Novel Reaction of Phosphinothioic Methanesulphonic Anhydride with Aluminium Halides. Stereoselective Synthesis of Phosphinothioic Halides

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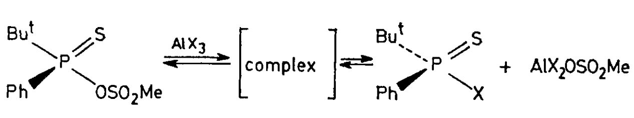
Summary Phosphinothioic methanesulphonic anhydrides (**1**) react with aluminium chloride or bromide to form complexes which after decomposition with water or methanol give halides (**2**) in high yield, with retention of configuration at phosphorus in the case of aluminium chloride.

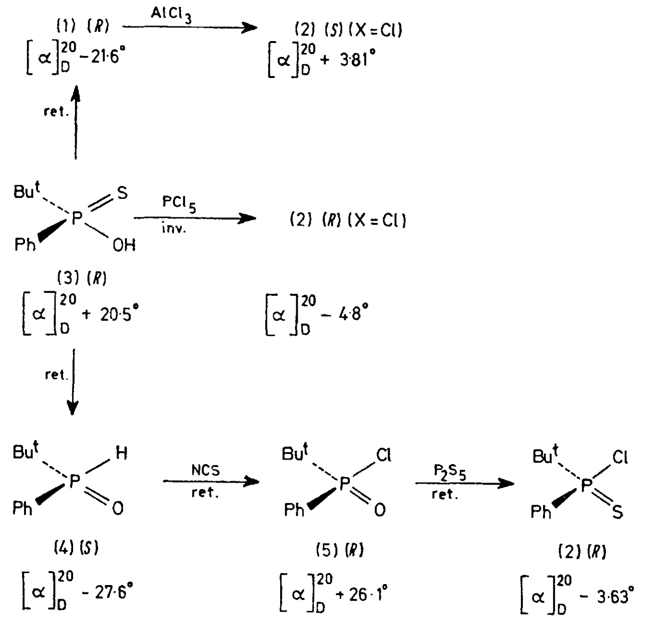
In connection with our studies of reactions of acid-catalysed nucleophilic displacement at four-co-ordinated phosphorus centres[1] we now report a novel displacement reaction with the aid of aluminium halides.



(1) (2)

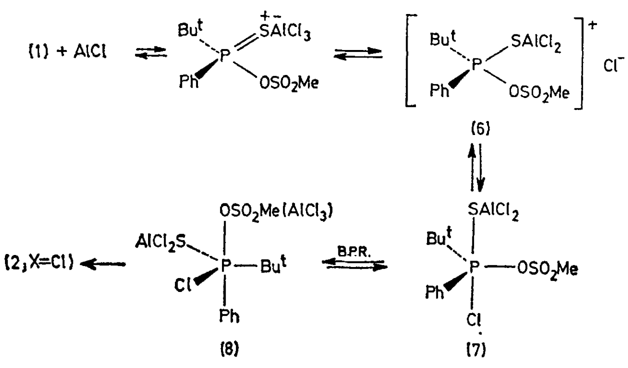
Racemic t-butylphenylphosphinothioic methanesulphonic anhydride (**1**) reacts with a small excess of aluminium chloride or bromide at ambient temperature in CH_2Cl_2, over 10 min, to give a complex which after decomposition by water or methanol and extraction with chloroform gives a high yield of corresponding chloride (**2**; X = Cl), or bromide (**2**; X = Br), finally purified by sublimation *in vacuo*. The stereochemistry of the reaction was studied using optically active (**1**) (Scheme 1).

Since the anhydride (**1**) is of the same configuration at the phosphorus atom as the starting phosphinothioic acid (**3**), the sign and rotation value of the chloride (**2**; X = Cl) are indicative of retention of configuration at phosphorus with relatively high stereoselectively.



NCS = N-chlorosuccinimide

Scheme 1



B.P.R. = Berry pseudo-rotation

Scheme 2

This assignment follows from the following stereochemical correlations. The chloridate (**2**; X = Cl) can be obtained by two independent routes of well established stereochemistry. The reaction of the acid (**3**) with phosphorus pentachloride leads to the chloride of the opposite configuration. This type of reaction is known to proceed with inversion of configuration at the phosphorus atom.[2] The chloride of the opposite configuration was also obtained by a series of reactions involving desulphurization of the thioic acid (**3**) to t-butylphenylphosphine oxide (**4**),[3,4] chlorination of (**4**) by *N*-chlorosuccinimide to the phosphinic chloride (**5**)[3,5] and finally replacement of oxygen by sulphur (P_2S_5).[5,6] All reactions of this series proceed with retention of configuration at the phosphorus centre. However the ligand metathesis, equivalent to an additional inversion, results in formation of (**2**) of opposite configuration to that observed in the reaction of (**1**) with aluminium chloride. It is of interest to note that optically active (**2**) undergoes slow racemisation in the presence of $AlCl_3$ under the reaction conditions lowering somewhat the stereoselectivity of the reaction under discussion.

These findings suggest that reaction of aluminium chloride with the anhydride (**1**) proceeds *via* complexation†

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† A similar complex is presumably formed with aluminium bromide but no reaction is observed using aluminium fluoride presumably as the result of lack of release of a suitable nucleophile from the reagent.

of the former at the sulphur atom attached to the phosphorus, leading to the phosphonium salt (**6**) which undergoes nucleophilic displacement *via* the five-co-ordinate intermediate (**7**) (Scheme 2). Co-ordination makes the sulphur atom highly apicophilic, forcing the sulphonic leaving group to enter an equatorial position. After one Berry-pseudorotation leading to the trigonal bipyramid (**8**), the sulphonic group may depart, assisted most likely by further complexation with $AlCl_3$.[7]

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