

## Cyclic Carboxylic Monophosphides: A New Class of Phosphorus Heterocycle

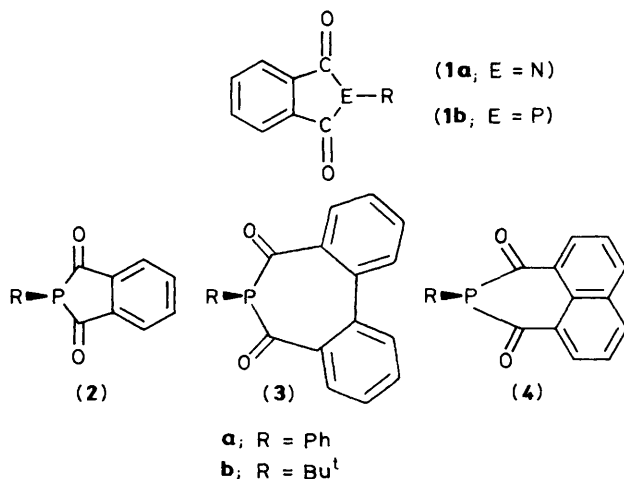
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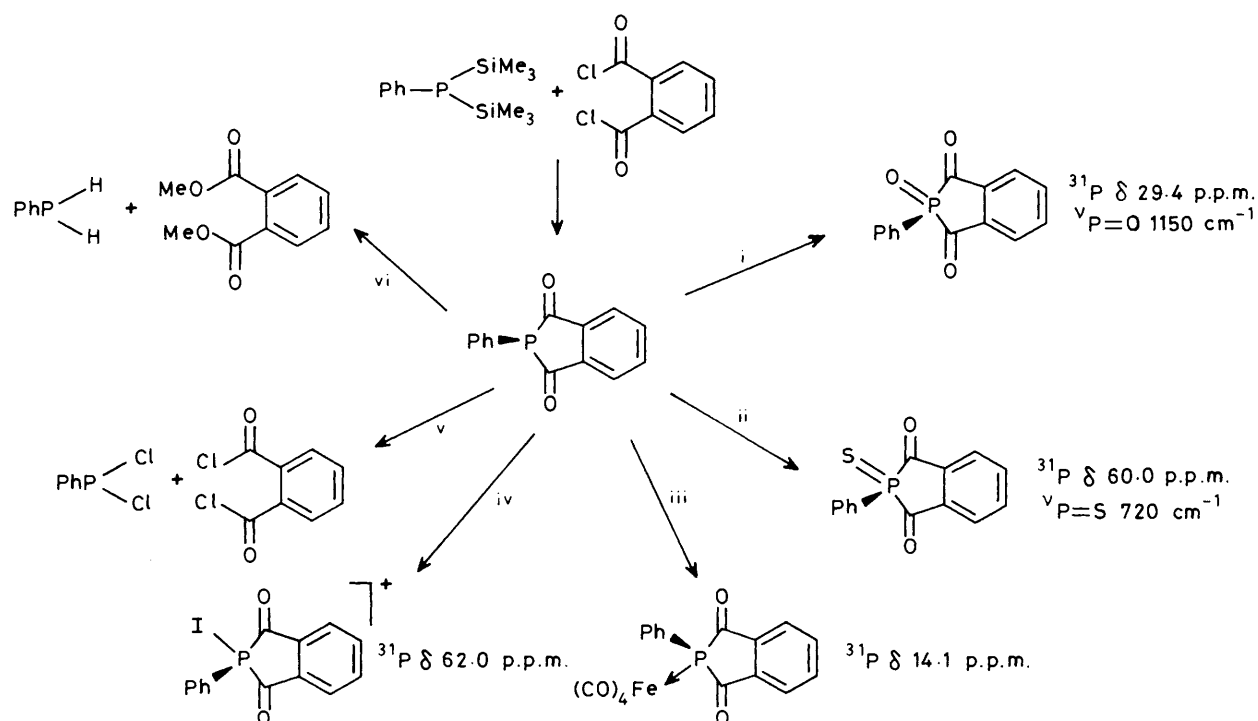
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Bis(trimethylsilyl)phosphines,  $RP(SiMe_3)_2$  ( $R = Ph, Bu^t$ ), react with di-acid chlorides or the corresponding acid anhydrides to afford cyclic carboxylic monophosphides featuring five-, six- or seven-membered phosphorus-containing rings; the reaction chemistry of the five-membered ring is discussed.

Cyclic carboxylic monoimides such as (**1a**) find extensive use as polymer precursors, fungicides, herbicides, and pharmaceuticals.<sup>1</sup> Interestingly, the corresponding phosphorus heterocycles, *e.g.* (**1b**), are unknown.

Our initial attempts to prepare cyclic carboxylic monophosphides were based on the method used for the synthesis of the analogous nitrogen compounds,<sup>1</sup> *viz* the reaction of a primary phosphine with the appropriate carboxylic acid or acid halide. However, this approach was unsuccessful on account of low reactivity. Attention was therefore turned to the somewhat more reactive bis(trimethylsilyl)phosphines,  $RP(SiMe_3)_2$ . Thus the reaction of  $RP(SiMe_3)_2$  ( $R = Ph, Bu^t$ ) with phthaloyl and diphenic chlorides in  $Et_2O$  at  $-78^\circ C$  affords heterocycles (**2**) and (**3**) respectively, in virtually quantitative yield. Compound (**4**) was prepared in *ca.* 50% yield by refluxing an equimolar mixture of  $RP(SiMe_3)_2$  ( $R = Ph, Bu^t$ ) and naphthalic anhydride in 1,2-dimethoxyethane. Compounds (**2**)—(**4**) are yellow solids which are soluble in,





**Scheme 1.** Conditions and reagents: i,  $\text{H}_2\text{O}_2$ , MeCN; ii,  $\text{S}_8$ , pyridine, toluene reflux; iii,  $\text{Fe}_2(\text{CO})_9$ , hexane; iv,  $\text{I}_2$ ,  $\text{Et}_2\text{O}$ ; v,  $\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ ; vi, MeOH, reflux.

**Table 1.**  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. data for compounds (2)–(4).<sup>b</sup>

Compound	$^{31}\text{P}$	$^{13}\text{C}$	$^1J_{\text{PC}}$
(2a)	-28.0	211.2	28.1
(2b)	-2.6	214.2	32.4
(3a)	10.24	212.0	36.9
(3b)	44.31	214.9	36.2
(4a)	51.15	211.8	35.1
(4b)	73.35	215.5	40.0

<sup>a</sup>  $\alpha$ -C of heterocyclic ring. <sup>b</sup> N.m.r. spectra were recorded at ambient temperature on Varian FT80 ( $^{31}\text{P}$ , 32.2 MHz) or GE 300 ( $^{13}\text{C}$ , 75.4 MHz) spectrometers,  $\delta$  in p.p.m. relative to 85%  $\text{H}_3\text{PO}_4$  external ( $^{31}\text{P}$ ) and  $\text{SiMe}_4$  ( $^{13}\text{C}$ ),  $J$  in Hz.

and can be recrystallised from, common organic solvents.† Unfortunately, it was not possible to produce crystals of (2)–(4) suitable for X-ray diffraction. However, the structure assignments shown are consistent with mass spectroscopic, n.m.r. ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ), and i.r. data. All six compounds exhibit a parent peak in the (70 eV) electron-impact mass spectra. Moreover, in each case fragmentation peaks are detected corresponding to  $[\text{M} - \text{CO}]^+$ ,  $[\text{M} - 2\text{CO}]^+$ , and  $[\text{M} - 2\text{CO} - \text{RP}]^+$ . The bonding of the acyl carbon to phosphorus is established by the existence of a low-field doublet in the  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. spectra. These and  $^{31}\text{P}\{^1\text{H}\}$

n.m.r. spectral data are summarised in Table 1. Compounds (2)–(4) exhibit two  $\nu_{\text{CO}}$  frequencies ( $1700 \pm 5$ ,  $1770 \pm 5 \text{ cm}^{-1}$ ).

*Ab initio* calculations (3–21  $\text{G}^*$ ) have been performed on the model systems  $\text{HEC}(\text{O})\text{CH}=\text{CHC}(\text{O})$  ( $\text{E} = \text{N}, \text{P}$ ).<sup>2</sup> The minimum energy structure for  $\text{E} = \text{N}$  possesses a planar nitrogen geometry as has been observed for succinimide.<sup>3</sup> In contrast, a pyramidal heteroatom geometry is computed for the analogous phosphorus compound. The implied reactivity of the phosphorus lone pair in (2)–(4) is confirmed by a preliminary reactivity study of (2a) (Scheme 1, reactions i–iv). Some electrophiles, however, cause ring cleavage (Scheme 1, reactions v–vi).

Finally we note that our synthetic procedure is unsuccessful when saturated organic halides such as  $\alpha, \alpha'$ -dichloro-*o*-xylene are employed. Possibly this implies the necessity for prior co-ordination of the bis(trimethylsilyl)phosphine followed by  $\text{Me}_3\text{SiCl}$  elimination. Significantly, when the phosphorus lone pair is involved in dative bonding, as in  $(\text{CO})_4\text{FeP}(\text{Bu}^t)(\text{SiMe}_3)_2$ , no reaction with phthaloyl chloride takes place.

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## References

- M. K. Hargreaves, J. G. Pritchard, and H. R. Dave, *Chem. Rev.*, 1970, **70**, 439.
- K. E. Dobbs, personal communication.
- R. Mason, *Acta Crystallogr.*, 1961, **14**, 720.

† Satisfactory elemental analyses have been obtained for (2)–(4).