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O-SULFINYLATION WITH METHANESULFONYL CYANIDE OR P-TOLUENESULFONYL CYANIDE AND DBU+.

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Abstract: Reaction of methanesulfonyl cyanide or p-toluenesulfonyl cyanide with alcohols in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gives sulfinates in good yield. A mechanistic scheme involving sulfinyl cyanates is suggested.

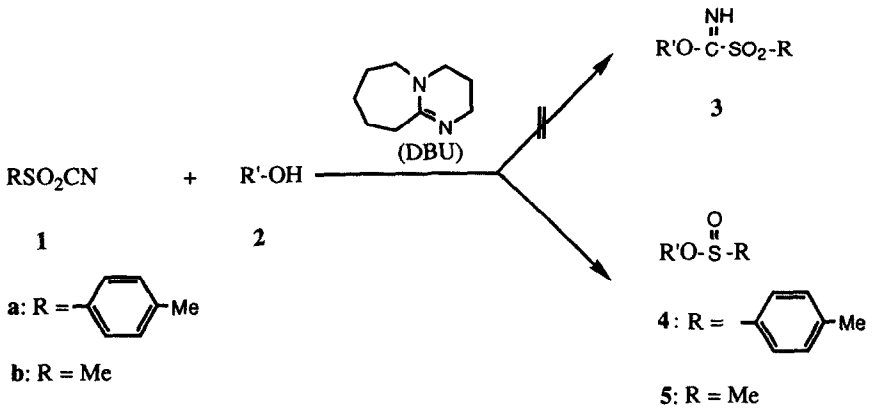
The synthesis of p-toluenesulfinate esters requires the activation[1,2] of p-toluenesulfinic acid, or the use of the corresponding sulfinyl chloride which is of limited stability[3]. More recently a one-pot synthesis of sulfinates from alcohols, sulfonyl chlorides and trimethyl phosphite has also been described[4]. Although most of the yields quoted are high, this method gives methanesulfinate esters in low yield[5]. The standard synthesis of methanesulfinates requires the somewhat tedious preparation of methanesulfinyl chloride[6].

In the course of the work on radical deoxygenation of alcohols[7] we have employed a series of derivatizing agents[8] making the alcohols suitable for this radical process. Thus, we attempted to react various alcohols with tosyl cyanide (**1a**) (Scheme 1) in order to obtain the corresponding imidates (**3**). In the presence of DBU, however, sulfinates of type **4** have been obtained in high yield (Table 1). Our data show that primary, secondary and tertiary alcohols are easily transformed to their p-toluenesulfinates. Similarly, methanesulfonyl cyanide (**1b**) reacted with alcohols in the presence of DBU resulting in the formation of methanesulfinates (**5**) (Scheme 1, Table 1).

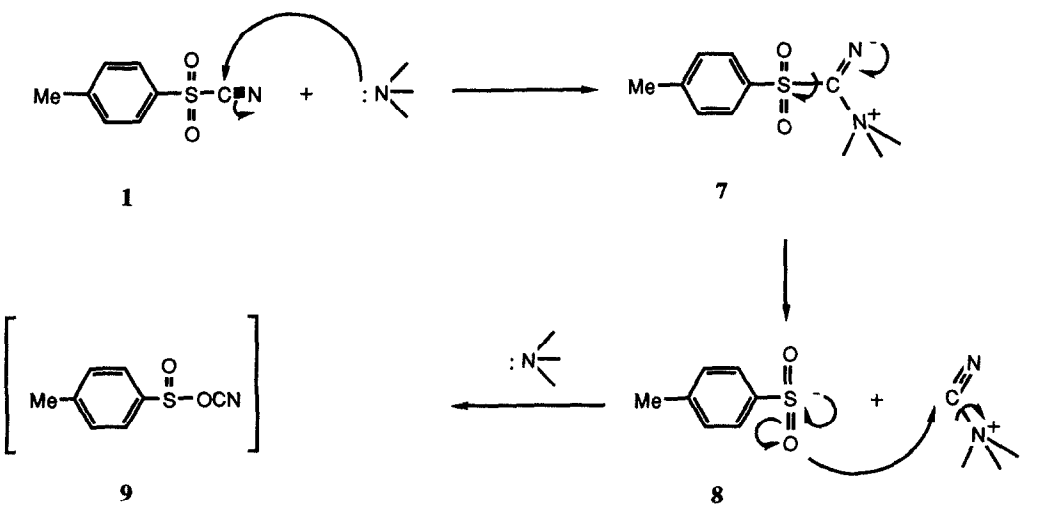
It is known[9] that tosyl cyanide reacts easily with suitable nucleophiles (ArO^-, RS^-, R_2N^-, ArMgX) giving rise to the formation of ArOCN, RSCN, R_2NCN, ArCN- type products. The only other product of these reactions is TsS-4Me-Ph[10], (**6**) indicating a more complex mechanism. We propose that the first steps of our new sulfination reactions are as shown in Scheme 2. Intermediates **7** and **8** give rise to the activated sulfinyl moiety of **9** which then affords the sulfinates **4**. Also the weak S-O single bond of **9** may undergo homolytic cleavage giving sulfinyl and cyanate radicals in the absence of an alcohol[11].

The sulphinates formed in our reactions have been identified (in addition to physical methods) by comparison with authentic compounds and also by oxidizing some of them to the known sulfonates (tosylates and mesylates) with 3-chloroperoxybenzoic acid (50-60%, Aldrich).

+Dedicated to the memory of the late Professor Rezső Bognár of Department of Chemistry, Kossuth Lajos University of Arts and Sciences, Debrecen, Hungary.

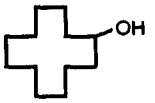
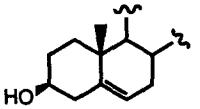
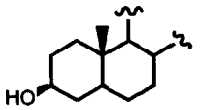
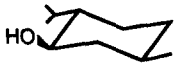
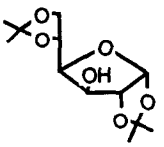
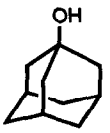


Scheme 1



Scheme 2

Table 1 Sulfinylation of alcohols with sulfonyl cyanides (1a and 1b) and DBU

Entry	Substrate 2		Isolated yield (%)		Identification	
			4	5	4	5
1	a		89	92	d, e, f	d,f,g
2	b	 3β - cholesterol	85[a]	91[a]	d	d
3	c	 3β - cholestanol	91[a]	98[a]	d, e, f	d,g
4	d		94[a]	93[a]	d	d
5	e	CH_3-$(CH_2)_{17}$-OH	92	90	d	d,g,h
6	f		91[a]	84[a]	d	d,g,h
7	g		70[b] (87.5)[c]	85	d	d,g,h

Notes: a: mixture of two diastereomers, b: 20% 1-adamantanol was recovered, c: yield based on the adamantanol consumed, d: m.p., IR, ^1H and ^{13}C NMR, MS, e: comparison with the independently prepared authentic compound, f: oxidation to the corresponding sulfonate ester and comparison with the authentic compounds prepared by direct sulfonylation, g: microanalysis, h: at 0°C 1.5 more equivalents of MsCN was added.

Typical procedure:

To the solution of the starting alcohol **2** (2 mmol) in dry methylene dichloride (8-10 ml), DBU (1.1 eq.) was added under argon at 0°C, followed by the addition of the corresponding cyanide[12] (**1**) (up to 4.0 equivalents of **1a** or 1.5 eq. of **1b**) in small portions. Then the pale yellow solution was allowed to warm up to room temperature and the reaction monitored by t.l.c. The reaction was complete in less than 2 hr. Then the mixture was concentrated in vacuum and the sulfinates isolated by column chromatography on silica gel (hexanes: ether = 8:2).

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5. In ref. 4 the molar ratio of methanesulfonyl chloride to menthol was 1.5:1.0. This was also the ratio in our case (Table 1, entry 4). However, the yield was increased from 22% to 93%.

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11. A detailed mechanistic study of this reaction will be reported in a full paper.

12. Reagents: 95% pure p-toluenesulfonyl cyanide was used as purchased (Aldrich Chemical Co., Inc.). Methanesulfonyl cyanide was prepared by the method of Vrijland, M. S. A. Organic. Syntheses; 1977; 57, 88. The reported yield was 67-72% after distillation. We found that the crude product (82%) is sufficiently pure for the sulfinylation step without further purification. In accordance with the finding of Vrijland, this compound can be stored (in our case in the freezer under dry argon) without decomposition for a long period of time. The starting cyanogen chloride, albeit a commercially available compound, was prepared by the method of Schröder, H. *Z. Anorg. Allg. Chem.* **1958**, *297*, 296.

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