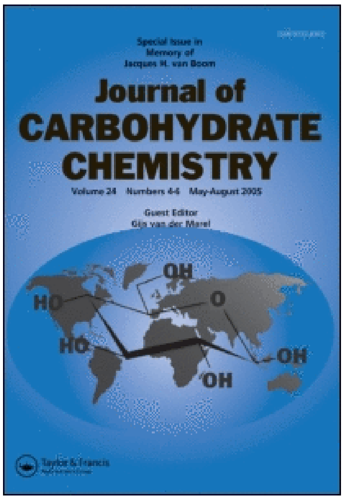

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COMMUNICATION

A NEW PHOTOCHEMICAL REACTION OF SULFONIC ACID ESTERS

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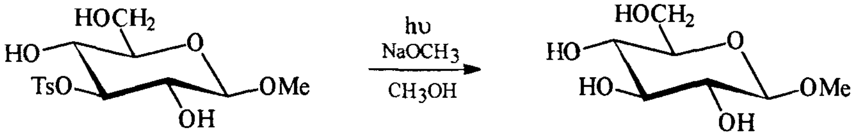
In 1968 Zen and coworkers reported that the *p*-tolylsulfonyl group could be removed from carbohydrate systems by photochemical reaction (eq 1).[1] Since then other investigators



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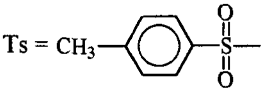
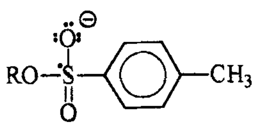


have used this deprotection process in carbohydrate synthesis.[2-10] Mechanistic studies[11-16] have shown that tosylate photolysis is promoted by compounds (e.g., triethylamine) that donate an electron to an excited *p*-toluenesulfonate to generate a radical anion (**1**). This



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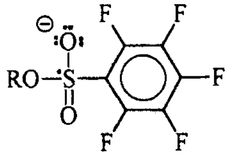
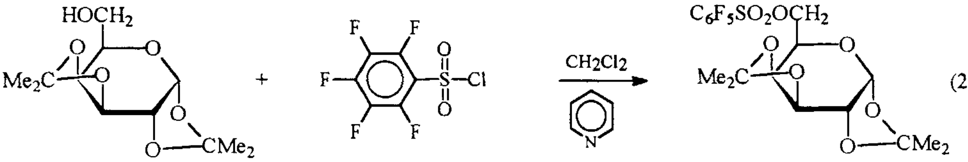


2

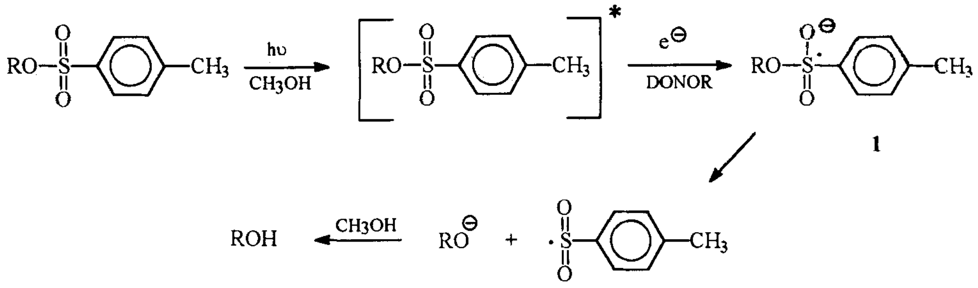
intermediate then fragments to form the anion of the deprotected sugar (Scheme 1). Since generating a radical anion is the central element in this photochemical process, structural changes that impact radical anion formation should influence the reaction. Replacing the *p*-tolylsulfonyl group with the pentafluorophenylsulfonyl group generates a more stable radical anion (**2**) because the electronegative fluorine atoms can help stabilize the negative charge. Since we have a continuing interest in the photochemistry of sulfonic acid esters, we synthesized the pentafluorobenzenesulfonates (pentaflates) **3-6** and studied their photochemistry under electron transfer conditions.

Pentaflates **3-6** were prepared by the procedure of Hall and Miller (eq 2).[17] Irradiation of these compounds (**3-6**) in methanol in the presence of triethylamine gave, in each case, two products.[18] One photoproduct (**7**, **8**, **9**, or **10**) from each irradiation was the corresponding starting sugar, and the other (**11**, **12**, **13**, or **14**) had a structure in which the pentafluorophenyl group had become bonded to an oxygen atom (Scheme 2).



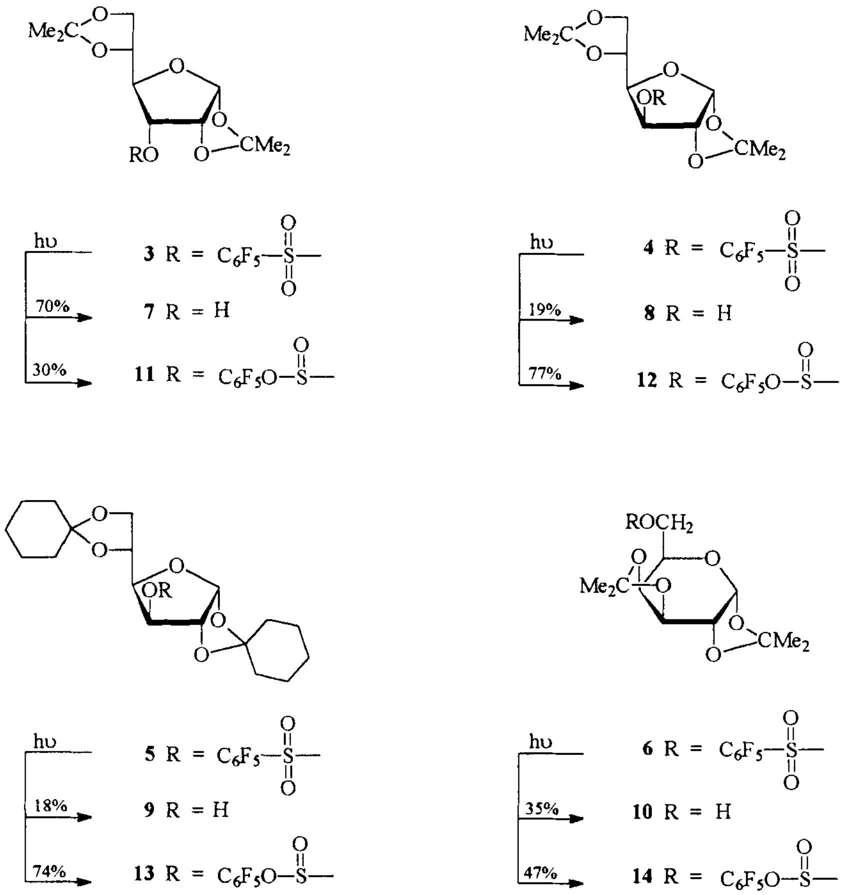
(2)

The structures of photoproducts **11-14** were determined from a combination of spectroscopic analysis and chemical reaction. The striking similarity between the NMR spectra of each pentaflate and its photoproduct required these compounds to be isomers that differed only in the noncarbohydrate portions of the molecules. (The ^{1}H and ^{13}C NMR spectra of pentaflate **3** and its photoproduct **11** are given in Tables 1 and 2. Similar relationships exist between spectra for the other pentaflates and their photoproducts.[19]) The primary difference in NMR spectra when comparing a pentaflate with its photoproduct was



e$^{\ominus}$ DONOR = $(CH_3CH_2)_3N$

Scheme 1



Scheme 2

Table 1. Significant ^{13}C NMR Chemical Shifts[a] for Compounds **3** and **11**[b]

	C-1	C-2	C-3	C-4	C-5	C-6	Aromatic Resonances			
3	104.0	77.83	79.65	77.33	74.76	65.68	136.3	139.8	143.2	147.0
11	104.0	77.94	79.14	77.32	74.85	65.66	138.5	141.9	143.7	147.2

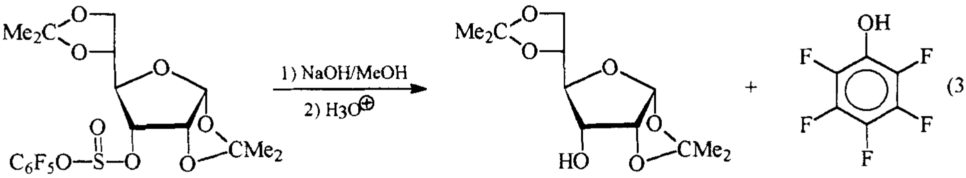
a. Recorded in $CDCl_3$ with TMS as the internal standard. b. See reference 19.

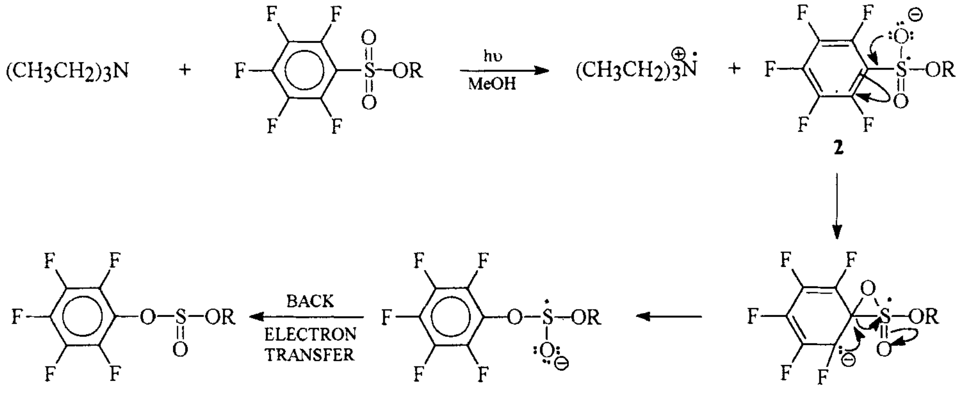
Table 2. ^{1}H NMR Chemical Shifts[a,b,c] for Compounds **3** and **11**

	H-1	H-2	H-3	H-4	H-5	H-6	H-6'
3	5.81 $J_{1,2} = 3.8$	4.76 $J_{2,3} = 5.0$	4.83 $J_{3,4} = 7.9$	4.14 $J_{4,5} = 4.9$	4.23 $J_{5,6} = 5.1$	3.90 $J_{5,6'} = 6.9$	4.08 $J_{6,6'} = 8.9$
11	5.80 $J_{1,2} = 3.6$	4.74 $J_{2,3} = 5.0$	4.78 $J_{3,4} = 7.7$	4.12 $J_{4,5} = 4.7$	4.19 $J_{5,6} = 5.3$	3.88 $J_{5,6'} = 6.8$	4.03 $J_{6,6'} = 8.8$

a. Recorded in $CDCl_3$ with TMS as the internal standard. b. See reference 19.
c. Coupling constants are in Hertz.

that photoproduct resonances in the aromatic region of the ^{13}C NMR spectrum occurred downfield from those in the pentaflate spectrum. This fact suggested that in the photoproduct an oxygen atom now was directly attached to the aromatic ring. Among the possible structures that contain such a change, the most probable ones were the sulfurous acid esters **11-14**. These structures were confirmed by hydrolysis of the photoproducts to give, in each case, pentafluorophenol and the starting sugar (eq 3).





Scheme 3

A possible mechanism for this new photochemical reaction is shown in Scheme 3. Supporting the suggested reaction pathway is the observation that triethylamine promotes the photochemical process; thus, an electron transfer reaction is indicated. The proposed nucleophilic addition to the aromatic ring draws analogy from nucleophilic aromatic substitution reactions in which fluorinated benzene rings react readily.[20] Back electron transfer to the triethylamine radical cation completes this new photochemical rearrangement of sulfonic acid esters.

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18. Photochemical reactions were conducted in a quartz vessel using Rayonet RPR-2537 mercury lamps. Reaction mixtures were purged with nitrogen for 1 h prior to photolysis, and the purge was continued during irradiation. Column chromatography was conducted with a 2.5 x 15 cm column of Baker 240-400 mesh silica gel.
19. All new compounds had ^{1}H and ^{13}C NMR spectra which were consistent with the proposed structures and gave satisfactory analytical data.
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