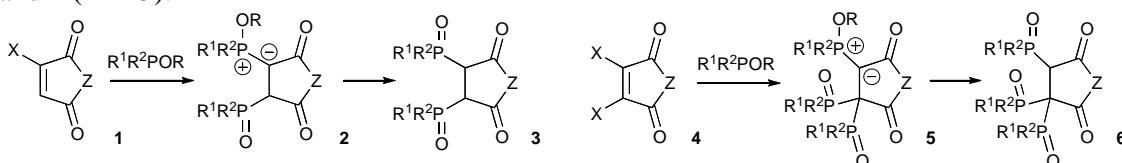


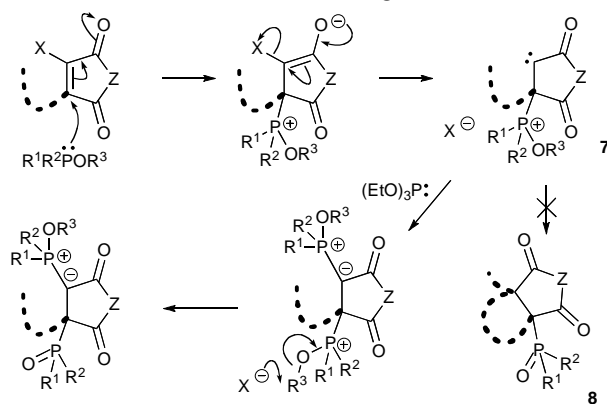
THE REACTION OF TRIVALENT PHOSPHORUS COMPOUNDS WITH HALOGENATED PYRROLE- AND FURAN-2,5-DIONES

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We have previously reported that 3-halogenated pyrrole-2,5-diones **1** ($Z = \text{NR}^3$) 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** ($Z = \text{NR}^3$) give rise to the ylides **5** and hence the trisphosphoryl systems **6**.^[1] We have also shown that analogous reactions occur with the corresponding furan systems **1** and **4** ($Z = \text{O}$).



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

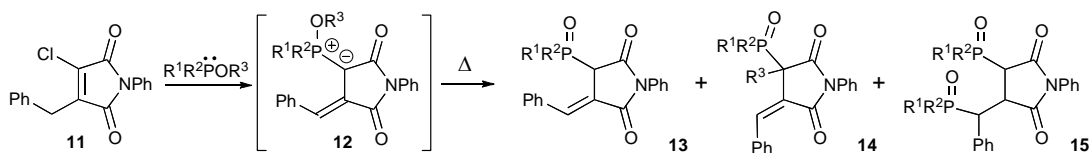
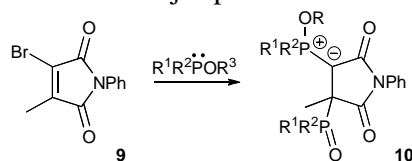


Scheme 1

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 Ph_2POMe and the case of **9**, where the 4-substituent 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** [$\text{R}^1=\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$]. 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** [$\text{R}^1=\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$], 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** [$\text{R}^1=\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$] was observed solely as its *Z* isomer, only the *E* isomer of the thermal rearrangement product **14** [$\text{R}^1=\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$] was observed. Such observations will be discussed.



[1] Y-K. Cheong, P. Duncanson and D. V. Griffiths, ICPC2007, Xiamen, China.