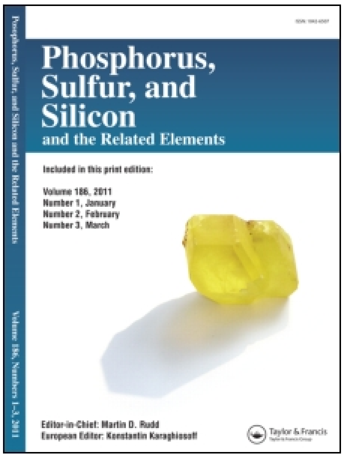

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Pyrolysis of Cyclic Polyoxo Phosphorus Ylides

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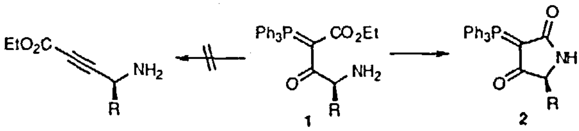
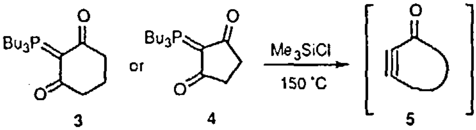
In an extension of our recent work on generating acetylenic amino acid derivatives by flash vacuum pyrolysis (FVP) of appropriate stabilised phosphorus ylides,[1] we examined the ylides **1** with a free amino group. Rather than the expected acetylenic product these gave the novel cyclic ylides **2** with loss of ethanol. Preliminary attempts to bring about extrusion of Ph_3PO from these gave rather confusing results so we have examined simpler cyclic ylides in an attempt to understand the processes involved.

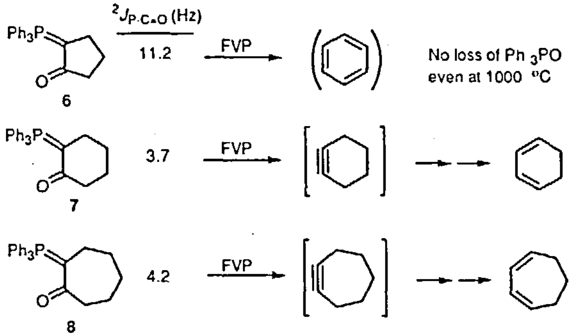


There has been little previous work on pyrolysis of cyclic β-oxo ylides but the possibility of generating cycloalkynes makes this an interesting area for study. A brief communication in 1988 reported that heating tributylphosphonium ylides such as **3** and **4** with Me_3SiCl in toluene at 150 °C led to generation of the cycloalkynones **5** which could be trapped by Diels Alder reaction with an added diene, but no mechanism for the elimination was proposed.[2]

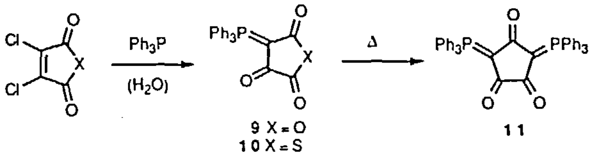


In previous work in our laboratory the series of cyclic ylides **6**–**8**[3] were subjected to FVP. As shown, the 6- and 7-membered ring compounds did undergo clean loss of Ph_3PO to give the cycloalkynes which isomerised to the corresponding 1,3-dienes.[4]

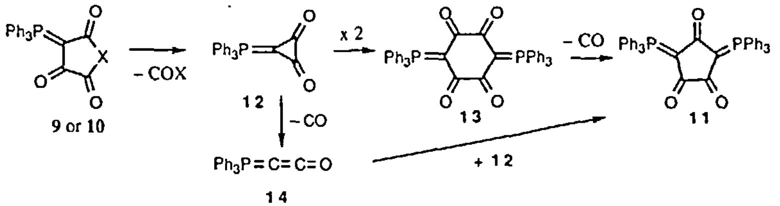
However the 5-membered ring compound 6 was completely resistant to extrusion even under the severest conditions. This is explained by the high value of $^2J_{P\text{-}CO}$ which indicates a negligible contribution from the phosphonium enolate tautomer necessary for the extrusion mechanism. Extensive studies on a wide variety of β-oxo ylides have shown that there is a good correlation between the value of this coupling constant and the pyrolytic behaviour of the ylides: Ylides with J < 10 Hz readily undergo thermal elimination of Ph_3PO, while those with J > 10 Hz do not. Bearing this factor in mind we would expect the heterocyclic ylides 9 and 10 to undergo thermal elimination of Ph_3PO since the values of $^2J_{P\text{-}CO}$ are < 10 Hz. We report here the pyrolytic behaviour of these two compounds which takes a most unexpected course.

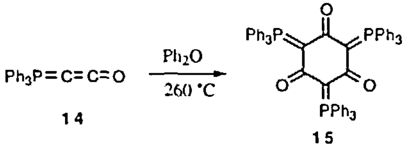


Reaction of dichloromaleic anhydride with triphenylphosphine in the presence of water[5] gave 9 while 10 was obtained by the corresponding reaction of dichlorothiomaleic anhydride.[6] Initial studies using FVP gave disappointing results but in one case a small amount of product from 9 was recovered from the inlet tube which proved to be the cyclic bis ylide **11**. Once it was clear that an intermolecular reaction was involved, much better results were obtained by heating 9 or 10 either neat at 150 °C or in boiling diphenyl ether at 260 °C. In this way **11** was obtained in up to 30% yield and had identical properties to those described in the literature for this compound.[7]

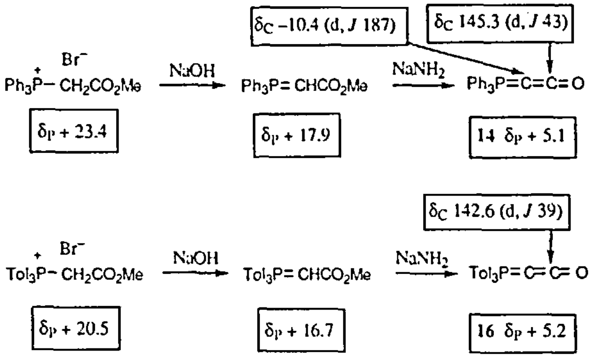


The mechanism of this process is of great interest and several possibilities can be identified. It seems clear that the first step is extrusion of CO_2 or COS to give an intermediate which can be formulated as **12**. This may then dimerise to give **13** which loses CO. An alternative is for **12** to lose CO giving the well known ketene ylide **14** and for this then to interact with **12** to afford **11** directly. Evidence in favour of the latter mechanism was obtained by heating **9** with **14** which gave **11** and no new product, implying that the **14** had been used up by reaction with **12**. Interestingly a control experiment of heating **14** alone in diphenyl ether led directly to the cyclic trimer **15**

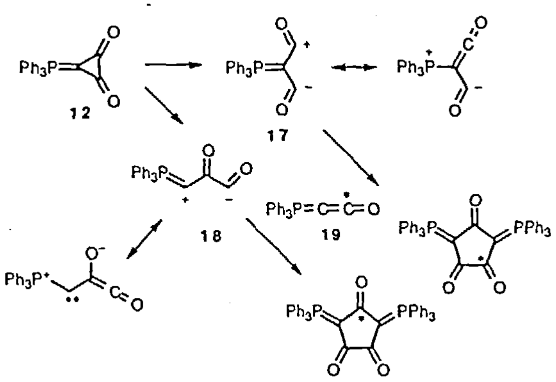




identical with an authentic sample and this is a much easier route to it than the published method.[7] In an attempt to further demonstrate the involvement of **14** in the formation of **11**, the tri-p-tolyl analogue **16** was prepared by the route shown below. The closely corresponding spectroscopic data for the two series leave little doubt that the new ketene ylide **16** has been formed but unfortunately it proved to be much more oxygen sensitive than **14** and all attempts at heating it with **9** in diphenyl ether with exclusion of air simply led to its conversion into tri-p-tolylphosphine oxide.



The interaction of **12** with **14** to give **11** clearly involves ring-opening of **12** and a number of intermediate forms can be envisaged. Either the ylide – CO bond or the CO – CO bond may break and the intermediate may be diradical or dipolar in nature. We favour a dipolar intermediate and, as shown, either **17** or **18** can be stabilised to some extent by delocalisation. Which one is involved should be easily determined by a ^{13}C labelling study and this is currently in progress using the CO labelled ketene ylide **19** prepared in a number of steps from ^{13}C enriched bromoacetic acid.



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