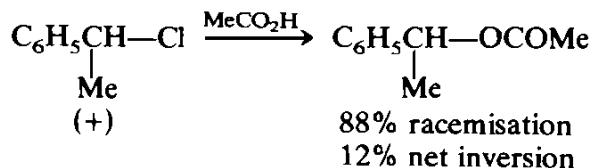


excess. This raises the question whether the mixture of racemisation/inversion observed in such cases stems from the simultaneous operation of  $S_N1$  and  $S_N2$  pathways for solvolysis, rather than *via* the relatively elaborate, variable ion pair hypothesis advanced above.

In some cases at least it is possible to demonstrate that a 'mixed'  $S_N1 + S_N2$  pathway is *not* operating. Thus solvolysis of the halide,  $(+)\text{C}_6\text{H}_5\text{CHMeCl}$ , mentioned above, but this time in  $\text{MeCO}_2\text{H}$ ,

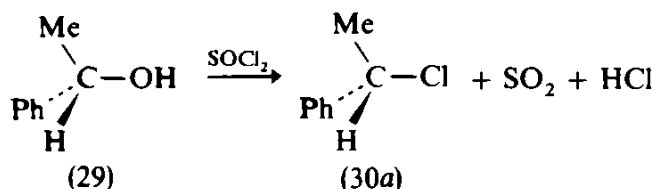


was found to lead to 88% racemisation, and 12% net inversion. Adding the much more powerfully nucleophilic  $\text{MeCO}_2^\ominus$  (as  $\text{MeCO}_2^\ominus\text{Na}^\oplus$ ) to the reaction mixture was found to result in: (a) no increase in the overall reaction rate, and (b) no increase in the proportion of net inversion. This strongly suggests that the inversion that is observed does *not* stem from part of the overall reaction proceeding *via* an  $S_N2$  pathway simultaneously with the (major)  $S_N1$  mode. If it did, we would expect the change to a much more powerful nucleophile ( $\text{MeCO}_2\text{H} \rightarrow \text{MeCO}_2^\ominus$ ) to lead to marked increases in both (a) and (b) above.

A good deal of interest, and controversy, has centred on whether in the last analysis there is perhaps a continuous spectrum of mechanistic pathways intermediate between  $S_N2$  and  $S_N1$ : these imperceptibly shading into each other *via* gradually varying transition states from the pure  $S_N2$  side, and *via* gradually varying ion pair/solvent combinations from the pure  $S_N1$  side. It is an area in which theory has shaded over into semantics if, indeed, not even into theology!

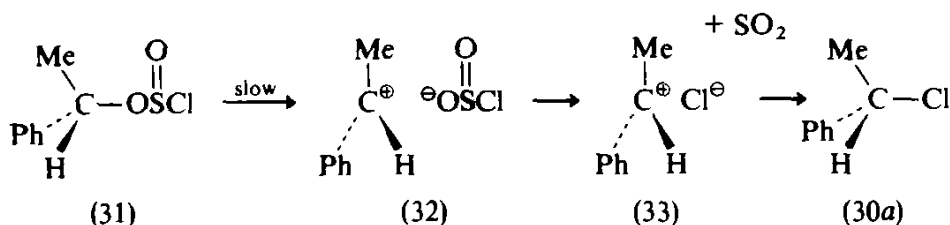
#### 4.4.5 $S_Ni$ mechanism: retention of configuration

Despite what has been said above about displacement reactions leading to inversion of configuration, to racemisation, or to a mixture of both, a number of cases are known of reactions that proceed with actual retention of configuration, i.e. in which the starting material and product have the same configuration. One reaction in which this has been shown to occur is in the replacement of OH by Cl through the use of thionyl chloride,  $\text{SOCl}_2$ :



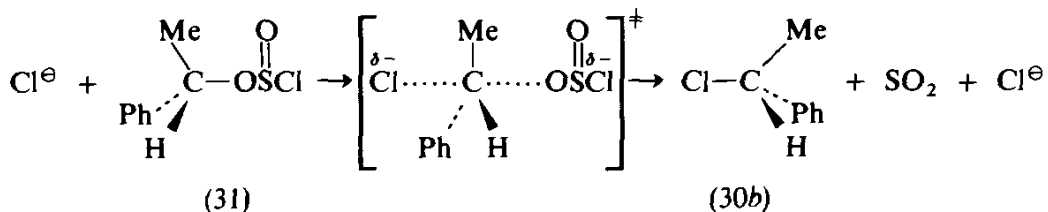
The reaction has been shown to follow a second order rate equation,  $\text{rate} = k_2[\text{ROH}][\text{SOCl}_2]$ , but clearly cannot proceed by the simple  $\text{S}_{\text{N}}2$  mode for this would lead to inversion of configuration (p. 87) in the product, which is not observed.

Carrying out the reaction under milder conditions allows of the isolation of an alkyl chlorosulphite,  $\text{ROSOCl}$  (31), and this can be shown to be a true intermediate. The chlorosulphite is formed with retention of configuration, the  $\text{R}-\text{O}$  bond not being broken during the reaction. The rate at which the alkyl chlorosulphite intermediate (31) breaks down to the product,  $\text{RCl}$  (30a), is found to increase with increasing polarity of the solvent, and also with increasing stability of the carbocation  $\text{R}^{\oplus}$ : an ion pair,  $\text{R}^{\oplus}\ominus\text{OSOCl}$  (32), is almost certainly involved. Provided collapse of the ion pair to products then occurs rapidly, i.e. in the intimate ion pair (33) within a solvent cage (*cf.* p. 90), then attack by  $\text{Cl}^{\ominus}$  is likely to occur on the same side of  $\text{R}^{\oplus}$  from which  $\ominus\text{OSOCl}$  departed, i.e. with retention of configuration:



Whether the breaking of the  $\text{C}-\text{O}$  and the  $\text{S}-\text{Cl}$  bonds occurs simultaneously, or whether the former occurs first, is still a matter of debate.

It is interesting that if the  $\text{SOCl}_2$  reaction on  $\text{ROH}$  (29) is carried out in the presence of pyridine, the product  $\text{RCl}$  is found now to have undergone inversion of configuration (30b). This occurs because the  $\text{HCl}$  produced during the formation of (31) from  $\text{ROH}$  and  $\text{SOCl}_2$  is converted by pyridine into  $\text{C}_5\text{H}_5\text{NH}^{\oplus}\text{Cl}^{\ominus}$  and  $\text{Cl}^{\ominus}$ , being an effective nucleophile, attacks (31) 'from the back' in a normal  $\text{S}_{\text{N}}2$  reaction with inversion of configuration:



#### 4.4.6 Neighbouring group participation: 'retention'

There are also some examples of retention of configuration in nucleophilic displacement reactions where the common feature is an atom or group—close to the carbon undergoing attack—which has an electron