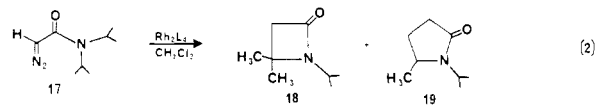

(2)

ratio was only 2.4, but the use of rhodium(II) 2-phenoxybenzoate provided an increase in this product ratio to 6.2. The diazoacetamide derived from *trans*-2,6-dimethylpiperidine also formed products from both β-C–H and γ-C–H (methyl) insertion, but because of piperidine ring constraints, the β-lactam/γ-lactam product ratio was already 16 in the $Rh_2(OAc)_4$-catalyzed reaction (92% isolated yield).

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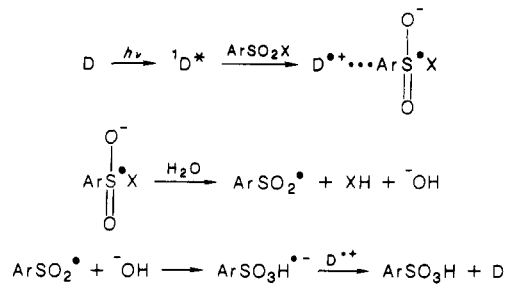
Hydrolysis of Tosyl Esters Initiated by an Electron Transfer from Photoexcited Electron-Rich Aromatic Compounds

Summary: Selective hydrolysis of tosyl esters was realized by irradiation of UV light (>300 nm) in the presence of electron-rich aromatic compounds and the reaction proceeds via an electron-transfer process.

Sir: The tosyl group is a unique protecting group for sugar and nucleic acid synthesis because of its ability to provide regioselective protection of hydroxy groups by means of the dibutylstannylene derivaties and its stability under solvolytic conditions.[1] However, the drastic conditions that have been employed for the detosylation step reduce the utility of this group.[2] Thus, development of a mild and selective method for the hydrolysis of the tosyl ester is still required.

Direct photolysis of tosyl esters in the presence of sodium methoxide has been reported,[3] and, recently, Masnovi showed that the mechanism of this type of reactions[4] involves an electron-transfer process. Unfortunately, utilization of 254-nm light limits the applicability of this reaction to substrates that have no chromophore other than the tosyl group.[5] Recently, we reported that the photohydrolysis of tosylamides[6] proceeds smoothly via electron-transfer from the excited electron-donating aromatic compounds such as *p*-dimethoxybenzene or 1,5-dimethoxynaphthalene (Scheme I, X = NRR′) and now we have extended this process to the hydrolysis of tosyl esters as shown in Scheme I (X = OR).

Scheme I[a]



[a] D, donor (dimethoxybenzenes, dimethoxynaphthalenes); X, NRR′ or OR.

The free energy change (ΔG) in the electron-transfer process from the singlet excited state of 1,5-dimethoxynaphthalene to methyl tosylate, calculated by the Weller equation,[7] was −14.5 kcal/mol in ethanol. This is obviously more negative than that for *N*-tosyl-*N*-methylphenethylamine (−5.79 kcal/mol).[6] Actually, fluorescence quenching experiments of 1,5-dimethoxynaphthalene by methyl tosylate gave a $k_q\tau$ from the linear Stern–Volmer plot of 43.8 M^{-1}. Hence, the k_q value was calculated to be 3.5×10^9 M^{-1} s^{-1} (τ = 12.6 ns), which means the process is occurring at nearly the diffusion-controlled rate and almost five times that of the rate of quenching by a tosylamide (MeNHTs). All of these results suggested that the hydrolysis of tosyl esters should be possible via a photosensitized electron-transfer process similar to that for tosylamides.

When tosyl esters of phenethyl alcohol, cyclohexanol, cholesterol, and cholestanol were irradiated under the conditions that were successful for the photosensitized cleavage of tosylamides,[6] the corresponding alcohols were obtained in good yield (Table I).[8] The reaction proceeded considerably slower in aqueous ethanol compared to the reactions of tosylamides, which were completed within 2 h.[9] However, employing acetonitrile as a solvent increased the rate of the reaction. As a coreductant,[10] hydrazine was

(1) (a) For the selective protection of the 2′-hydroxy group of nucleosides: Wagner, D.; Verheyden, J. P. H.; Moffatt, J. G. *J. Org. Chem.* **1974**, *39*, 24. (b) The protection of hexopyranosides: Munavu, R. M.; Szmant, H. H. *J. Org. Chem.* **1976**, *41*, 1932.

(2) Detosylation of 2′-*O*-tosyladenosine derivative using sodium amalgam has been reported: Ranganathan, R.; Larwood, F. *Tetrahedron Lett.* **1978**, 4341. However, this reaction is only applicable to purine nucleosides.

(3) (a) Zen, S.; Tashima, S.; Koto, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3025. (b) Izawa Y.; Kuromiya, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3197. (c) Pete, J. P.; Portella, C. *Bull. Soc. Chim. Fr.* **1980**, 275.

(4) Masnovi, J.; Koholic, D. J.; Binkley, R. *J. Am. Chem. Soc.* **1987**, *109*, 2851.

(5) Attempts to sensitize the detosylation reaction by using electron-transfer sensitizers such as phenothiazine, 9,10-dimethoxyanthracene, and *p*-dimethoxybenzene were reported to be unsuccessful.[4]

(6) (a) Hamada, H.; Nishida, A.; Matsumoto, Y.; Yonemitsu, O. *J. Am. Chem. Soc.* **1980**, *102*, 3978. (b) Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140.

(7) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(8) Without donor, no reaction occurred.

(9) The efficiency of the photolysis of methyl tosylate (10 mM) in the presence of DMN (10 mM) and ammonia borane (10 mM) in 95% ethanol was measured and the quantum yield was ϕ = 0.003 (extrapolated to infinite concentration of methyl tosylate, ϕ_{lim} = 0.26) which is considerably smaller when compared to that of methyl tosylamide (ϕ_{lim} = 0.83). The reason for this low efficiency may be due to the presence of competing electron back-donation from the cation radical to the anion radical (Scheme I).

(10) The presence of coreductant was required for efficient reaction. The role of the coreductant may be the reduction of radical species, such as $D^{\bullet+}$ or the tolyl sulfonyl radical.

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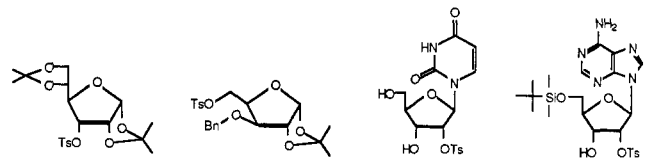
Table I. Photosensitized Cleavage of Tosyl Esters



[A] [B] [C] [D]

run	substrate (mM)	solvent	donor[a] (mM)	reductant (mM)	time (h)	yield (%)
1	*O*-tosylcyclohexanol (10)	70% EtOH	DMNP (10)	$NaBH_4$ (1 M)	7.0	85[b,c]
2	*O*-tosylphenethyl alcohol (10)	70% EtOH	DMNP (10)	$NaBH_4$ (0.5 M)	7.0	90[b,c]
3	*O*-tosylcholesterol (2.0)	H_2O–Et_2O–DMF (1:2.1:6.9)	DMNP (2)	$NaBH_4$ (12)	6.0	86[b]
4	*O*-tosylcholestanol (4.6)	CH_3CN	DMN (4.6)	$NaBH_4$ (46)	5.4	97[b]
5	*O*-tosylcholestanol (1.4)	97% CH_3CN	DMNP (1.7)	H_2NNH_2 (44)	1.5	93[d]
6	A (2.0)	90% CH_3CN	DMNP (2.4)	H_2NNH_2 (62)	2.0	65[d]
7	B (1.8)	90% CH_3CN	DMN (2.7)	H_2NNH_2 (50)	2.6	68[d]
8	B (3.0)	MeOH	DABCO (6.6)	none	1.8	59[e]
9	C (2.3)	90% CH_3CN	DMNP (2.7)	H_2NNH_2 (90)	1.6	76[d]
10	C (3.9)	MeOH	DABCO (6.6)	none	2.0	*e,f*
11	D (1.1)	90% CH_3CN	DMNP (2.2)	H_2NNH_2 (43)	2.0	84[d]
12	D (2.4)	MeOH	DABCO (4.1)	none	4.0	*e,g*

[a] DMNP = (4,8-dimethoxynaphthyl)propionic acid, DMN = 1,5-dimethoxynaphthalene. [b] 300-W high pressure mercury lamp, Pyrex filter. [c] Determined by GLC. [d] 500-W lamp, Pyrex filter. [e] 60-W low pressure mercury lamp (254 nm).[4] [f] Complex mixture was obtained. [g] No desired product was detected and 37% of the starting material was recovered.

superior to sodium borohydride or amine borane, which were employed for the tosylamide reaction, because of less reactivity with carbonyl compounds and of the lack of formation of precipitates.

Under these conditions, primary and secondary tosylates of sugar derivatives, even a sterically hindered tosylate (run 6), afforded the corresponding alcohols in satisfactory yields. Deprotection of the tosylates of nucleosides also proceeded without any difficulties. There was no evidence for the reduction of the pyrimidine ring in the reaction of 2′-*O*-tosyluridine (run 9).[11,12] On the other hand, irradiation of the nucleosides using 254-nm light in the presence of 1,4-diazabicyclo[2.2.2.]octane (DABCO)[4] afforded complex mixtures of the products (run 10 and 12).

In summary, we have shown that tosyl esters can be hydrolyzed via a photosensitized electron-transfer process and that this new reaction is applicable to the deprotection of the tosylates of sugar and nucleoside derivatives.

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(11) (a) Photohydration and photodimerization are the typical reaction observed on irradiation of pyrimidine nucleosides: Fisher, G. J.; Johns, H. E. *Photochemistry and Photobiology of Nucleic Acids*; Wang, S. Y.; Ed.; Academic Press: New York, 1976; pp 169–294. (b) The reduction of uridine by UV irradiation in the presence of sodium borohydride has been reported: Cerutti, P.; Ikeda, K.; Witkop, B. *J. Am. Chem. Soc.* **1965**, *87*, 2505. Cerutti, P.; Kondo, Y.; Landis, W. R.; Witkop, B. *J. Am. Chem. Soc.* **1968**, *90*, 771.

(12) Typical reaction procedure: A mixture of 5′-*O*-(*tert*-butyldimethylsilyl)-2′-*O*-tosyladenosine (92 mg, 1.1 mM), DMNP (2.2 mM), and hydrazine hydrate (43 mM) in 140 mL of 90% acetonitrile was irradiated with a 500-W mercury lamp through a Pyrex filter at ambient temperature under an argon atmosphere for 2 h. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography, eluting with ethyl acetate, yielding 56 mg (84%) of 5′-*O*-(*tert*-butyldimethylsilyl)adenosine.

Extractive workup to remove DMNP and hydrazine is also applicable in a larger scale reaction.

Catalytic Siloxymethylation of Glycosides by the $HSiR_3/CO/Co_2(CO)_8$ Reaction. A New Entry to *C*-Glycosyl Compounds

Summary: The acetoxy group at the anomeric center of glycosides can be replaced with a siloxymethyl group by $Co_2(CO)_8$-catalyzed reaction with carbon monoxide and a hydrosilane.

Sir: Carbon–carbon bond formation at the anomeric sites of saccharides is of great importance for preparation of *C*-glycosyl compounds[1] including *C*-nucleosides[2] as well as

(1) For examples, see: (a) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111. (b) Goodchild, J. *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Ellis Horword: Chichester, 1982; Vol. 6, p 105. (c) Lichtenthaler, W. In *Natural Products Chemistry*; Atta-Ur-Rahman, Ed.; Springer-Verlag: Berlin, 1986; p 227.

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