

MECHANISM OF THE CLAY-KINNEAR-PERREN CONDENSATION

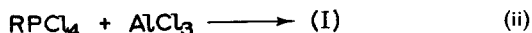
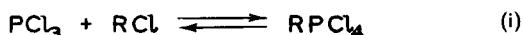
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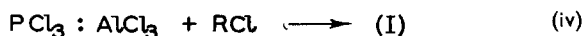
(Received 4 September 1957)

Abstract—Several apparently unrelated aspects of the process whereby complexes of the type $[\text{RPCl}_3]^+[\text{AlCl}_4]^-$ are formed from phosphorus trichloride, aluminium chloride and an alkyl halide, are shown to be compatible in terms of a mechanism involving preliminary formation of a carbonium cation.

CLAY,¹ and independently Kinnear and Perren,² have prepared alkylphosphonyl dichlorides, $\text{RPO}\cdot\text{Cl}_2$, by controlled hydrolysis of the complexes formed by interaction of alkyl halides with phosphorus trichloride and aluminium chloride, the latter authors demonstrating the wide application of the reaction. Evidence was provided to show that the intermediate complexes, which were isolated in specific examples of the reaction, might be formulated $[\text{RPCl}_3]^+[\text{AlCl}_4]^-$ (I), and recent work³ on the mechanism of the hydrolysis tends to support this. Clay proposed that the formation of complex occurred by the sequence:



Kinnear and Perren suggested the alternative reactions:



The originators considered a process involving intermediate formation of carbonium cation unlikely, on the grounds that if the alkyl halide and aluminium chloride are first mixed together, a lower yield of product is obtained than if the reactants are mixed in any other order.

There is little evidence however, that phosphorus trichloride will react with either alkyl halide or aluminium chloride alone, and a carbonium cation mechanism appears more likely for the following reasons:

(a) The formation exclusively of alkyl-2-phosphonyl dichloride when an *n*-alkyl is employed in the reaction, because of the greater comparative stability of the secondary cation, and related phenomena such as the behaviour of allyl chloride, can be better understood.

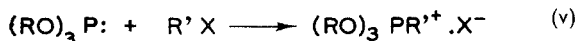
(b) It explains the low reactivity of poly-halogeno compounds and the complete inactivity of vinyl chloride in the reaction.

¹ J. P. Clay *J. Org. Chem.* **16**, 892 (1951).

² A. M. Kinnear and E. A. Perren *J. Chem. Soc.* 3437 (1952).

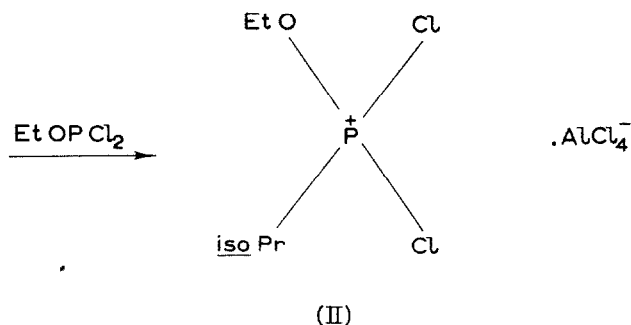
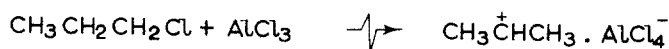
³ F. W. Hoffman, T. C. Simmons and L. J. Glunz III *J. Amer. Chem. Soc.* **79**, 3570 (1957).

(c) It may be correlated with the mechanistic interpretation placed upon the first stage (v) of the Arbusov reaction:



In triphenyl phosphite, the nature of R is such that the first step is undoubtedly bimolecular, since the resonance stabilised phosphonium salt, which is not susceptible to the subsequent elimination (vi) can be isolated in good yield.⁴ There is no real evidence that such a phosphonium salt has more than transitory existence in the reaction involving trialkyl phosphites, but Gerrard and Green⁵ have shown that when triethyl phosphite and optically active (+)-1-phenylethylchloroethane interact, the products include diethyl 1-phenylethylphosphonate possessing a small but definite degree of activity. One may infer that the first step proceeds at least partly by an SN_2 mechanism, which accounts for this product, if predominantly by an SN_1 process. In species in which one or more RO groups are replaced by electron attracting atoms, their nucleophilic power is thereby reduced and the SN_2 character of the primary process is still further suppressed. Thus a dialkyl phosphorochloridite, $(\text{RO})_2\text{PCl}$, will not react with an alkyl halide⁵ unless some agent facilitating preliminary carbon-halogen bond fission in the latter is present, as in the subject reaction. Phosphorus trichloride evidently represents a limiting case in this respect, and it is reasonable to assume that a carbonium cation must be produced before reaction with alkyl halide will take place.

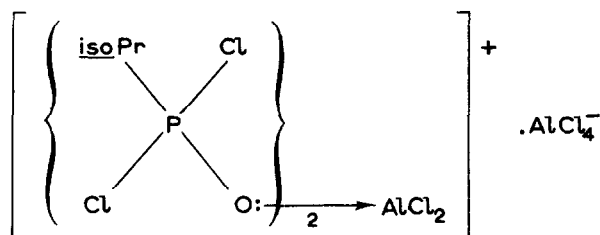
(d) The same mechanism may be invoked to account for the behaviour of an alkyl phosphorodichloridite, ROPCl_2 , in the reaction:



In this case however, it follows that the nature of the complex, (which on hydrolysis gives *isopropylphosphonyl dichloride*), may be different from (I), and better represented:

⁴ A. Michaelis and R. Kähne *Ber.* 31, 1048 (1898).

⁵ W. Gerrard and W. J. Green *J. Chem. Soc.* 2550 (1951).

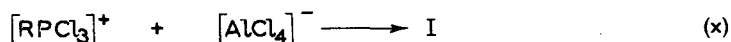
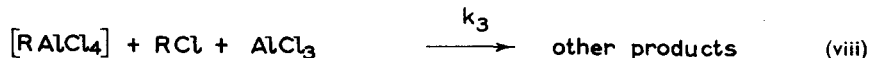


It depends at what stage (II) decomposes to give ethyl chloride, a point yet to be investigated.

(e) It provides a partial explanation of the fact that a diphosphono derivative cannot be obtained from, for instance, chloromethylphosphonyl dichloride, $\text{ClCH}_2\text{PO}\cdot\text{Cl}_2$. Formation of the cation in this case would necessitate like charges on the adjacent carbon and phosphorus atoms, which experience shows to be a very unstable arrangement.⁶ The situation is however, more complex than this as the effect would diminish rapidly down side chains of increasing length, whereas even pentamethylene dibromide gives only 5-bromopentylphosphonyl dichloride.

(f) It explains new observations on the behaviour of trimethylchlorosilane, Me_3SiCl , and chloromethyldimethylchlorosilane, $\text{ClCH}_2\text{Si}(\text{Me})_2\text{Cl}$, in the reaction. The former takes part in the reaction very sluggishly and in its presence (1 mole), aluminium chloride (1 mole) in excess phosphorus trichloride dissolves completely only after six hours heating under reflux. Even after twenty hours, some trimethylchlorosilane can be recovered. Its carbon isologue, *tert.*-butyl chloride, gives an almost quantitative yield of complex in ten minutes. This difference in reactivity may be attributed to the difference in ease of formation between the carbonium and silylium cations in these circumstances, arising from the relative electronegativities of the carbon (2.5), silicon (1.8) chlorine (3.0) and aluminium (1.5) atoms. On the other hand, chloromethyldimethylchlorosilane (1 mole) gives after less than one hour of heating with aluminium chloride (1 mole) and excess trichloride, a complex which on alcoholysis affords a good yield of dialkyl alkoxydimethylsilylmethylphosphonate $(\text{RO})_2\text{PO}\cdot\text{CH}_2\text{Si}(\text{Me})_2\text{OR}$ ⁷ showing that the chlorine atom attached to the carbon atom reacts preferentially.

The carbonium cation mechanism is not put forward without reservation, but formation of the complex may be provisionally considered to take place in the following manner:



where $k_4 \gg k_3 < k_2$.

⁶ A. E. Remick *Electronic Interpretations of Organic Chemistry*. p. 115, Wiley, New York (1949).

⁷ C. W. Jefford Private communication.

Such a scheme provides for the observed effect upon yield of the order in which reactants are mixed, the "other products" in (viii) being the more intricate polynuclear complexes envisaged by Wertyporoch,⁸ and recently substantiated, by Korshak and Lebedev;⁹ complexes which although effective in promoting Friedel-Crafts alkylation are apparently ineffective in the subject reaction. This conclusion is compatible with a current view that Friedel-Crafts alkylation can occur by a dual mechanism, which results in formation of the mixture of *n* and *sec* substitution products obtained from an *n*-alkyl halide.

⁸ E. Wertyporoch *Ber. Dtsch. Chem. Ges.* **64**, 1372 (1931).

⁹ V. V. Korshak and N. N. Lebedev *Zhur. Obs. Khim. SSSR* **18**, 1766 (1948); *Chem. Abstr.* **43**, 2930 (1949).