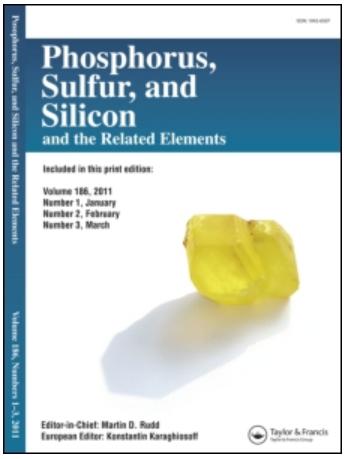

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THE REACTION OF PHOSPHITES WITH AROYLPHOSPHONATES IN THE PRESENCE OF PROTON DONORS-REVERSE NUCLEOPHILIC ADDITION TO CARBONYL GROUPS

D. V. Griffiths[a]; H. A. R. Jamali[a]; J. C. Tebby[b]
[a] Department of Chemistry, University of Keele, Staffordshire, England [b] Department of Chemistry and Biology, North Staffordshire Polytechnic, Staffordshire, England

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THE REACTION OF PHOSPHITES WITH AROYLPHOSPHONATES IN THE PRESENCE OF PROTON DONORS–REVERSE NUCLEOPHILIC ADDITION TO CARBONYL GROUPS

D. V. GRIFFITHS* and H. A. R. JAMALI

Department of Chemistry, University of Keele, Staffordshire ST5 5BG, England

J. C. TEBBY

Department of Chemistry and Biology, North Staffordshire Polytechnic, Stoke-on-Trent, Staffordshire ST4 2DE, England

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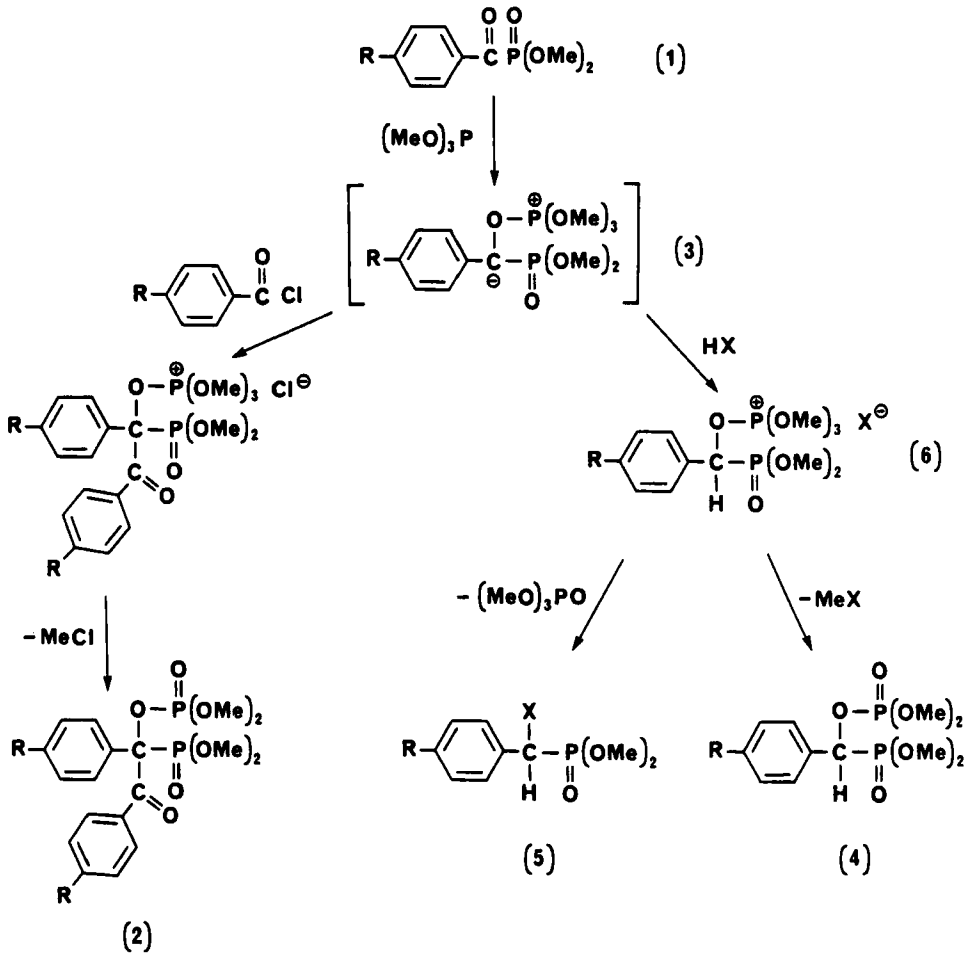
Trimethyl phosphite attacks the carbonyl oxygen of aromatic α-ketophosphonates in the presence of proton donors such as carboxylic acids. The intermediate quasi-phosphonium salts (**6**) either demethylate to a diphosphorus compound (**4**) in the normal Arbusov manner or dealkylate to give a phosphonate (**5**) and trimethyl phosphate.

Dimethyl aroylphosphonates (**1**) are readily prepared by the reaction of trimethyl phosphite with aroyl chlorides. However, we have previously reported[1] that this approach cannot be used for the formation of the aroylphosphonate (**1**; R = NO_2). In the reaction of trimethyl phosphite with 4-nitrobenzoyl chloride the aroylphosphonate initially formed reacted further to give the diphosphorus compound (**2**; R = NO_2). This unexpected reaction appears to proceed via the anionic intermediate (**3**; R = NO_2) which is formed by reaction of the initially formed aroylphosphonate (**1**; R = NO_2) with a molecule of trimethyl phosphite. This anionic intermediate then attacks the electrophilic 4-nitrobenzoyl chloride to give the diphosphorus compound (**2**; R = NO_2) (see Scheme 1).

This unusual reactivity of the carbonyl group of the α-ketophosphonate (**1**, R = NO_2) towards phosphite can be explained in terms of enhanced stability of the anionic intermediate (**3**; R = NO_2) as a result of the nitro substituent. However, it has been suggested that the reaction of diethyl 2-methoxybenzoylphosphonate with triethyl phosphite to give diethyl 2,3-dihydro-3-phosphonobenzofuran also proceeds via an anionic intermediate.[2] Clearly, in this latter case, we would expect the methoxy substituent to destabilise rather than stabilise the proposed anionic intermediate.

The reluctance of other aroyl chlorides to react with phosphite in a manner analogous to 4-nitrobenzoyl chloride may therefore depend not only on the stability of the anionic intermediate (**3**) but also on the electrophilicity of the acid chloride in its reaction with the anionic intermediate. If this is the case phosphites should react

*Author to whom all correspondence should be addressed.



SCHEME 1

with a wide range of aroylphosphonates providing that a good electrophile is present to trap the anionic intermediates as they form.

We have now confirmed that a range of aroylphosphonates react rapidly with trialkyl phosphites in the presence of proton donors such as carboxylic acids and alcohols. For the aroylphosphonates (**1**; R = H, Cl, Me), and with benzoic acid as the proton donor, the reaction with trimethyl phosphite proceeded rapidly in the manner previously reported for dimethyl 4-nitrobenzoylphosphonate[1] to give the diphosphorus compounds (**4**; R = H, Cl, Me). However, with (**1**; R = MeO) under similar conditions the reaction was very much slower and the product was not the diphosphorus compound (**4**; R = OMe) but the phosphonate (**5**; R = OMe, X = $PhCO_2$) and trimethyl phosphate.

Although at first sight this appears to be a quite different reaction route it can be seen (Scheme 1) that the routes differ merely in the mode of dealkylation of the intermediate (**6**). The reason for dealkylation of (**6**; R = OMe) by attack on

the carbon adjacent to the benzene ring rather than the methoxy groups on the quasi-phosphonium salt is not readily apparent. Clearly, the ease of dealkylation of the intermediate (**6**; R = OMe) by attack of the benzoate anion on the methoxy groups at the quasi-phosphonium centre should not be significantly slower than in the other systems studied. The much reduced rate of reaction of the aroylphosphonate (**1**; R = OMe) with phosphite in the presence of benzoic acid relative to the aroylphosphonates (**1**; R = H, Cl, Me, NO_2) therefore probably reflects the low concentration of the intermediate (**6**; R = OMe) in solution at any given time. The preference for attack on the carbon adjacent to the benzene ring in the intermediate (**6**; R = OMe) rather than attack on the methoxy groups as in the intermediates (**6**; R = H, Cl, Me, NO_2) is less easy to explain. We have established that the nature of the nucleophile is important since the reaction of (**1**; R = OMe) with trimethyl phosphite in the presence of methanol proceeds more rapidly than with benzoic acid to give the diphosphorus compound (**4**; R = OMe) rather than the phosphonate (**5**; R = X = OMe).

Further work is in progress to clarify the mechanism of dealkylation and the factors which determine the preferred site of attack.

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