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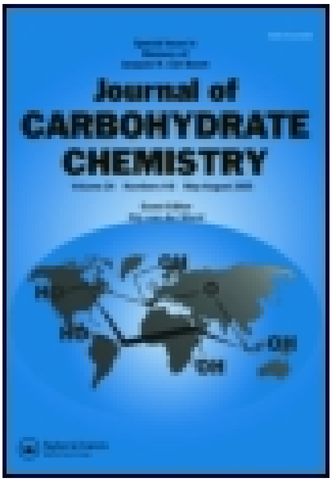

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A Mechanistic Study of the Photochemistry of Carbohydrate p-Toluenesulfonates

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A MECHANISTIC STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATE *p*-TOLUENESULFONATES

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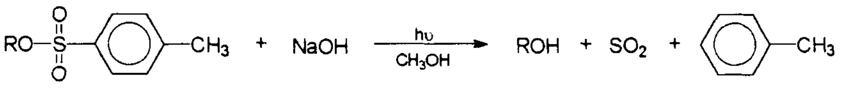
ABSTRACT

Photolysis of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-galactopyranose (**5**) in methanol under nitrogen in the presence of sodium hydroxide or diazabicyclo[2.2.2]octane (**3**, DABCO) produces toluene and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**6**). Electron transfer from DABCO or hydroxide ion to singlet excited **5** to generate a radical anion is the first step in this reaction. The radical anion rapidly fragments to give the *p*-tolylsulfonyl radical (**2**) and deprotonated **6**, which accepts a proton from the solvent. The *p*-tolylsulfonyl radical (**2**) then abstracts a hydrogen atom from the solvent to give *p*-toluenesulfinic acid, a compound that is converted to the *p*-toluenesulfinate anion (**8**) under the basic reaction conditions. Photolysis of **8** completes the reaction sequence by forming toluene.

INTRODUCTION



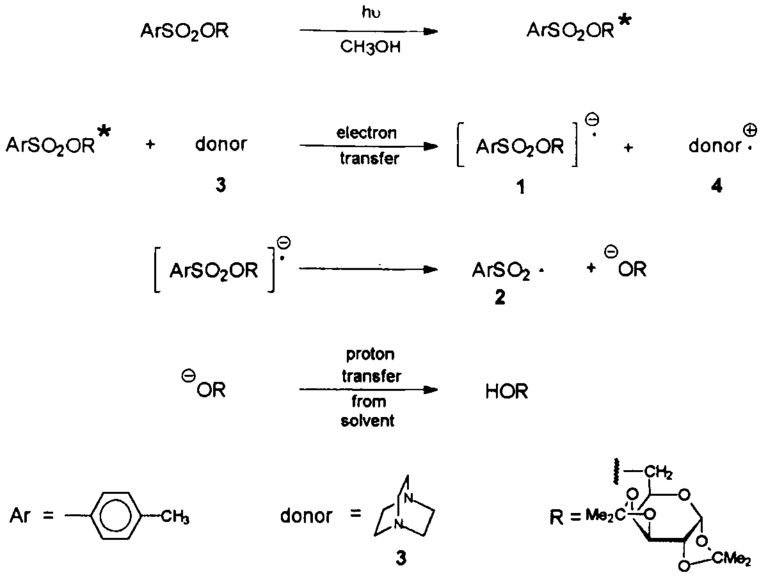
(1)

During the past twenty-five years various research groups have studied the mechanism of *p*-toluenesulfonate photoreaction.[1-7] The first four of these studies established that the singlet excited state of the tosylate interacted with an added base to generate the deprotected compound along with sulfur dioxide and toluene (eq 1).[1-4] More recent investigations have focused attention on the details of the mechanistic process.[5-7]

Several years ago we conducted an investigation of tosylate photoreaction using flash photolysis and pulse radiolysis techniques to detect reactive intermediates.[5] With this approach, we were able to determine that tosylate photolysis under typical reaction conditions involves the transfer of an electron from a donor ion (*e.g.*, methoxide or hydroxide) or neutral molecule (*e.g.*, an amine) to an excited tosylate to generate a radical anion (**1**). Fragmentation of this radical anion (**1**) then produces the anion of the deprotected sugar and the *p*-tolylsulfonyl radical (**2**) (Scheme 1). Although these experiments determined that an electron-transfer process was occurring, they left unanswered the question of how toluene and sulfur dioxide were being produced. As a result of our most recent studies, we now can answer this question.

Results and Discussion

Since the *p*-tolylsulfonyl radical (**2**) is a logical precursor to toluene and sulfur dioxide, the first experiments conducted were designed to identify the reactions of **2** under the photolysis conditions. Flash photolysis of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-galactopyranose (**5**) under nitrogen in methanol containing sodium hydroxide produced the characteristic UV absorption for **2** (λ_{max} 320 nm);[5,8] however, this absorption was absent in experiments conducted in the presence of oxygen. A possible explanation for these results was that oxygen was quenching the excited tosylate, thus, preventing electron transfer. In order to test this possibility, the sodium hydroxide (i.e., the electron-transfer agent) in the photolysis mixture was replaced by diazabicyclo[2.2.2]octane (**3**, DABCO). The reason for this change was that when DABCO functions as a donor in electron-transfer reactions, the DABCO radical-cation (**4**), with its characteristic UV absorption at 420 nm,[5,9] is formed. [In contrast, when hydroxide ion is the electron donor, it is difficult to verify that electron transfer has occurred because the reaction product (the hydroxy radical) does not have a detectable UV absorption.] When flash photolysis of **5** was conducted in an oxygen-containing atmosphere with DABCO present, the 420-nm absorption was produced; thus, electron transfer was occurring under these conditions. Once it was determined that electron transfer

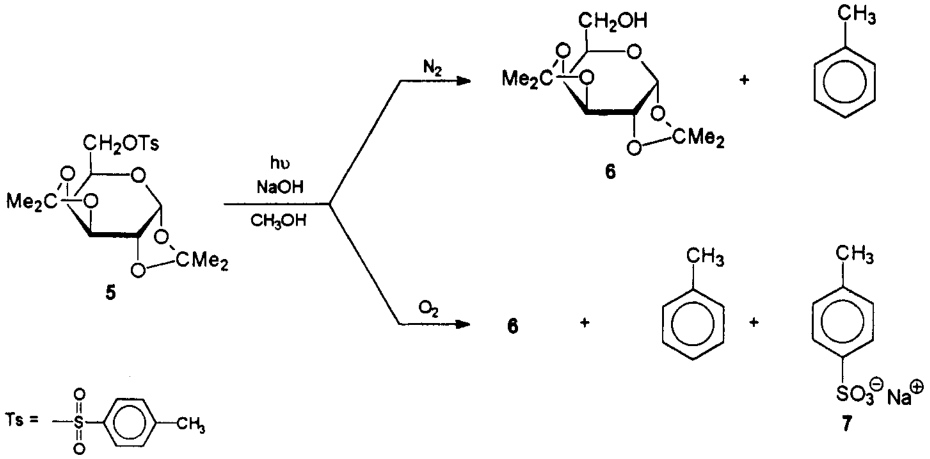


Scheme 1

was taking place, a logical explanation for the absence of the *p*-tolylsulfonyl radical (**2**) in reactions where oxygen was present, was that **2** was being converted rapidly into a new product by reaction with oxygen. We investigated this possibility by identifying the products formed from irradiating **5** in the presence of oxygen.

When **5** was photolyzed in an oxygen-containing atmosphere with sodium hydroxide (or DABCO) as the electron-transfer agent, the only carbohydrate formed was 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**6**). The other organic products were toluene (29%) and sodium *p*-toluenesulfonate (7, 50%). Photolysis under the same conditions in a nitrogen atmosphere produced **6** (100%) and toluene (70%) without any 7 being formed (Scheme 2, Table 1). These results showed that oxygen was interrupting formation of toluene by reacting with the *p*-tolylsulfonyl radical (**2**) to form the *p*-toluenesulfonate ion (7).

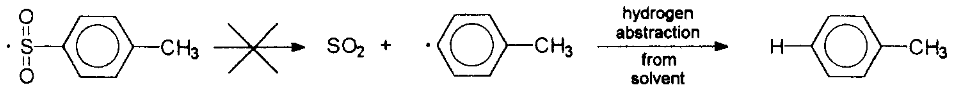
Even with this clear relationship between the *p*-tolylsulfonyl radical (**2**) and toluene, the actual steps involved in the formation of toluene remained uncertain. [The possibility of simple C–S bond homolysis in **2** to give the tolyl radical and sulfur dioxide (Scheme 3) already had been shown to be unlikely by Izawa and Kuromiya.[3]] Identifying the salts produced by photolysis of **5** under nitrogen, however, established the relationship between



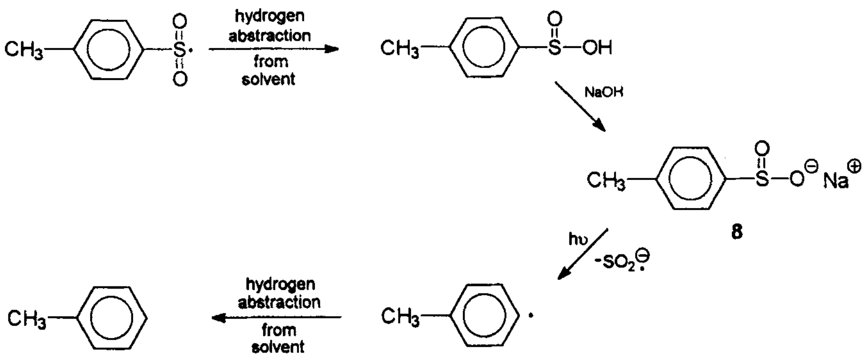
Scheme 2

Table 1. Non-carbohydrate Product Yields from Photolysis of **5**[a]					
Atmosphere	Conversion	Time[b]	Percent Yield of Products		
			Toluene	**7**	**8**
nitrogen	100%	180	70	none	none
nitrogen	62%	90	41	none	27
nitrogen	48%	60	32	none	55
oxygen[c]	85%	180	29	50	none
oxygen[c]	55%	60	25	54	none

a. 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**6**) was formed quantitatively.
b. Time is given in minutes.
c. When oxygen was present, the reaction mixture became yellow.



Scheme 3



Scheme 4

2 and toluene. No carbon containing salts were detected in reactions run to completion but in reactions run to partial completion, sodium *p*-toluenesulfinate (**8**) was present (Table 1). When **8** was irradiated by itself, toluene was formed.[10] These results identify **8** as an intermediate in the conversion of the *p*-tolylsulfonyl radical (**2**) into toluene. Since sulfonyl radicals are known to abstract hydrogen atoms from donors as effective as methanol,[11,12] a logical sequence of events is that **2** abstracts a hydrogen atom from methanol to give *p*-toluenesulfinic acid,[13] which reacts immediately with base to give sodium *p*-toluenesulfinate (**8**). Photolysis of **8** produces toluene (Scheme 4).

CONCLUSION

When the results from the present study are added to all those from earlier investigations,[1-7] the combined information provides a detailed understanding of the photodeprotection process of *p*-toluenesulfonates. The critical step in this reaction is the transfer of an electron from a donor to an excited *p*-toluenesulfonate to form the sulfonate radical anion. The actual deprotection step occurs during the fragmentation of this radical anion. The mechanism for the entire process is summarized in Schemes 1 and 4.

Experimental

General Procedures:

Flash Photolysis. Flash photolysis was performed using the frequency quadrupled (266 nm) output of a Quantel YG481 Nd:YAG laser (11 ns, Q-switched). The probe assembly consisted of a 150-W Xenon lamp, SPEX minmate monochrometer, Hamamatsu R928 Nm photomultiplier, and a Biomation 8100 waveform recorder.[14] Digitized signals were averaged and analyzed by a PDP11/70 computer.[15] A resolution of 100 ns was obtained by averaging 10 channels per point. Light intensity was attenuated with wire mesh filters (4%–100% transmission). A 0.5 cm x 1.0 cm fluorescence cuvette was charged with 1.0 or 2.0 mL of ethanol solution and purged with nitrogen or air for 20 min. Gentle purge was continued throughout the experiment. The concentration of tosylate was 2 mM for the flash photolysis experiments.

Gas Chromatography/Mass Spectrometry. GC/MS analyses were performed using a Finnigan TSQ-45 triple quadrupole mass spectrometer coupled to a Finnigan 9610 gas chromatograph. The GC column employed was a Hewlett-Packard fused silica capillary [25 m x 0.25 mm (i.d.)] coated with 5% phenyl methyl silicone. Samples were injected in the splitless mode and the column temperature was programmed for a 75 ^{0}C to 295 ^{0}C rise at a rate of 10 ^{0}C/min. The mass spectrometer was operated in the Q1-MS, positive-ion, electron-impact mode. The instrument was scanned from 35 to 650 amu with one scan every two seconds. Electron energy was kept at 70 eV. Quantitation was performed using the area-ratio method.

Nuclear Magnetic Resonance. NMR spectra were determined in D_2O using a Varian FT-80A spectrometer.

Irradiations of 1,2:3,4-Di-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-galactopyranose (5).[16]

a) In the Presence of Diazabicyclo[2.2.2]octane (DABCO, 3) in a Nitrogen Atmosphere. Compound **5** (0.83 g, 2.0 mmol) and DABCO (**3**, 4.5 mmol) were dissolved in 75 mL of methanol, purged with nitrogen for 1 h, and then irradiated for 180 min under continuous nitrogen purge using a Rayonet Photochemical Reactor equipped with 16 RPR 2537-A lamps. After photolysis, the solvent was distilled to leave a residue which was chromatographed on a 2.5 x 15 cm column of 230-400 mesh silica gel using hexane–ethyl acetate (4/1). The only material eluted from the column was 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**6**)[16] in quantitative yield. (^{13}C NMR spectra of the crude reaction mixture prior to chromatography also showed that **6** was the only carbohydrate present.)

(b) In the Presence of Sodium Hydroxide in a Nitrogen Atmosphere. Compound **5** (1.00 g, 2.5 mmol) and 1.0 g (25 mmol) of sodium hydroxide were dissolved in 375 mL of methanol, purged with nitrogen for 1 h and irradiated through a Corex filter (240 nm cutoff) using a 450-W Hanovia, mercury-vapor lamp. (Irradiation times are given in Table 1.) After irradiation, the solvent was distilled under reduced pressure and the distillate was analyzed by GC/MS to determine the yield of toluene (Table 1). The residue was partitioned between ethyl ether (100 mL) and water (20 mL). The layers were separated and the water layer washed twice (20 mL) with ether. The combined ether extracts were analyzed by GC/MS to determine the yield of compound **6** and the amount of unreacted **5** (in those reactions not run to completion). In every instance, **6** was the only carbohydrate produced and its yield, based on starting material reacted, was quantitative. The solvent was removed from the aqueous layer under reduced pressure and the residue analyzed by ^{13}C and ^{1}H NMR. In reactions not run to completion, the residue was shown to contain sodium *p*-toluenesulfinate (**8**), by NMR comparison with an authentic sample.[17] Product yields, determined by NMR analysis of the residue after addition of an internal standard, are given in Table 1.

(c) In the Presence of Sodium Hydroxide and Oxygen. Reactions and analyses were conducted as described in the preceding paragraph, except that the reaction mixture was purged with air. The results are given in Table 1.

Irradiation of Sodium *p*-Toluenesulfinate (8). Compound **8**[17] (445 mg, 2.5 mmol) was dissolved in 375 mL of methanol, purged with nitrogen for 1 h, and irradiated under continuous nitrogen purge through a Corex filter for 30 min with a Hanovia 450-W, mercury-vapor lamp. After irradiation, the solvent was distilled under reduced pressure and the distillate found by GC/MS to contain 64 mg (0.70 mmol, 70%) of toluene. The residue consisted of 267 mg (1.5 mmol) of unreacted **8**.

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