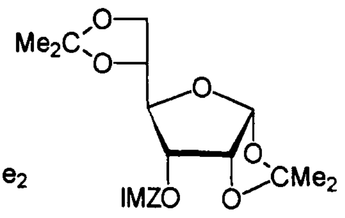
	1	**2**	**3**
Et_3N Absent	95% (25)[a]	96% (35)[a]	98% (18)[a]
Et_3N Present	100% (8)[a]	100% (8)[a]	98% (8)[a]

a. The numbers in parenthesis are irradiation times in hours.

It was possible that intramolecular electron transfer was occurring but that back electron transfer (or another reaction that regenerated starting material) was the major process after the initial electron-transfer took place (eq 1). Since deprotection was slow when imidazylates were irradiated by themselves, we decided to test their photochemical reactivity during photolysis in the presence of triethylamine. Under these conditions photochemical deprotection was essentially quantitative and required substantially shorter irradiation times (Table 1).



1



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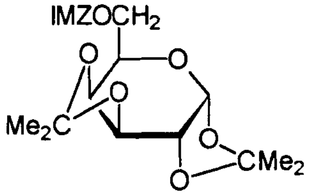

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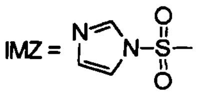

It is clear from these results that the imidazylsulfonyl group can be removed very effectively by photolysis and that the preferred conditions are those that involve irradiation in the presence of an electron donor. The ease of formation of imidazylates and their stability in the absence of nucleophiles suggests that they could be used as photoremovable protecting groups in appropriate situations.

EXPERIMENTAL

General Procedures. Column chromatography was conducted with a 2.5 x 15 cm column of 240-400 mesh silica gel (Baker) developed with 1:3 ethyl acetate–hexane. TLC was done with Whatman silica gel 60A plates developed with 1:3 ethyl acetate–hexane. NMR spectra were determined with a Brucker AC300F spectrometer with deuterochloroform as the solvent. Mass spectra were obtained with a Finnigan TSQ-45 mass spectrometer.

General Photochemical Procedures. Photochemical reactions were conducted in a quartz vessel (2.5 x 25 cm) with a Rayonet, Srinivasan-Griffin apparatus equipped with 16 Rayonet RPR-2537A UV lamps. All photochemical reaction mixtures were purged with nitrogen for 1 h prior to photolysis, and the purge was continued during irradiation. In each case the photochemical reaction mixture consisted of 0.50 mmol of the imidazylate and 1.5 mmol of sodium bicarbonate dissolved in 75 mL of methanol. (In reactions conducted in the presence of an electron donor, 10 mmol of triethylamine was added to the reaction mixture.) After irradiation, the solvent was evaporated under reduced pressure and the residue was chromatographed with ethyl acetate–hexane (1:3) to give the products shown in Table 1 in the indicated yields. Product identities were established by comparison of their ^{1}H and ^{13}C NMR and their electron-impact mass spectra with those of authentic samples. Compounds **1-3** were stable under the reaction conditions in the absence of light.

Synthesis of Imidazylates 1-3. The imidazylates **1-3** were synthesized according to the procedure of Vatèle and Hanessian (method A).[7]

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