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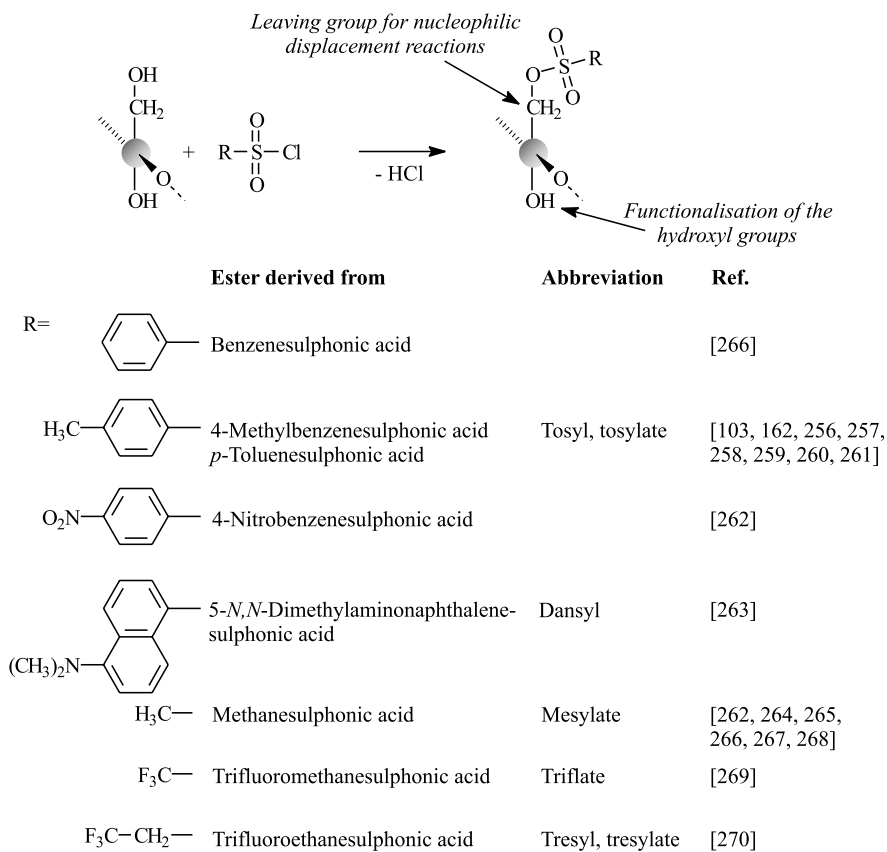
## 6 Sulphonic Acid Esters

Typical structures of sulphonic acid esters used in polysaccharide chemistry are shown in Fig. 6.1. The most widely used are the *p*-toluenesulphonic- and the methanesulphonic acid esters, due to their availability and hydrolytic stability. The formation of sulphonic acid esters is carried out heterogeneously by conversion with sulphonic acid chlorides in a tertiary organic base, in aqueous alkaline media (NaOH, Schotten-Baumann reaction), or completely homogeneous in a solvent such as DMAc/LiCl. A major drawback of heterogeneous procedures is that long reaction times and a high molar excess of reagent, mostly sulphonic acid chloride, are necessary for significant conversion. Sulphonic acid esters are reactive and may be attacked by unmodified OH groups in situ, yielding cross-links. Hence, the products obtained are insoluble. In addition, they contain a high chlorine content formed by the nucleophilic attack of chloride ions. In contrast, the homogeneous conversion, e.g. of cellulose dissolved in DMAc/LiCl, yields soluble sulphonic acid esters [162]. In particular, homogeneous tosylation applying TosCl in the presence of TEA is very efficient.

It is well known from the chemistry of low-molecular alcohols that hydroxyl functions are converted to a good leaving group by the formation of the corresponding sulphonic acid esters, and hence nucleophilic displacement reactions can be carried out. In the case of polysaccharides, nucleophiles such as halide ions may attack the carbon atom, leading to the corresponding deoxy compound with substitution of the sulphonate group (Fig. 6.2). It is also possible to modify the remaining hydroxyl groups prior to the S<sub>N</sub> reaction.

### 6.1 Mesylates

The heterogeneous conversion of mercerised cellulose (cotton linters) with MesCl (6 mol per mol AGU) in Py slurry affords cellulose mesylate with DS<sub>Mes</sub> values up to 1.7 after reaction for several days at RT [264]. A crucial point is the activation of the starting cellulose. It was found that the treatment of cellulose with aqueous NaOH increases the reactivity [264]. In order to gain higher DS values, subsequent solvent exchange with anhydrous methanol and Py is necessary. The alkali content of the activated cellulose on the DS<sub>Mes</sub> is unimportant (Table 6.1).



**Fig. 6.1.** Typical sulphonic acid esters of polysaccharides

**Table 6.1.** Influence of reaction time and temperature on the conversion of mercerised cellulose (cotton linters) with MesCl in Py (adapted from [265])

Conditions	Time (h)	Temperature (°C)	Reaction product			
			S (%)	Cl (%)	DS <sub>Mes</sub>	DS <sub>Cl</sub>
	4	28	20.0	1.42	2.00	0.11
	17	28	23.0	2.91	2.74	0.29
	2	57	12.0	10.73	0.93	0.72
	20	57	12.5	12.93	1.00	0.86