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STEREOELECTRONIC SUPPRESSION OF AN ARBUSOV-TYPE REACTION

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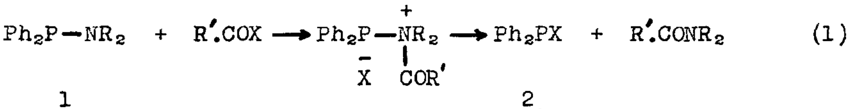
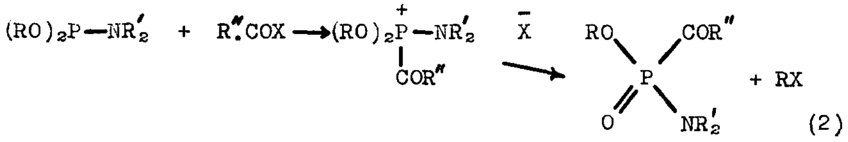
We have recently shown[1] that 5-membered cyclic phosphites exhibit greatly reduced nucleophilic reactivity compared with their acyclic analogues. We attributed this effect to increased ring strain in the former following quaternisation at phosphorus. In the present communication we wish to report that this ring-strain can suppress the normally exothermic Arbusov-type reaction of phosphoramidites.

We have shown[2,3] that whereas phosphinous amides **1** reacted with acid halides to give phosphinous halides **2** and amides (eq.1) phosphoramidites **3** reacted differently,[4] by way of an Arbusov reaction without P-N bond cleavage to give **4**.



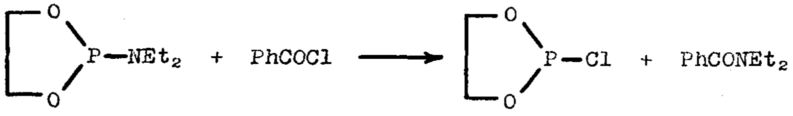
$$Ph_2P{-}NR_2 + R'.COX \longrightarrow \underset{\bar{X}}{Ph_2P}{-}\underset{COR'}{\overset{+}{N}}R_2 \longrightarrow Ph_2PX + R'.CONR_2 \qquad (1)$$

1 **2**



3 **4**

However, when the alkoxy substituents of **3** were incorporated into a 5-membered ring, as in 2-diethylamino-1,3,2-dioxaphospholane **5**, the Arbusov reaction (eq. 2) was suppressed and acylation at nitrogen occurred with formation of 2-chloro-1,3,2-dioxaphospholane **6**.



5 **6**

Thus when **5** in benzene was treated with one equivalent of benzoyl chloride at 20° **6** was formed in *ca*. 95% yield, together with *ca*. 5% of the Arbusov product. On the other hand, under the same conditions **3** (R = R' = Et) reacted with benzoyl chloride to give **4** (R = R' = Et, R" = Ph) as the only detectable phosphorus-containing product.† Assuming that no more than 2-3% of $(EtO)_2PCl$ could remain undetected by the analytical method used (^{31}P NMR), and that the rates of acylation at nitrogen in **3** and **5** would be comparable,‡ we can calculate that the Arbusov reaction of **3** with benzoyl chloride proceeds some 10^3 times faster than that of **5**. This rate ratio compares well with the value of 200 obtained for the reaction of phosphites with benzoyl chloride in acetonitrile.[1]

When the experiment with **5** was repeated at higher temperatures, the product contained up to 50% of the Arbusov product. This indicates that differences in activation energy are at least partly responsible for the difference in reactivity between the cyclic and acyclic phosphoramidites. This important point is now being studied in our laboratory as part of our general program in this area.

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† Satisfactory analytical and spectroscopic data have been obtained for all compounds cited.

‡ Experiments in this Laboratory indicate that this is the case (C. Brown and A. R. Thompson, unpublished work).

References

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3. C. Brown, M. Murray and R. Schmutzler, *J.Chem.Soc.(C)*, 1970, 878.
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