Direct Cleavage of Esters to Acid Halides

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Summary Esters and lactones can be directly cleaved to acid halides with Ph_3PCl_2, Ph_3PBr_2 and $Ph_3{}^+PCl(BF_3Cl)^-$.

Although dihalogenophosphoranes have been utilized for the cleavage of the carbon-oxygen bond,[1] direct conversion of an ester or lactone to an acid halide has not been reported.

We report that the compounds Ph_3PCl_2 (I), Ph_3PBr_2 (II) and Ph $^+PCl[BF_3Cl]^-$ (III)† readily effect this type of conversion. The choice of reagent is dictated by the type of

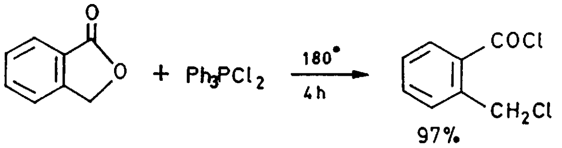
$$RCO_2R' + Ph_3PX_2 \longrightarrow RCOX + R'X + Ph_3PO \qquad (1)$$

substitution in the acyl portion of the ester. Halogenation in the acyl portion facilitates cleavage with (I) and (II), and halogenated esters (R = CF_3, CCl_3, CH_2Cl, $CHCl_2$) are readily cleaved in refluxing acetonitrile by these reagents. Reagent (III) is relatively ineffective for the cleavage of halogenated esters.

$$(E)\ PhCH{=}CHCO_2Et + Ph_3PCl_2 \xrightarrow[8\ h]{150^\circ} (E)\ PhCH{=}CHCOCl\ (69\%) \qquad (2)$$

$$(E)\ PhCH{=}CHCO_2Et + (III) \xrightarrow[1{\cdot}5\ h]{150^\circ} (E)\ PhCH{=}CHCOCl\ (92\%) \qquad (3)$$

In contrast to the behaviour of halogenated esters, nonhalogenated esters, (R = alkyl or aryl) are cleaved by (I) and (II) only at high temperatures (150—180°) and long reaction times, reaction (2); whereas, reagent (III) readily cleaves nonhalogenated esters, reaction (3). In addition, (III) does not consume the acid halide formed, whereas (I) and (II) appear in some cases to react with the acid halide product.



(4)

Similarly, lactones can be readily cleaved to dihalides [reaction (4)]. These reagents provide a convenient method for the regeneration of an active acid derivative when an ester function has been employed as a protecting group.

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† (III) can be conveniently prepared from Ph_3PCl_2 and BF_3.

[1] For example, G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, 1964, **86**, 964; D. Levy and R. Stevenson, *J. Org. Chem.*, 1965, **30**, 3469; *ibid.*, 1967, **32**, 1265; J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, 1965, **30**, 2639; D. Brett, I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. and Ind.*, 1969, 1017; H. J. Bestmann and L. Mott, *Annalen*, 1966, **693**, 132; *cf.* also S. Trippett in Organophosphorus Chemistry, Vol. 1, The Chemical Society, 1970, p. 60; A. G. Anderson, Jr. and F. J. Freenor, *J. Org. Chem.*, 1972, **37**, 627.