Phosphoryl Transfer using *gem*-Dihalides

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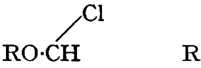
PHOSPHORYL transfer promoted by nitriles in the presence of highly reactive halides was recently reported.[1] We now record that suitably reactive *gem*-dihalides (I) are capable of promoting phosphoryl transfer, even in the absence of a nitrile.

Gross and co-workers observed[2] the formation of an unstable orthoformyl chloride (II) on treatment of an αα-dichloro-ether with a carboxylic acid; (II) decomposed to an acyl chloride and a formate ester. Using these reagents, peptides have been synthesised.[3,4]

$RR'CCl_2$
(I)



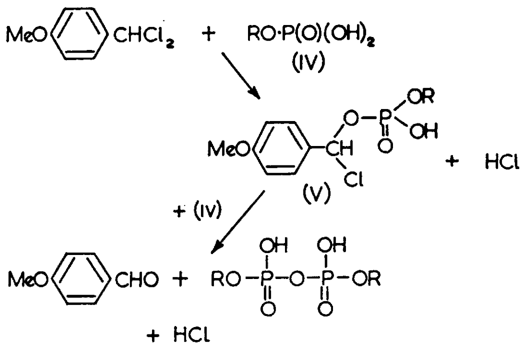
$$RO\cdot CH\begin{cases} Cl \\ O\cdot CO\cdot R' \end{cases}$$

(II)

$RO\cdot CH(O\cdot CO\cdot R')_2$
(III)

With a salt of the carboxylic acid, a stable diacyloxy-ether (III) was isolated. Pyrolysis then yielded the corresponding symmetrical anhydride.[5]

Hine and Rosscup[6] showed that α-chloro-substitution markedly increased the reactivity of benzyl chlorides, and, in our hands, treatment of *p*-methoxybenzal chloride (I; R=H, R'=*p*-$MeOC_6H_4$) with an excess of a monoester of phosphoric acid (IV; R=Ph, or *p*-$Cl\cdot C_6H_4$) in benzene under reflux gave the symmetrical diester of pyrophosphoric acid in quantitative yield. Though copious fumes of hydrogen chloride were evolved, anisaldehyde was the only other product. An equally effective reaction was observed with *o*-methoxybenzal chloride. Under comparable conditions, the parent chloride (I; R=H, R'=Ph) gave a yield of only 5%. The system can be used to phosphorylate alcohols. Thus, phenylphosphoric acid, and *o*-methoxybenzal chloride were used to acylate *p*-nitrobenzyl alcohol, the product, *p*-nitrobenzylphenylphosphoric acid, being isolable in 70% yield.



The reaction presumably occurs through the formation of (V): phosphoryl transfer may then occur by direct attack on (V), or by prior formation of a phosphorochloridate.

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[4] K. Poduška and H. Gross, *Chem. Ber.*, 1961, **94**, 527.
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