Structural Effects on the Complexing Ability of Alkyl Diphenylphosphinates with Magnesium Iodide

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THE complexation chemistry of phosphorus esters and oxides is both of theoretical and practical value.[1-4] We have isolated stable complexes of alkyl diphenylphosphinates with magnesium iodide when the alkyl substituent is n-propyl, isopropyl, isobutyl, or neopentyl. These complexes were generated by reaction of anhydrous magnesium iodide with a tenfold excess of phosphinate in anhydrous benzene. Elemental analyses for phosphorus and magnesium content indicated a 3 : 1 ratio of phosphinate to magnesium iodide, respectively. The i.r. spectrum of the complex is very similar to the uncomplexed phosphinate with the exception that the phosphoryl band is somewhat broadened and shifted to lower frequency. The Table summarizes the data on the complexes.

In the case of methyl diphenylphosphinate (I), the complex could not be obtained free from the magnesium salt of diphenylphosphinic acid, $[Ph_2P(O)O]_2Mg$. When anhydrous magnesium iodide and (I) were allowed to react for 12 hr. in benzene at room temperature, the pure magnesium salt of the phosphinic acid was obtained. Analysis by n.m.r. of the benzene solution showed the presence of methyl iodide. The action of magnesium iodide on t-butyl diphenylphosphinate, under the same conditions, also resulted in the formation of the magnesium salt of diphenylphosphinic acid. The presence of isobutene and t-butyl iodide in the filtrate was also indicated by n.m.r. analyses.

Pyrolytic decomposition, at 5° above the melting point, of the complexes (II—V) gave the

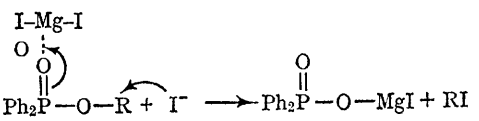
TABLE

Data on the complexes of $Ph_2P(O)OR$

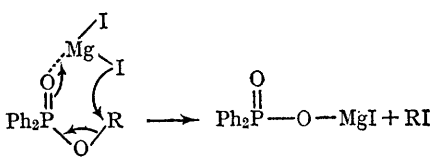
R		M.p. °c	Infrared Data: Free P=O[a]	Complexed P=O	Δν,
			cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
Me	(I)	.....	1225	1200	−25
Pr^n	(II)	110—112	1222	1208	−14
Pr^i	(III)	115—117	1221	1213	−8
Bu^i	(IV)	125—128	1221	1210	−11
Neopentyl	(V)	137—141	1227	1219	−8

[a] I.r. absorption frequencies were measured on KBr pellet using a Beckman IR-7. Nujol mulls of the complexes revealed P=O absorption at the same positions as observed with KBr discs of the complexes.

corresponding alkyl iodides in 80—85% yield. In all these pyrolytic decompositions, no isomeric alkyl iodides were detected. It does seem feasible that the formation of the alkyl halides proceeds by nucleophilic attack by the iodide moiety on carbon.[5] This can conceivably follow an ordinary S_N2 (a) or type of S_Ni (b) mechanism. However, because of the expected difficulty in a back-side attack on sterically hindered groups like neopentyl, we favour reaction pathway (b).

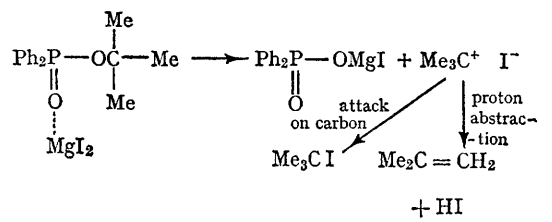


(a)



(b)

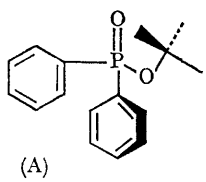
The formation of isobutene and t-butyl iodide, in the attempted complexation of t-butyl phosphinate with magnesium iodide at room temperature, could be envisaged as following the following steps:



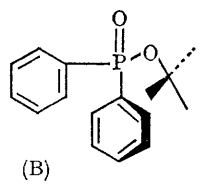
It is conceivable that the stability of the tertiary carbonium ion and the relief of *B*-strain in the molecule provides the driving force of the reaction.

The inherent steric interactions in the complexes is reflected in the magnitude of the phosphoryl shifts (Δν) compared to the uncomplexed ester. The decrease in the magnitude of the i.r. shifts of the complexes, as more bulky groups are introduced, could be interpreted to mean a parallel decrease in the complexing ability. On the basis of pure inductive effect, one might expect the reverse order for complexation. The observed results seem to indicate partial screening of the phosphoryl group by the alkyl substituents. Comparison of the shifts for the complexes of (II—V) suggests that methyl groups on the α-carbon are much more effective in screening the phosphoryl group than methyl substituents on the β-carbon. It is also somewhat surprising to find a considerable difference in the phosphoryl shifts for (I) and (II).

Siddall and Prohaska[6] have postulated the existence of rotamers in several phosphorus esters. Of the two energetically possible conformations (structures A and B), structure (A) is favoured over that of (B) as there is considerable interaction between the phenyl and alkyl groups in (B). In structure (A) the phosphoryl group is



(A)



(B)

partially screened by the alkyl group and the approach by a reactant is made difficult. In any event as R increases in size, ease of complex formation should decrease. Although the n.m.r. data for the esters do not infer a high population of a preferred conformation (by virtue of non-equivalence of protons in the alcohol portion), the

complex (ester–magnesium iodide) may indeed assume a rigid geometrical configuration in the solid state. Thus, free rotation around C_α–C_β bonds [P–O–C_α–C_β] in solution may result in a weaker Mg–O bond and decomposition of most of the complexes is not easy at room temperature. However, although the small methyl group in (I) probably is the least restricted in regard to rotation, the unhindered carbon atom of the methyl group is more accessible to attack so rapid formation of methyl iodide results at room temperature. In the t-butyl diphenylphosphinate, partial ionization of the O–C bond could yield the t-butyl cation which could form isobutene and/or t-butyl iodide which were both identified by n.m.r.

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