Reaction of Alkyl Benzoates with Diphenylphosphinous Chloride

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Summary The dealkylation of alkyl benzoates by diphenylphosphinous chloride results in the formation of varying yields of benzoyl chloride, alkyl diphenylphosphine oxides, and alkyl halides.

IN the recent interest in the organic chemistry of phosphorus, little attention has been paid to the reactions of carboxylic esters with tervalent phosphorus compounds.[1,2] We report that alkyl benzoates are dealkylated by heating with diphenylphosphinous chloride (I). Since one of the reaction products is benzoyl chloride, these dealkylations represent an unusual one-step conversion of an ester to an acid halide.

When benzyl benzoate and diphenylphosphinous chloride (I) were heated at 160° in a sealed tube, the formation of benzyl diphenyl phosphine oxide (II; $R = CH_2Ph$)(80%) and of benzyl chloride (20%) was observed by n.m.r. Similar treatment of methyl benzoate with diphenylphosphinous chloride (I) gave methyl diphenyl phosphine oxide (II; $R = CH_3$) (40%) and methyl chloride (60%). In each of these reactions, benzoyl chloride was identified as part of the product, and the phosphine oxides purified by chromatography and recrystallization.

Since the yields of benzoyl chloride (*ca* 75 and 40%) were of the same order as those of the benzyl and methyl diphenyl phosphine oxides, respectively, we believe that the benzoyl chloride and the appropriate phosphine oxide are formed in the same sequence of reactions. The variation in yield of the phosphine oxides seems to be best explained by a reaction sequence initiated by attack of the tervalent phosphorus on the alkyl carbon of the ester, followed by steps analogous to those believed to occur in the Arbusov and related reactions.[3] (Scheme 1.)

$$\mathrm{PhCO_2R + Ph_2PCl\ (I) \longrightarrow PhCO_2^- + R\overset{+}{P}Ph_2Cl}$$
$$\longrightarrow \mathrm{PhCO_2\overset{+}{P}Ph_2R + Cl^-}$$
$$\longrightarrow \mathrm{PhCOCl + Ph_2P(O)R\ (II)}$$

SCHEME 1

The formation of alkyl halide is clearly the result of a different reaction sequence, which may be initiated by attack of the tervalent phosphorus at the carbonyl carbon of the ester. (Scheme 2.)

$$\mathrm{PhCO_2R + Ph_2PCl \longrightarrow PhCO\overset{+}{P}Ph_2Cl + OR^-}$$
$$\longrightarrow \mathrm{PhCOPPh_2OR + Cl^-}$$
$$\longrightarrow \mathrm{PhCOP(O)Ph_2 + RCl}$$

SCHEME 2

All attempts to isolate benzoyl diphenyl phosphine oxide were unsuccessful. This is not surprising in view of the failure of attempts, both in our laboratory and elsewhere,[4] to synthesise it by standard, mild methods.

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[1] A. J. Kirby and S. G. Warren "Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967.

[2] R. F. Hudson "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, 1963.

[3] G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, 1964, **18**, 38.

[4] K. Issleib and E. Priebe, *Chem. Ber.*, 1959, **92**, 3183.