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

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

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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 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. 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

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$$R - \bigvee_{C} P(OMe)_{2} \qquad (1)$$

$$(MeO)_{3}P \downarrow$$

$$Q - P(OMe)_{3} \qquad (3)$$

$$R - \bigvee_{C} CCI$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (3)$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (6)$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (7)$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (8)$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (9)$$

$$R - \bigvee_{C} P(OMe)_{2} \qquad (1)$$

$$R - \bigvee_{C} P(OMe)_{$$

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-nitrobenzoylphosphonate¹ 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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