Cleavage and Formation of P-C Bonds During an Unusual Kinnear-Perren Reaction

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Z. Naturforsch. **53 b,** 1265–1266 (1998); received June 25, 1998

Kinnear-Perren Reaction, Triphenylmethyl

Treatment of triphenylmethyldichlorophosphine **1** with aluminium trichloride in the presence of *tert*-butyl chloride leads, after hydrolysis, with high selectivity to di-*tert*-butylphosphinic chloride **5**. The reaction is suggested to proceed via a chlorophosphinidene intermediate which is trapped by the alkyl chloride.

Introduction

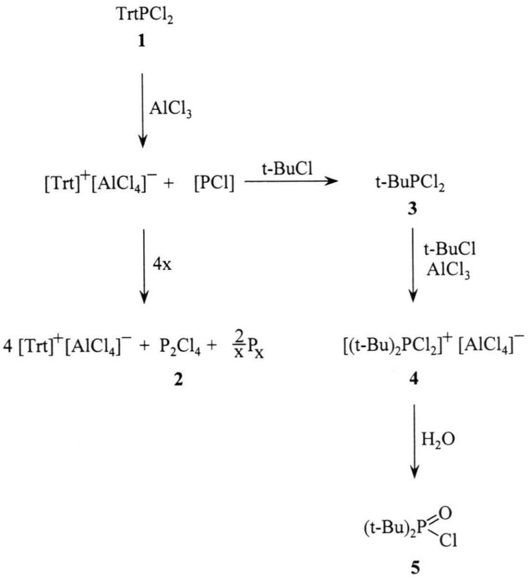
Formation of a phosphorus-carbon bond is observed when phosphorus trichloride as a nucleophile attacks the electrophilic carbon atom of an activated alkyl halide. If the Lewis acid aluminium trichloride is used, in order to activate the alkyl halide, and the ionic intermediate complex is finally hydrolyzed to give alkylphosphonic dichlorides, this sequence is known as the Clay or Kinnear-Perren reaction [1, 2].

Several variations of this important reaction are known. Instead of phosphorus trichloride other P-nucleophiles can be used: phosphorus tribromide leads (after hydrolysis) to alkylphosphonic dibromides [3], dichlorophosphines to diorganophosphinic chlorides [4 - 7]. Aluminium trichloride was successfully substituted by aluminium tribromide [8], and also by anhydrous sulfuric acid [4 - 6, 9, 10]. Treatment of the ionic intermediate with thiourea [11] or thiols [12] gives access, in certain cases, to alkylthiophosphonic dichlorides.

It is important that a carbocation of high stability can be derived from the alkyl halide employed. Accordingly, isomerization is observed in cases in which the formation of a thermodynamically more stable carbocation from the primary ionic intermediate is possible [3, 4, 13 - 15].

Results

We tried to achieve the formation of a phosphorus-carbon bond under Kinnear-Perren conditions using *tert*-butyl chloride as an alkyl halide, and triphenylmethyldichlorophosphine **1** [16] as a nucleophile. Surprisingly, after hydrolysis, di-*tert*-butylphosphinic chloride **5** [17, 18] was obtained as the only phosphorus-containing compound. Apparently, cleavage of the P-C-bond between the triphenylmethyl group and phosphorus was accompanied by the formation of P-C bonds between two *tert*-butyl groups and the latter.



Scheme 1.

This observation becomes understandable if one takes into consideration that the P-C bond in triphenylmethyldichlorophosphine **1** [16] is readily

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0932–0776/98/1100–1265 $ 06.00

cleaved upon treatment of **1** with aluminium chloride [19]. Abstraction of Cl^- from **1** by the Lewis acid aluminium trichloride, and elimination of Trt^+ from **1** leaves a putative chlorophosphinidene fragment (Scheme 1). In the absence of a suitable trapping agent, this fragment is known to disproportionate yielding tetrachlorodiphosphine **2** and amorphous phosphorus P_n [19]; in the presence of *tert*-butyl chloride it is readily inserted into the carbon-chlorine bond of the latter, yielding *tert*-butyldichlorophosphine **3** [17] which was observed by ^{31}P NMR spectroscopy in low concentration during the reaction. In the following step **3** acts as a nucleophile. It attacks the carbon center of another molecule of *tert*-butyl chloride whose electrophilicity is enhanced by complex formation with aluminium trichloride. This leads to di-*tert*-butyldichlorophosphonium tetrachloroaluminate **4**, from which di-*tert*-butylphosphinic chloride **5** is obtained by hydrolysis.

The course of this reaction strongly depends on the correct stoichiometry. If the amount of *tert*-butyl chloride and/or aluminium trichloride employed in the reaction is reduced, the formation of tetrachlorodiphosphine **2** is always observed.

Experimental

The working conditions are described elsewhere [20]. Triphenylmethyldichlorophosphine **1** was synthesized as previously described [16].

Reaction of triphenylmethyldichlorophosphine **1** *with tert-butyl chloride and aluminium trichloride, followed by hydrolysis; formation of di-tert-butylphosphinic chloride*

To a mixture of 0.772 g (5.8 mmol) of aluminium trichloride and 0.54 g (5.8 mmol) of *tert*-butyl chloride was added at r. t. a solution of 1.0 g (2.9 mmol) of triphenylmethyldichlorophosphine **1** in 10 ml of dichloromethane. The mixture was stirred for 2 h at r. t., and hydrolyzed by addition of 10 ml of water. After separation of the layers, the solvent was removed from the organic layer, and the remaining oily substance was investigated by ^1H and ^{31}P NMR spectroscopy. Di-*tert*-butylphosphinic chloride **5** was identified by its NMR parameters [17, 18].

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