

Catalysis Phenomena and Intermediates in the Reaction of Phosphorus Trichloride with Aldehydes

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Both hydrogen chloride and tertiary amines have been found to catalyse the reaction of PCl_3 with aldehydes; two types of intermediate not previously observed have been synthesized.

The phosphite structures (4) have been postulated as intermediates in the reaction of phosphorus trichloride (1) with aldehydes (2).¹ Miller *et al.* proposed that (4a) should react rapidly with a second aldehyde molecule to give 1-chloro-1-chloroalkoxyalkanes (6).² The phosphite structure (5) was expected to be the precursor of (6).

Commercial phosphorus trichloride (1) was found to be

contaminated with HCl, even after multiple distillation. The HCl can be removed from commercial (1) and other P^{III} chlorides by treatment with *N,N*-diethylaniline.[†] Refined (1)

[†] Compound (1) and tertiary amine (3) were mixed in a 1:0.15 ratio and PCl_3 was distilled directly into the reaction flask.

