THE REACTION OF TRIVALENT PHOSPHORUS COMPOUNDS WITH HALOGENATED PYRROLE- AND FURAN-2,5-DIONES

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We have previously reported that 3-halogenated pyrrole-2,5-diones 1 (Z = NR₃) react with trialkyl phosphites, dialkyl phosphonites and alkyl phosphinites to give the corresponding ylides 2 and hence the bisphosphoryl systems 3. Similarly, the dihalogenated heterocycles 4 (Z = NR₃) give rise to the ylides 5 and hence the trisphosphoryl systems 6. We have also shown that analogous reactions occur with the corresponding furan systems 1 and 4 (Z = O).

Since the mechanism we proposed to explain the formation of 2 involves an initial attack at C-4, as in Scheme 1, leading to carbene formation 7, we were interested to investigate whether the presence of a suitable substituent (-----) at this position would also result in some intramolecular cyclisation 8 or whether its presence would inhibit attack at the C-4 site leading to alternative products.

For Ph₂POMe and the case of 9, where the 4-substitutent was methyl, the mode of attack was not affected and the product proceeded cleanly to give the crystalline ylide 10. However, in the corresponding reaction when the 4-substituent was benzyl and the halogen was Cl, as in 11, the reaction was much slower and the outcome was temperature dependent. Interestingly, at 150 °C the major products were the three phosphoryl compounds 13 – 15 [R₁=R²=Ph, R³=Me]. The formation of these components, whose structures were established by X-ray crystallography, can be explained by proposing that they are derived from the initially formed ylide 12 [R₁=R²=Ph, R³=Me], which can be rationalised as involving an initial attack at C-3 rather than C-4. It is also interesting to note that while the phosphoryl compound 13 [R₁=R²=Ph, R³=Me] was observed solely as its Z isomer, only the E isomer of the thermal rearrangement product 14 [R₁=R²=Ph, R³=Me] was observed. Such observations will be discussed.