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Chemoselective and scalable preparation of alkyl tosylates under solvent-free conditions

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Abstract—The improved method for the efficient tosylation of alcohols has been reported using two procedures (A and B). Procedure A: methanol, ethanol, benzyl alcohols, and valuable ethylene glycols can be converted into their corresponding alkyl tosylates in very fast, simple, and efficient grinding method using potassium carbonate as solid base. Other primary and secondary alcohols need to add potassium hydroxide to reaction mixture (procedure B). High selectivity of tosylation was observed for these two procedures. Scale up ability was found in this method even in 100 mmol of substrate. The present method is the example of solid-state tosylation using tosyl chloride, and is a green chemical process due to solvent-free conditions.

1. Introduction

Sulfonate derivatives, which are precursors of cyclic crown ethers, azacrown ethers, and lariat ethers, are widely used in polyether chemistry and many other organic transformations as the tosylate anion makes a good leaving group.[1] Among the sulfonates, tosylate is selected for its physical properties, availability of its reagent, and appropriate reactivity. Tosylate derivatives have three clear advantages. First, crystallinity (they are often crystalline and have low vapor pressure), therefore, can be obtained in high purity. Second, significant addition to the mass of parent compound (a mole of diethylene glycol weighs 106.1 g, its ditosylate derivatives, 414.5 g) causes more accuracy in handling. Finally, the tosylate salts form as insoluble precipitates upon reaction with the nucleophilic salts such as alkali metal salts of alcohols and phenols in non-aqueous solvents. As a result, simple filtration followed by solvent removal is often all that is necessary to isolate the product.[1d] Also, in comparison with alkyl halides, tosylate is often the leaving group of choice as its preparation from the corresponding alcohol takes place under mild conditions, which avoids the stereochemical uncertainties and skeletal rearrangements associated with the conversion of an alcohol to a halide.[2] There are two general methods for tosylation according to tosylating agent: (i) using reactive agent such as *p*-toluenesulfonyl chloride (or anhydride) in the presence of a base; (ii) using *p*-toluenesulfonic acid[3] in the presence of silica chloride[3b] or Lewis acids such as $CoCl_2$.[3c] The first method is used frequently due to its simplicity and generality. In this method, using triethylamine or especially pyridine, as a base, is often common.[1] The use of an equimolar amount of wasted organic amine reagent necessitates a large amount of BOD and COD (biological and chemical oxygen demands). In order to avoid using toxic material, application of aqueous sodium or potassium hydroxide,[4] $Me_3N\cdot HCl$,[5a] and $Me_2N(CH_2)_nNMe_2$[5b] was also reported. Also, Tanabe et al. reported the water–solvent method for tosylation of alcohols promoted by KOH and catalytic amines such as *N*,*N*-dimethyl aniline.[5c] Their method only works efficiently for primary alcohols, for example, tosylation of 2-octanol provides its product in 27% yield. The control of pH is necessary to avoid hydrolysis of sulfonyl chloride. $TsCl/NEt_3$ in the presence of catalytic amounts of Bu_2SnO_4,[6] ring opening of dibutylstannylene acetal with sulfonyl chloride,[7] Ag_2O/KI/sulfonyl chloride,[8] and zinc tosylate in a Mitsunobu type reaction[9] are the other modifications. Difficulties such as tedious procedure to remove hazardous materials (e.g., pyridine), unavailability of reagents, side reactions, necessary of control of pH and temperature, long reaction times encourages development of this transformation.

Recently considerable attention has been paid to solvent-free reactions. These reactions are not only of interest from an environmental point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure.[10] There are a few reports[11] about solvent-free tosylation of alcohols such as using heteropolyacids.[11a]

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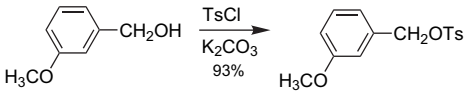
2. Results and discussion

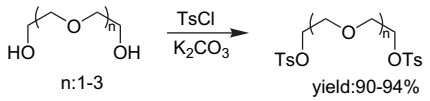
Tosyl chloride/potassium carbonate combination was used successfully in anhydride and sulfonamide preparations at solvent-free conditions by us.[12] Using potassium carbonate as cheap, weak basic solid support has advantages such as controlled promotion of reaction and simplicity. In order to develop the applications of $TsCl/K_2CO_3$ combination, we decided to try it for tosylation of alcohols. Methanol as volatile and cheap alcohol was used as first starting material. The well mixed K_2CO_3 and tosyl chloride was wetted with methanol and grinded (procedure A). Surprisingly, according to TLC, the reaction was completed in about 5 min and the corresponding tosylate was obtained very easily in high yield without any other basic additive (Table 1, entry 1). Ethanol and benzyl alcohols are also quantitatively converted into their corresponding tosylates using this method (Scheme 1, Table 1). In the case of benzyl alcohols, the 1.5 equimolar of TsCl was used and the reaction was completed in about 5 min.



Scheme 1.

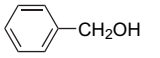
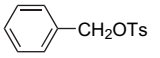
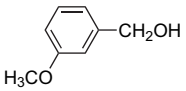
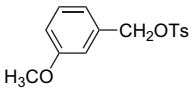
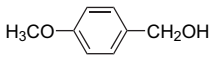
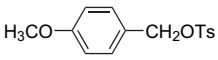
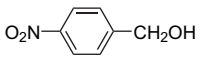
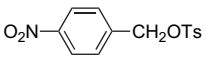
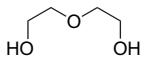
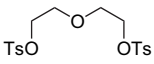
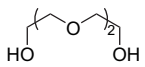
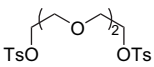
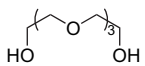
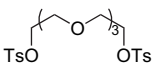
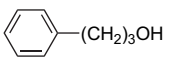
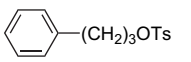
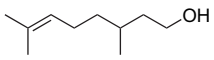
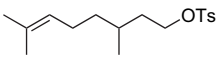
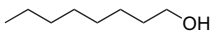
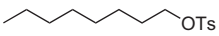
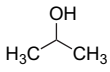
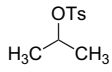
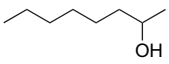
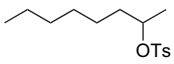
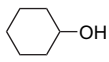
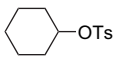
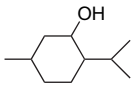
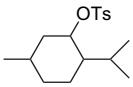
For removing the remaining TsCl, in addition to known method, using *N*,*N*-dimethylethylenediamine,[5c] we found that addition of KOH and grinding were very efficient. Interestingly, up to 5 equimolar of KOH was examined successfully without considerable hydrolysis of tosylate. Also, we found that wetting the reaction mixture with *t*-BuOH and irradiation under microwave (900 W for 2 min) can be used for removing the remaining TsCl without reducing the yield of the product. It might be owing to tosylation of *t*-BuOH followed by elimination reaction that produces volatile isobutene (bp −6.9 °C) and salt of tosylate, which do not cause any problem in the work up process.

More surprisingly, in extending this procedure to other alcohols we found that valuable ethylene glycols that are very important in macrocycle, rotaxane, and cryptand syntheses as building block can be prepared as simple as benzylic alcohols. The equimolar amount of them against 3 equimolar of TsCl can be converted into their corresponding ditosylates in very short reaction times (Table 1, Scheme 2). According to the literature, the ditosylate derivatives can be prepared with pyridine as base,[13] or they are synthesized more effectively in higher yield using aqueous sodium hydroxide and tetrahydrofuran.[4a] In this method, the excess of sodium hydroxide is used, reaction temperature must be controlled, and the yield of some ditosylates is not very high, e.g., 79% for diethylene glycol ditosylate. Then, present method has superiority to the current methods due to simplicity, reaction time, solvent-free conditions, and free base additive.



Scheme 2.

Table 1. Tosylation of alcohols with *p*-toluenesulfonyl chloride (1.5 equiv) on potassium carbonate at solid-state conditions

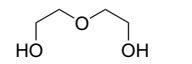
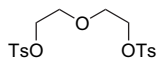
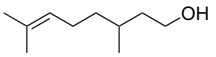
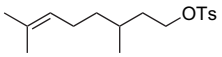
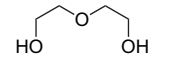
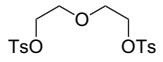
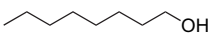
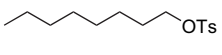
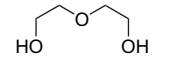
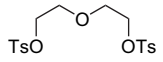
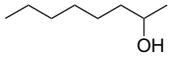
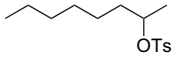
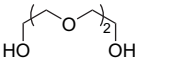
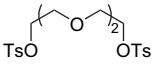
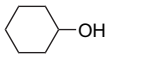
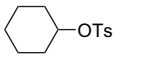
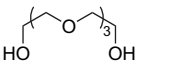
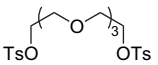
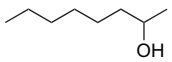
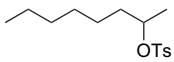
Entry	Alcohol	Alkyl tosylate	Yield (%)
1	CH_3OH	CH_3OTs	94[a]
2	C_2H_5OH	C_2H_5OTs	92[a]
3			91[a]
4			93[a]
5			89[a]
6			87[a]
7			95[a]
8			94[a]
9			90[a]
10			89[b]
11			93[b]
12			92[b]
13			90[b]
14			85[b,c]
15			88[b]
16			81[b,c]

[a] Reaction carried out without KOH (procedure A).
[b] Reaction carried out in the presence of KOH (procedure B).
[c] 2.5 equiv of TsCl was used.

It was found that addition of KOH to K_2CO_3 (TsCl/KOH/K_2CO_3 combination, procedure B) can increase the ability of present method for tosylation of alcohols that were not successful at tosylation reaction using $TsCl/K_2CO_3$ combination (procedure A). For example, citronellol, 1- and 2-octanol, and cyclohexanol quantitatively can be converted into the corresponding tosylate, respectively, in high yields and very short reaction times (Table 1, entries 11, 12, 14, and 15).

The necessity of using KOH in procedure B, and importance of selectivity in organic chemistry encouraged us to consider

Table 2. Consideration of selectivity in tosylation of alcohols in the absence of KOH

Entry	Mixture of alcohols	Product(s)	Conversion (%)
1			100
			Trace
2			100
			Trace
3			100
			0
4			100
			0
5			100
			0

the selectivity of tosylation of different alcohols. Several reactions were carried out and surprisingly, the excellent selectivity was found according to TLC and ^{1}H NMR of alcohol mixtures (1:1) (Table 2). For example, triethylene glycol and tetraethylene glycol quantitatively can be converted into their ditosylates in the presence of cyclohexanol and 2-octanol, respectively (Table 2, entries 4 and 5).

To show another advantage of present tosylation method and because of the importance of scale up ability for laboratory and industrial purposes, several alcohols were tosylated in large scale and as shown in Table 3 all of the alcohols were tosylated successfully without considerable limitation. For example, 1-octanol, citronellol, and diethylene glycol were converted into their tosylates at 100 mmol scale of substrate. The scales in this table are optional and we have not encountered with special limitation.

Table 3. Consideration of ability of the present tosylation method in large scale

Entry	Alkyl tosylate	Scale (mmol)	Yield (%)
1	3-Phenyl-1-propyl tosylate	30	89
2	1-Octyl tosylate	100	92
3	3,7-Dimethyl-6-octene-1-tosylate (citronellol tosylate)	100	92
4	Diethyleneglycol ditosylate (DEG ditosylate)	100	89
5	Cyclohexyl tosylate	50	86
6	(−)-Menthyl tosylate	50	77
7	3-Methoxybenzyl tosylate	100	90
8	4-Nitrobenzyl tosylate	100	88
9	Benzyl tosylate	100	91
10	Triethylene glycol ditosylate (TEG ditosylate)	50	87

3. Conclusion

In conclusion, we have demonstrated that solvent-free tosylation of wide range of 1° and 2° alcohols on K_2CO_3 is practical and very good alternative for previous reports. The major advantages of this method are: (i) simplicity of procedure; (ii) high yields and purity of products; (iii) it can be used for both 1° and 2° alcohols; (iv) solvent-free conditions, therefore, good choice according to green chemistry point of view; (v) short reaction times; (vi) scale up ability without considerable limitation; (vii) high selectivity; (viii) very simple and fast removing the excess of tosyl chloride at the end of reaction.

4. Experimental

4.1. General

All chemicals were commercial products and distilled or recrystallized before use. All melting points were obtained by a Buchi 510 and are uncorrected. IR spectra were recorded on a BOMEM (MB102) spectrophotometer; and NMR spectra were recorded on a Bruker Avance DPX instrument (400 MHz). Chemical shifts (δ, ppm) were reported downfield from tetramethylsilane (0 ppm) for ^{1}H NMR and were reported in the scale relative to $CDCl_3$ (77.00 ppm) for ^{13}C NMR.

4.2. Procedure A: tosylation of alcohols without KOH

A mortar was charged with dry K_2CO_3 (5 g), alcohol (10 mmol), TsCl (15 mmol), and grinded vigorously for 5 min. After the completion of tosylation, remaining tosyl chloride was removed by addition of powdered KOH (50 mmol) and vigorously grinded (2 min), addition of a few drops of *t*-BuOH accelerates the disappearance of TsCl, or the removing of tosyl chloride can be carried out by wetting the reaction mixture with *t*-BuOH and irradiating (900 W) in domestic microwave oven for 2 min. The product was extracted by addition of ether (50 ml), filtered, and finally by the evaporation of organic solvent. Further purification can be carried out on the crude solid tosylate by recrystallization in *n*-hexane or by column chromatography over silica gel (hexane/diethyl ether=10:1) for oily tosylates. The yields were 88–91%.

4.3. Procedure B: tosylation of alcohols using KOH

A mortar was charged with a finely powder potassium hydroxide (50 mmol) and corresponding alcohol (10 mmol), grinded with a pestle for 5 min, then dry potassium carbonate (5 g) was added, and mixed thoroughly. Tosyl chloride (15 ml) was added in one portion and grinded vigorously for 3 min (*caution: a highly exothermic reaction was happened*). Reaction progress was monitored by TLC

(CCl_4/EtOAc). Remaining tosyl chloride was removed by the addition of powdered KOH (50 mmol) and vigorously grinded (2 min), addition of a few drops of *t*-BuOH accelerates the disappearance of TsCl. After completion of the reaction, the reaction mixture was stirred and filtered with ether (50 ml). The combined organic layer was collected by sintered glass in vacuo and the resulting product was concentrated by evaporation of the ether using a rotary evaporator. The obtained crude tosylate was sufficiently pure. If necessary, more purification can be carried out by silica-gel chromatography for oily tosylates or by recrystallization in *n*-hexane on solid tosylates.

4.4. Large scale synthesis of diethylene glycol ditosylate

A mortar was charged with dry K_2CO_3 (50 g), diethylene glycol (9.47 ml, 100 mmol), and TsCl (57.19 g, 300 mmol), and grinded vigorously for about 10 min. After the completion of tosylation, remaining tosyl chloride was removed by the addition of powdered KOH (50 mmol) and vigorously grinded (2 min), addition of a few drops of *t*-BuOH accelerates the disappearance of TsCl. The product was extracted by the addition of ether (50 ml), filtered, and finally by the evaporation of organic solvent. Further purification can be carried out on the crude solid tosylate by recrystallization in *n*-hexane. The yields were 89%.

4.4.1. Methyl tosylate (1).[3a] Thick oil; IR (film) 1178, 1362 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s, CH_3), 3.59 (3H, s, OCH_3), 7.24 (2H, d, *J* 8 Hz, *m*-H), 7.64 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.38, 56.25, 127.68, 130.16, 131.98, 144.98.

4.4.2. 3-Methoxybenzyl tosylate (4).[14] Pale yellow crystal; IR (film) 1178, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (3H, s, CH_3), 3.70 (3H, s, OCH_3), 5.04 (2H, s, OCH_2), 7.21–7.82 (8H, m); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.60, 55.24, 71.80, 113.73, 114.75, 120.65, 127.96, 129.71, 133.30, 134.75, 144.84, 159.76.

4.4.3. Diethyleneglycol ditosylate (7).[13] Colorless crystal; mp 87–89 °C; IR (film) 1165, 1352 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (6H, s, CH_3), 3.62 (4H, t, *J* 4 Hz, OCH_2), 4.09 (4H, t, *J* 4 Hz, OCH_2), 7.34 (4H, d, *J* 8 Hz, *m*-H), 7.77 (4H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.67, 68.71, 69.04, 127.94, 128.34, 129.91, 132.75, 145.

4.4.4. Triethyleneglycol ditosylate (8).[1e] Colorless crystal: mp 78–81 °C; IR (film) 1177, 1354 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (6H, s, CH_3), 3.47 (4H, s), 3.54 (4H, t, *J* 4 Hz, OCH_2), 4.01 (4H, t, *J* 4 Hz, OCH_2), 7.25 (4H, d, *J* 8 Hz, *m*-H), 7.67 (4H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.56, 70.34, 70.47, 71.20, 127.82, 129.87, 132.72, 144.92.

4.4.5. Tetraethylene glycol ditosylate (9).[1e] Thick oil; IR (film) 1178, 1358 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.22 (6H, s, CH_3), 3.35 (8H, m, *J* 12 Hz), 3.44 (4H, t, *J* 8 Hz, OCH_2), 3.94 (4H, t, *J* 8 Hz, OCH_2), 7.145 (4H, d, *J* 8 Hz, *m*-H), 7.56 (4H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.40, 68.36, 69.44, 70.23, 70.62, 128.16, 129.83, 132.78, 144.8.

4.4.6. Isopropyl tosylate (10).[3a] Thick oil; IR (film) 1177, 1362 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (6H, d, *J* 4 Hz, $CHMe_2$), 2.32 (3H, s, CH_3), 4.60 (1H, h, *J* 4 Hz, CHO–), 7.25 (2H, d, *J* 8 Hz, *m*-H), 7.67 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.43, 22.38, 22.59, 127.76, 130.02, 134.37, 144.46.

4.4.7. Citronellol tosylate (12).[15] Thick oil; IR (film) 1178, 1362 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (3H, d, *J* 4 Hz, CH_3), 0.84–1.87 (15H, m), 2.38 (3H, s, CH_3), 4.01 (2H, t, *J* 4 Hz), 4.98 (1H, t, *J* 8 Hz), 7.28 (2H, d, *J* 8 Hz, *m*-H), 7.74 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 17.52, 19.52, 21.47, 25.43, 25.50, 29.55, 36.62, 37.19, 69.05, 124.78, 127.77, 129.78, 131.19, 133.21, 144.63.

4.4.8. 1-Octyl tosylate (13).[5c] Thick oil; IR (film) 1178, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (3H, t, *J* 8 Hz, CH_3), 1.12–1.55 (12H, m), 2.34 (3H, s, CH_3), 3.92 (2H, t, *J* 8 Hz), 7.25 (2H, d, *J* 8 Hz, *m*-H), 7.68 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 13.98, 21.43, 22.59, 25.24, 26.17, 29.24, 28.7, 29.41, 29.74, 31.78, 70.79, 127.74, 129.76, 133.14, 144.59.

4.4.9. 2-Octyl tosylate (14).[3a] Thick oil; IR (film) 1178, 1362 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.66 (3H, t, *J* 7 Hz, CH_3), 0.98–1.38 (13H, m), 2.23 (3H, s, CH_3), 4.38 (1H, m, CHO–), 7.26 (2H, d, *J* 8 Hz, *m*-H), 7.62 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 13.94, 21.30, 22.30, 22.47, 23.33, 24.63, 25.66, 31.37, 80.33, 127.49, 129.60, 136.28, 144.27.

4.4.10. Cyclohexyl tosylate (15).[3a] Thick oil; IR (film) 1177, 1360 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.74 (10H, m, $-(CH_2)_5$), 2.40 (3H, s, CH_3), 4.48 (1H, m, CHO–), 7.28 (2H, d, *J* 8 Hz, *m*-H), 7.74 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.58, 23.32, 24.10, 24.97, 32.10, 32.26, 81.58, 127.79, 129.74, 134.70, 144.35.

4.4.11. Menthyl tosylate (16).[5b] Colorless crystals: mp 92–93 °C; IR (film) 1178, 1366 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.52 (3H, d, *J* 6.4 Hz), 0.70–2.25 (15H, m), 2.37 (3H, s, CH_3), 4.32 (1H, m, OCH–), 7.26 (2H, d, *J* 8 Hz, *m*-H), 7.73 (2H, d, *J* 8 Hz, *o*-H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 15.21, 21.52, 22.21, 22.91, 23.13, 25.42, 31.57, 33.72, 41.91, 50.0, 83.50, 127.87, 129.64, 134.74, 144.31.

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