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THE SYNTHESIS OF CARBON-PHOSPHORUS HETEROCYCLES WITH MEDIUM-SIZE RINGS

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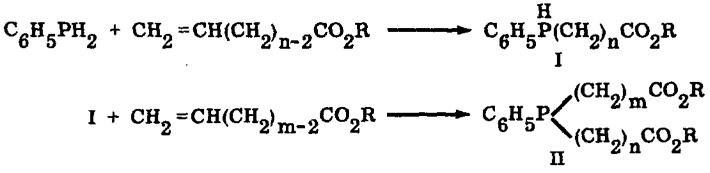
Although phosphorus-containing heterocyclic compounds are known with ring sizes varying from three to seven atoms, no methods have been described for the synthesis of larger rings (1). We have found that carbon-phosphorus heterocycles with seven to eleven atoms can be prepared by acyloin condensation.

The starting materials were synthesized by addition of phenylphosphine to terminally unsaturated carboxylic esters (2,$^{+}$,$^{++}$).



$$C_6H_5PH_2 + CH_2{=}CH(CH_2)_{n-2}CO_2R \longrightarrow C_6H_5\overset{H}{P}(CH_2)_nCO_2R$$

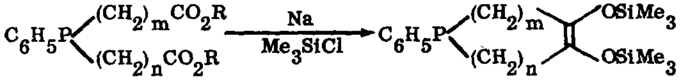
I

$$I + CH_2{=}CH(CH_2)_{m-2}CO_2R \longrightarrow C_6H_5P\begin{matrix}(CH_2)_mCO_2R\\(CH_2)_nCO_2R\end{matrix}$$

II

$m = 2, 3, 4;\ n = 2, 3, 4;\ R = C_4H_9$

The acyloin condensations were carried out by the method of Rühlmann (3), i.e. in the presence of trimethylsilyl chloride with toluene as the solvent. The expected bis(trimethylsiloxy)phosphacyclo-alkenes III a-e were obtained in 44-14 % yields (see Table).



II III

The presence of the phosphorus atom constitutes a special problem in this reaction. If the normal procedure is followed, that is, if the ester II is gradually added to the sodium, the product will be contaminated with substances containing an R_2PH group (IR absorption at 2280 cm^{-1}). Probably, such compounds result from reductive fission of carbon-phosphorus bonds by sodium. This side reaction can be suppressed, however, by adding the starting material all at once, in a small excess to the sodium. The ester groups are apparently far more reactive towards sodium than the phosphine groups. Unfortunately, this procedure prohibits working in high dilution, as is usually done in the acyloin condensation (4). As a result, with growing ring size polymerization becomes an increasingly productive side reaction and the yields of monomeric products decrease accordingly, as is shown in the Table.

The products III are colourless liquids or low-melting solids, thermally quite stable, but extremely reactive towards oxidizing agents. When exposed to the atmosphere, they polymerize within a few minutes to a white solid; consequently, fully satisfactory combustion analyses are difficult to obtain. However, the spectral data (IR, NMR, MS) are all in accordance with the proposed structures (+++).

Experiments aimed at transforming the enediol-bis(trimethylsilyl)ether moieties of III a-e into other functional groups by hydrolysis (3) or reaction with bromine (3, 5) only yielded intractable products. Reaction with sulphur quite readily gave the corresponding phosphine sulphides (+).

TABLE

Synthesis of 1-phenyl-(m+2), (m+3)—bis(trimethylsiloxy)phospha—(m+2)-cycloalkenes (III)

	m	n	Ring size	Yield, %	bp, °C (p, mbar)	mp of sulphide, °C
IIIa	2	2	7	44	118-128 (0.16)	103-106
IIIb	3	2	8	30	124-125 (0.04)	-
IIIc	3	3	9	23	134-137 (0.09)	108-110
IIId	4	3	10	23	142-152 (0.05)	-
IIIe	4	4	11	14	152-166 (0.04)	100-102

References and footnotes

1. For a recent review see F. G. Mann, "The heterocyclic derivatives of phosphorus, arsenic, antimony and bismuth", Wiley-Interscience, New York (1970).

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[+] Satisfactory analytical and spectral data were obtained for these substances.

[++] The n-butyl esters were chosen because their boiling points are about 40 °C higher than those of the cyclic phosphines III resulting from them. This allows a convenient isolation of the cyclization products by distillation.

[+++] e.g. IIIc: Analysis C 60.2 % (calcd. 60.9), H 8.5 (8.9), P 7.9 (7.9); IR 1680 cm^{-1} (m, C=C str.), 1250, 1260 (s, CH$_3$ symm. deform.), 850 (s, Si-CH$_3$ str.); NMR: δ 7.2-7.7 (multiplet, 5 H, C$_6$H$_5$), 1.8-3.0 (multiplet, 12 H, ring protons), 0.3 (singlet, 18 H, SiMe$_3$); MS: M/e 394 (parent), 379 (P-CH$_3$), 305 (P-Me$_3$SiO).