1,4-Diazabicyclo[2.2.2]octane (DABCO) – an Efficient Reagent in the Synthesis of Alkyl Tosylates or Sulfenates

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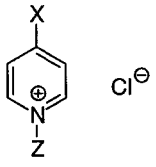
Dedicated to Professor Dr. Peter Welzel on the occasion of his 60th birthday.

The bicyclic tertiary amine 1,4-diazabicyclo[2.2.2]octane (DABCO) is a promising substitute not only for the widely used but hazardous and hygroscopic base pyridine in the syntheses of alkyl tosylates **3** but also for triethylamine in the preparation of alkyl sulfenates **4** from sterically hindered alcohols **2**. In several provided examples the substrates **2** were completely converted into the desired products, e.g. the respective tosylates **3**, which minimized subsequent separation processes. The current protocol points, in a number of cases, to nonchlorinated solvents as good alternatives to chloroform or dichloromethane and offers a workup procedure for a larger scale reaction which relies on the removal of the side products by filtration instead of the traditional extraction method using several aqueous washings.

The conversion of alcohols into esters by acid chlorides in the presence of a tertiary amine is one of the most fundamental and most widely employed transformations in organic chemistry.[1] Pyridine[2] and 4-dimethylaminopyridine (DMAP)[3] are still the amines of choice since they catalyze these esterfications of alcohols (or amidation of amines)[3–5] by the well-known pyridinium type intermediates **1** (Figure). Probably the significant positive partial charge of the ring nitrogen atom in pyridinium salts **1** is responsible for the dominating position of these compounds in the synthesis of esters although the sensitivity of arylsulfonyl pyridinium salts towards a nucleophilic ring opening has been known for many years.[6]

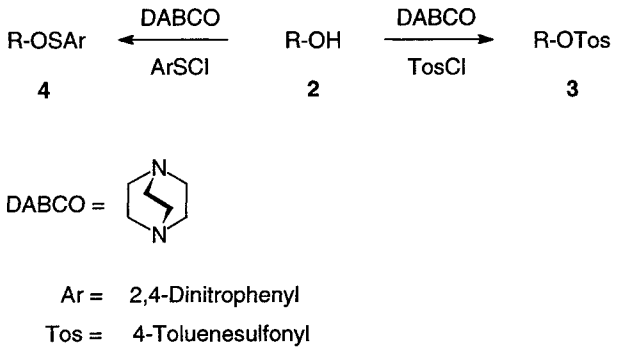


1

X = H, $N(CH_3)_2$, NC_4H_8
Z = H_3CCO, C_6H_5CO, $H_3CC_6H_4SO_2$

Figure

The toxicological data of pyridine and especially of DMAP call for a judicious and careful handling of these chemicals. In the case of 4-dimethylaminopyridine particularly, severe health-hazardous effects are well-documented.[7] Thus, methods were developed which require only substoichiometric to catalytic amounts of the nonvolatile base DMAP in acylation reactions.[3] In addition, a polymer-bound derivative of DMAP is commercially available and can be used in esterfication reactions. In the course of the revision of a laboratory manual,[8] a less hazardous base was needed for the synthesis of *trans*-4-*tert*-butylcyclohexyl tosylate (**3b**) and (−)-menthyl tosylate **3d** (Table 1) from the respective alcohols **2b** and **2d** and tosyl chloride. According to our results, 1,4-diazabicyclo[2.2.2]octane (DABCO) turned out to be the reagent of choice (Scheme 1). If pK_a data were taken as a guide for the efficiency of nitrogen bases in esterfication reactions our results called for an investigation of DABCO [pK_a = 8.9 (DMSO)] as a general substitute for pyridine [pK_a = 3.4 (DMSO)].[9] Apart from the conversion of phenols, naphthols,[10] or selected polymer-bound alcohols into the respective tosylates[11] no detailed study about the use of DABCO in tosylation reactions has been published so far. The present work discloses our latest results concerning the application of 1,4-diazabicyclo[2.2.2]octane in organic synthesis. The major work contributes to the synthesis of tosylates **3** from sterically demanding alcohols **2** followed by the synthesis of 2,4-diitrobenzenesulfenates **4** (Scheme 1).

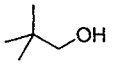
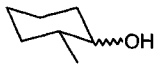
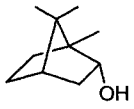
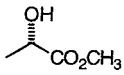
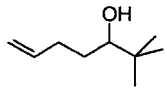
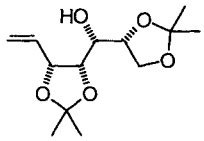


Preparation of alkyl tosylates **3** or alkyl sulfenates **4** from alcohols **2** using DABCO and the respective acid chlorides as reagents

Scheme 1

The tosylation of neopentyl alcohol **2a** and of *trans*-4-*tert*-butylcyclohexanol (**2b**) in chloroform using an excess of pyridine as base was satisfactory. However, the conversion of all the remaining alcohols of our study, i.e. 2-methylcyclohexanol (**2c**) (*cis*/*trans* = 26 : 74), (1*R*,2*S*,-5*R*)-(−)-menthol (**2d**), (*S*)-(−)-methyl lactate (**2f**), 2,2-dimethylhept-6-en-3-ol (**2g**), and the mannose-derived heptenol **2h**, to the respective sulfonic acid esters **3** in the presence of pyridine as base and chloroform as solvent[4] was not very successful (Table 1).[12] The synthesis of **3** either failed completely (preparation of **3h**), was inefficient (**3c**, **3f**), or showed the formation of the respective alkene presumably due to subsequent elimination of the respective tosylate under the basic conditions as a significant side reaction (synthesis of **3g**). The yields of tosylates **3** were significantly increased when 2 equivalents of DABCO were used as base instead of pyridine. At first glance dichloromethane seems to be the best reaction medium for the tosylation of **2**. However, we conclude from our detailed study of the tosylation of (−)-menthol

Table 1. Yields of Alkyl Tosylates **3a–h** in Different Solvents Using DABCO or Pyridine as Base (Scheme 2)

3	ROH 2	$CHCl_3$[a] C_5H_5N (%)	*t*-BuOMe[b] DABCO (%)	EtOAc[b,c] DABCO (%)	MeCN[b] DABCO (%)	CH_2Cl_2[b] DABCO (%)
a		99	66	**97**	79	87
b		81	80	–	–	**85**
c		34[d]	45[d]	**95**[e]	73[d]	81[f]
d		–	**93**	**96**	–	–
e		–	46	–	–	**87**
f		26	63	66	71	**79**
g		37	16	45	72	**88**
h		0	82	–	–	**92**

[a] Ratio of reagents: 10 mmol of ROH **2**, 15 mmol of TosCl, 10 mL of pyridine, 15 mL of $CHCl_3$.
[b] Ratio of reagents: 10 mmol of ROH **2**, 15 mmol of TosCl, 20 mmol of DABCO, 10 mL of solvent.
[c] 4 d reaction time.
[d] *trans*-**3c**.
[e] *cis*-**3c**/*trans*-**3c** = 22:78.
[f] *cis*-**3c**/*trans*-**3c** = 5:95.

2d (Table 2) that *tert*-butyl methyl ether (*t*-BuOMe) or, in other instances, ethyl acetate (Table 1) are always worth being considered as good alternatives to chlorinated solvents. This is especially noteworthy because *t*-BuOMe and EtOAc are the preferred organic solvents in chemical courses in academic institutes or for larger scale purposes in industry. The first set of experiments (Table 1) indicated that molar ratios of 1.0 equivalent of alcohol **2**, 1.5 equivalents of tosyl chloride, and 2.0 equivalents of DABCO in dichloromethane allowed the complete conversion of the substrates **2** to the respective esters **3** (TLC analysis). This fact was often of major importance in continuing studies using the tosylates **3** as substrates since some products **3**, e.g. the mannose-derived ester **3h**, could not be separated from the starting alcohol **2**, by means of chromatography or by crystallization. Elimination and the formation of alkenes from **3** was never a problem in our experiments in spite of the excess of DABCO employed. The optical rotations which were obtained for (−)-menthyl tosylate **3d** $\{[\alpha]_D^{20} - 68.4$ (c = 0.99, $CHCl_3$)$\}$ and for lactic acid derivative **3f** $\{[\alpha]_D^{20} - 6.0$ (c = 0.95, $CHCl_3$)$\}$ are well in accord with the literature values for the respective optically pure compounds.[12,13]

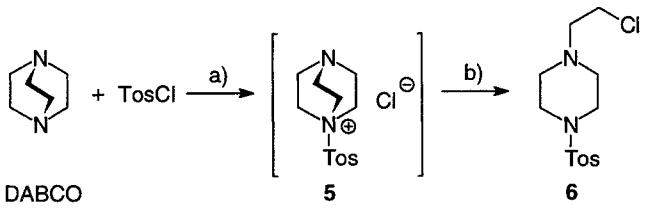
Several experiments were devised to reduce the amount of DABCO below 2.0 equivalents. Triethylamine as an auxiliary base ($pK_a = 9.0$[14]), which was successful with DMAP,[3] or potassium carbonate failed to replace the excess of DABCO.[15] However, lowering the amount of DABCO from 2.0 to 1.5 equivalents with a simultaneous reduction of the amount of TosCl (from 1.5 to 1.3 equivalents) still allowed the conversion of **2d** to **3d** within 24 h (Table 2, entry 3). If the reaction time was extended to 48 h the amount of reagents could be even further reduced without a significant drop in yield of **3d** (Table 2, entry 4). The complete conversion of alcohol **2d** using equimolar amounts of DABCO and tosyl chloride (Table 2, entries 7–9) could not be achieved under the reaction conditions summarized in Tables 1 and 2. The major reason for this finding presumably was a side reaction starting from the adduct **5** of DABCO and tosyl chloride which precipitated immediately upon addition of tosyl chloride to the reaction mixture. According to TLC analysis, the formation of the primary precipitate was not paralleled by the formation of the product **3d**.[16,17] Thus, the major reaction pathway of ammonium salt **5** should, in any case, be the conversion of **2** → **3**. However, in tosylation reactions which took longer time to comple-

tion the sulfonamide **6** was isolated as a side product (Scheme 2).[18] Thus, not all of the initially available tosylation reagent contributed to the formation of ester **3d** and obviously a complete conversion of **2d** to the tosylate **3d** was only possible if an excess of tosyl chloride and of the base DABCO was employed.[16,17] These mechanistic considerations also indicated that the suitability of solvents for the investigated tosylation reactions (Table 1) probably seemed to be dependent on their ability to dissolve the polar ammonium salt **5** for the reaction with the alcohol **2**.[19]

Table 2. Tosylation of (−)-Menthol **2d** in *t*-BuOMe at Ambient Temperatures (20 °C) (Scheme 2)

Entry	TosCl (equiv.)	DABCO (equiv.)	React. Time (h)	Yield **3d** (%)
1	1.5	2.0	24	93
2	1.5	1.7	24	95
3	**1.3**	**1.5**	**24**	**98**
4	1.1	1.3	48	94
5	1.0	1.5	48	76
6	1.0	1.3	48	76
7	1.0	1.0	108	79
8	1.0	1.0	24[a]	45
9	1.0	1.0	24[b]	75

[a] Reaction was performed at 55 °C.
[b] Ultrasound.



DABCO **5** **6**

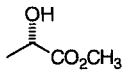
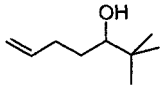
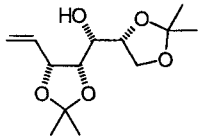
reagents and conditons: a) $CHCl_3$ or $CDCl_3$; b) 7 d, 25 °C.

Scheme 2

No complications were observed on scaling the synthesis of (−)-menthyl tosylate **3d** up to 0.06 moles. In order to adapt this method for organic chemistry courses we refrained from using anhydrous *t*-BuOMe in the experiment. The experiments, however, indicated that *purum grade t*-BuOMe was sufficient to afford the tosylate **3d** $\{[\alpha]_D^{20} - 68.4\ (c = 0.99, CHCl_3)\}$ in 98 % yield. The product **3d** was, in this case, isolated by filtration of the reaction mixture, washing of the precipitate, and subsequent concentration of the filtrate in vacuo.

Besides tosylates **3**, several sulfenic acid *O*-esters **4** were needed in our ongoing studies. However, the syntheses of these compounds according to the standard methods of Reich[20] and of Pasto[21] always led, in our cases to the formation of multiple side products which were sometimes hard to separate from the desired compounds **4**. Application of our protocol for the synthesis of tosylates **3** from alcohols **2** using 2,4-dinitrobenzenesulfenic acid chloride instead of tosyl chloride led to reaction mixtures which afforded, upon workup, the sulfenates **4** in high yields and as analytically pure samples (Table 3).[22]

Table 3. Synthesis of 2,4-Dinitrobenzenesulfenic Acid *O*-Esters **4f–h** (Scheme 2)

4	ROH **2**	Yield (%) **4**
f		79
g		92
h		92

An extension of the sulfonylation or the sulfenylation methods described above efficiently allowed benzoylation reactions of **2**.[23,24] Likewise, this new protocol can also be applied to amines. The successful preparation of sulfonamides by a procedure similar to the one reported has been published for several examples using optically active amines.[25]

In conclusion, 1,4-diazabicyclo[2.2.2]octane (DABCO) served as a useful substitute for pyridine in tosylations and for triethylamine in sulfenylation reactions. It should be pointed out that DABCO is a chemical convenient to handle. It is a colorless, crystalline, only weakly hygroscopic base with little, non-aminelike odour. If necessary, the reagent can be purified and dried by sublimation at 100 °C/0.1 mbar,[26] – conditions that are usually readily available in almost every research laboratory.

NMR spectra were recorded at 20 °C in $CDCl_3$ on Bruker WM 400 or AC 250 instruments. UV spectra were measured in EtOH in 1-cm quartz cuvettes using a Perkin-Elmer Spectrophotometer 330, and IR spectra in CCl_4 in NaCl cuvettes (0.5 mm) on a Perkin-Elmer 1600 FTIR machine. Optical rotations were measured on a Perkin-Elmer Spectrophotometer (1-mm split) at $\lambda = 546$ nm and at $\lambda = 579$ nm. The obtained values were converted to the respective values at $\lambda = 589$ nm using Drude's equation.[27]

The following abbreviations have been used throughout the present work: 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-dimethylaminopyridine (DMAP). Silica gel for column chromatography (0.063–0.200 mm) was obtained from Woelm. DABCO was purchased from Merck and was used as obtained. Sublimation of DABCO prior to use did not raise the yields of products **3**–**4**. Pyridine was distilled from Na under Ar and used immediately. CH_2Cl_2 and MeCN were distilled from CaH_2 (Ar), EtOAc was fractionally distilled prior to use. Anhydrous *t*-BuOMe (Na) was used for the experiments summarized in Tables 1 and 2, *purum grade t*-BuOMe (> 98 %) was used for the larger scale tosylation. TosCl was recrystallized from cyclohexane. 2,2-Dimethylhept-6-en-3-ol (**2g**),[28] (2*R*,3*R*,4*R*,5*R*)-1,2:4,5-di(isopropylidenedioxy)hept-6-en-3-ol (**2h**)[29] were prepared according to literature procedures. Neopentyl tosylate **3a**,[30] 2-methylcyclohexyl tosylate **3c**,[12] and (*S*)-(−)-methyl 2-(*p*-toluenesulfonyloxy)propanoate (**3f**)[13,31,32] have been prepared previously. Petroleum ether refers to the fraction boiling between 45–55 °C.

Synthesis of *O*-Esters (3, 4); General Procedure:
A round-bottom flask was charged with a solution of DABCO (2.24 g, 20 mmol, 10 mL of anhydrous solvent) and alcohol **2** (10 mmol) and was stoppered with a drying tube ($CaCl_{22}$). The mixture was cooled to 0 °C (ice bath). The respective acid chloride (15 mmol, neat) was added in small portions over a period of 5 min which was paralleled by the formation of a precipitate. The slurry was stirred for 1h at 0 °C and after removal of the ice bath until all starting alcohol **2** has been consumed [15 min for the formation of sulfenates **4**, and 14–24 h for tosylates **3**;[33] the alcohols **2** were detected on TLC plates using the 4-methoxybenzaldehyde sulfuric acid reagent[34] (Ekkert's reagent)]. The mixture was filtered and the precipitate was repeatedly washed with *t*-BuOMe (total volume of 50 mL). The filtrate was extracted with 2 M HCl (2 × 20 mL), with 5% $NaHCO_3$ (20 mL) and with H_2O (20 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The oily to solid residues were purified by column chromatography (silica gel) using the given eluent.

Larger Scale Synthesis of (−)-Menthyl Tosylate 3d:
A 250-mL round-bottom flask was charged with (−)-menthol **2d** (9.37 g, 0.06 mol) and DABCO (8.75 g, 0.08 mol). The solids were dissolved in *t*-BuOMe (*purum grade*, 60 mL), the flask was stoppered with a drying tube ($CaCl_2$), and was cooled to 0 °C. TosCl (recrystallized from cyclohexane, 12.58 g, 0.07 mol) was added in small portions (15 min). Stirring was continued for 1 h at 0 °C and for 48 h at 20 °C. The solids were removed by filtration over Celite (Buchner funnel, 7 cm in diameter, charged to a height of 1 cm with Celite). The precipitate was washed with small portions of *t*-BuOMe (a total volume of 300 mL, no vacuum was applied during the washing procedure). The clear filtrate was concentrated in vacuo to afford (−)-menthyl tosylate **3d** as colorless crystals (18.27 g, 98%); mp 92–93 °C; $[\alpha]_D^{20}$ −68.4 (c = 0.99, $CHCl_3$) {Lit.[13] mp 92.5–93.5 °C; $[\alpha]_D^{20}$ −68.2– −69.5 ($CHCl_3$)}.

2,2-Dimethylhept-6-en-3-yl p-Toluenesulfonate (**3g**): toluene as eluent; mp 43–45 °C.

$C_{16}H_{24}SO_3$ (296.4), calc. C 64.83, H 8.16, S 10.82
found C 64.77, H 8.42, S 10.74.

^{1}H NMR (250 MHz) δ = 0.88 (s, 9 H, CH_3), 1.59–1.72 (m, 2 H, CH_2), 1.93–2.21 (m, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 4.51 (m_c, 1 H, CH), 4.93–5.02 (m, 2 H, CH_2), 5.73 (ddt, J = 6.4, 10.7, 19.1 Hz, 1 H, CH), 7.31 (d, J = 7.9 Hz, 2 H, CH), 7.79 (d, J = 8.6 Hz, 2 H, CH).

^{13}C NMR (63 MHz) δ = 23.3, 27.8, 31.8, 32.3, 37.0, 93.8, 116.9, 129.1, 131.2, 136.9, 139.3, 145.7.

MS (EI, 70 eV): m/z (%) = 216 (16), 155 (27), 57 ($C_4H_9^+$, 100).

(2R,3R,4R,5R)-(−)-1,2:4,5-Di(isopropylidenedioxy)hept-6-en-3-yl p-Toluenesulfonate (**3h**): pentane/EtOAc, 9:1 (v/v) as eluent; colorless oil; $[\alpha]_D^{20}$ −4.7 (c = 0.65, $CHCl_3$).

$C_{20}H_{28}SO_7$ (412.5), calc. C 58.23 H 6.84 S 7.77
found 57.93 6.83 7.71.

IR (NaCl): ν = 3020, 2960, 2900, 1570, 1320, 1160 cm^{-1}.

^{1}H NMR (250 MHz) δ = 1.24 (s, 6 H, CH_3), 1.33 (s, 6 H, CH_3), 2.42 (s, 3 H, CH_3), 4.10–4.24 (m, 4 H, CH), 4.56 (t, J = 7.0 Hz, 1 H, CH), 4.79 (t, J = 6.0 Hz, CH), 5.33 (d, J = 9.9 Hz, 1 H, CH), 5.41 (d, J = 17.0 Hz, 1 H, CH), 5.92 (ddt, J = 7.0, 10.0, 17.0 Hz, 1 H, CH), 7.30 (d, J = 7.9 Hz, 2 H, CH), 7.81 (d, J = 8.5 Hz, 2 H, CH).

^{13}C NMR (63 MHz) δ = 21.5, 25.3, 25.4, 26.0, 26.9, 66.4, 74.5, 76.5, 78.7, 79.1, 109.1, 109.7, 120.5, 127.9, 129.3, 130.2, 132.9, 144.4.

MS (EI, 70 eV): m/z (%) = 397 ($M^+ - H_3$, 50), 155 (87), 127 (44), 101 (100).

(S)-(−)-Methyl 2-(2,4-Dinitrobenzenesulfenyloxy)propanoate (**4f**): CH_2Cl_2 as eluent; mp 109–111 °C; yellow crystals; $[\alpha]_D^{20}$ −146.5 (c = 0.27, CH_2Cl_2).

$C_{10}H_{10}N_2O_7S$ (302.3), calc. C 39.70 H 3.33 N 9.27 S 10.62
found 39.40 3.16 9.58 10.71.

^{1}H NMR (250 MHz) δ = 1.66 (d, J = 7.0 Hz, 3 H, CH_3), 3.80 (s, 3 H, CH_3), 4.36 (q, J = 7.0 Hz, 1 H, CH), 8.08 (d, J = 9.0 Hz, 1 H, CH), 8.51 (dd, J = 2.1, 9.0 Hz, 1 H, CH), 9.07 (d, J = 2.1 Hz, 1 H, CH).

^{13}C NMR (63 MHz) δ = 19.3, 53.1, 80.9, 121.4, 124.5, 128.4, 139.6, 145.2, 153.9.

MS (EI, 70 eV): m/z (%) = 302 (M^+, 3), 243 (7), 198 (26), 87 (100).

2,2-Dimethylhept-6-en-3-yl 2,4-Dinitrobenzenesulfenate (**4g**): CH_2Cl_2/petroleum ether, 1:1 (v/v) as eluent; orange crystals; mp 40–41 °C.

$C_{15}H_{20}N_2O_5S$ (340.4), calc. C 52.93 H 5.92 N 8.23 S 9.42
found 53.05 5.85 8.10 9.44.

IR (CCl_4) ν = 3090, 2970, 2870, 1600, 1590, 1520, 1340, 1300 cm^{-1}.

UV/Vis (EtOH): λ_{max} (ε) = 420 (3350)sh nm, 400 (4320)sh, 350 (9690), 250 (8440)sh.

^{1}H NMR (250 MHz) δ = 1.03 (s, 9 H, CH_3), 1.72–1.89 (m, 2 H, CH_2), 2.06–2.34 (m, 2 H, CH_2), 3.55 (m_c, 1 H, CH), 4.91–5.03 (m, 2 H, CH_2), 5.65–5.85 (m, 1 H, CH), 8.08 (d, J = 9.2 Hz, 1 H, CH), 8.48 (dd, J = 2.4, 9.2 Hz, 1 H, CH), 9.11 (d, J = 2.4 Hz, 1 H, CH).

^{13}C NMR (63 MHz) δ = 26.2, 30.5, 31.5, 36.3, 95.7, 115.7, 120.9, 123.7, 127.5, 137.4, 138.1, 144.0, 154.3.

MS (EI, 70 eV): m/z (%) = 340 (M^+, 0.2), 199 (5), 69 (100).

(2R,3R,4R,5R)-(−)-1,2:4,5-Di(isopropylidenedioxy)hept-6-en-3-yl 2,4-Dinitrobenzenesulfenate (**4h**): recrystallized from EtOH; yellow needles mp 65–67 °C; $[\alpha]_D^{20}$ −173.1 (c = 0.29, $CHCl_3$).

$C_{19}H_{24}N_2O_9S$ (456.5), calc. C 49.99 H 5.30 N 6.14 S 7.02
found 49.80 5.39 5.85 6.82.

^{1}H NMR (250 MHz) δ = 1.40 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 4.01–4.27 (m, 5 H, CH, CH_2), 4.60 (dd, J = 6.1, 8.2 Hz, 1 H, CH), 5.31 (d, J = 10.7 Hz, 1 H, CH_2), 5.39 (d, J = 16.8 Hz, 1 H, CH_2), 5.80 (ddd, J = 8.2, 10.7, 16.8 Hz, 1 H, CH), 8.43 (dd, J = 2.4, 9.2 Hz, 1 H, CH), 8.61 (d, J = 9.2 Hz, 1 H, CH), 9.10 (d, J = 2.4 Hz, 1 H, CH).

^{13}C NMR (100 MHz) δ = 25.1, 25.5, 26.2, 27.3, 64.3, 75.6, 77.7, 79.0, 84.1, 109.4, 109.7, 120.6, 121.1, 125.1, 127.3, 132.6, 138.4, 144.4, 154.5.

MS (EI, 70 eV): m/z (%) = 456 (M^+, 4), 441 (28), 199 (25) 185 (100), 101 (75).

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(16) Treatment of a solution of DABCO (2 equivalents) with TosCl (1.5 equivalents) afforded a colorless precipitate which was stirred for 18 h at ambient temperatures. Hereafter 1 equivalent of (–)-menthol **2d** was added and the slurry was allowed to stir for 14 h at r.t.. Workup of the reaction mixture afforded 72% of (–)-menthyl tosylate **3d**.

(17) The mixtures remained, however, thick slurries throughout the reaction periods because of the formation of hardly soluble DABCO · HCl during the course of the conversion of the alcohols **2**.

(18) The formation of **6** from equimolar amounts of DABCO and TosCl was monitored by NMR in $CDCl_3$. Within 7 d at ambient temperatures approximately half of the amount of DABCO was transformed into the sulfonamide **6**. 4-(2-Chloroethyl)piperazino-1-*p*-toluenesufonamide (**6**): colorless needles; mp 140–141 °C; $C_{13}H_{19}ClN_2O_2S$ (302.8), calc. C 51.56, H 6.32, N 9.25, S 10.59, found C 51.23, H 6.26, N 9.09, S 10.56. 1 H NMR (250 MHz, $CDCl_3$) δ = 2.43 (s, 3 H, CH_3), 2.59 (m_c, 4 H, CH_2), 2.71 (t, 2 H, J = 6.5 Hz, CH_2), 3.03 (m_c, 4 H, CH_2), 3.52 (t, J = 6.6 Hz, 2 H, CH_2), 7.32 (d, J = 8.0 Hz, 2 H, CH), 7.63 (d, J = 8.0 Hz, 2 H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.5, 40.7, 45.9, 52.2, 59.2, 127.9, 129.7, 132.5, 143.7. MS (EI, 70 eV): m/z (%) = 302 (M+, 7), 253 (40), 147 (100).

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(22) The synthesis of the secondary neopentyl type ester **4g** according to the method of Reich[20] afforded only 61% of **4g**. This finding shows that the new method is more than a simple substitute for Et_3N which is commonly used in the synthesis of 2,4-dinitrobenzenesulfenates **4**.

(23) For example (*S*)-(+)-methyl 2-(benzoyloxy)propanoate was prepared in 92% yield from (*S*)-(–)-methyl lactate (**2f**) {$[\alpha]_D^{20}$ +12.8 (c = 1.05, $CHCl_3$) [Lit.[24] $[\alpha]_D^{20}$ +11.2 ($CHCl_3$)]}.

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