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A CONVENIENT SYNTHESIS OF SPIROPHOSPHORANES

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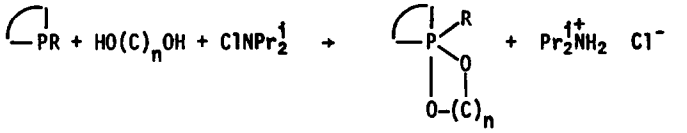
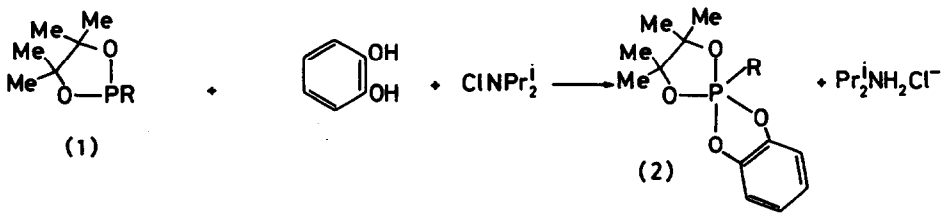
Castro, Chapleur, and Gross[1] have used N-chlorodi-isopropylamine in the synthesis of alkoxyphosphonium salts according to the equations

$$(Me_2N)_3P + ClNPr^i_2 + R^1R^2CH(OH) \rightarrow [\ ] \xrightarrow[NH_4ClO_4]{H_2O} (Me_2N)_3\overset{+}{P}OCHR^1R^2\ \ ClO_4^-$$

We have applied N-chlorodi-isopropylamine in a convenient synthesis of spirophosphoranes which can be summarised by the equation



Thus equimolar quantities of the phosphite (1; R = OPh), catechol, and N-chlorodi-isopropylamine in ether at -40° gave a precipitate of di-isopropylammonium chloride. Filtration and evaporation gave an 80% yield of the phosphorane (2; R =OPh). The Table includes other spirophosphoranes prepared in a similar way. Some, e.g. those from experiments 3, 4, 7, and 8, have not been accessible hitherto; their dynamic n.m.r. spectra will be described elsewhere. The method works well with 1,2- and 1,3-glycols and is the easiest route to many spirophosphoranes.

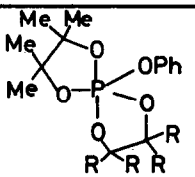
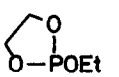
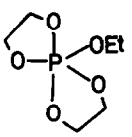
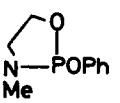
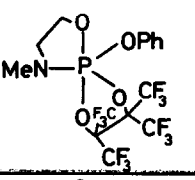
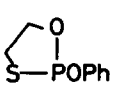
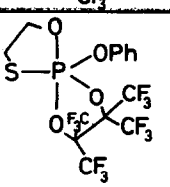
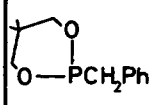
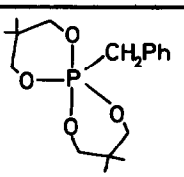


(1) (2)

References

1. B. Castro, Y. Chapleur, and R. Gross, Tetrahedron Letters, 1974, 2313.
2. S. Bone, S. Trippett, and P.J. Whittle, J.C.S. Perkin 1, 1974, 2125.
3. B.C. Chang, W.E. Conrad, D.B. Denney, D.Z. Denney, R. Edelmann, R.L.Powell, and D.W. White, J. Amer. Chem. Soc., 1971, 93, 4004.

$$R_3P + HO(C)_nOH + ClNPr^i_2 \rightarrow R_3P\begin{smallmatrix}O\\O\end{smallmatrix}(C)_n$$

Exp.	R_3P	$HO(C)_nOH$	Spirophosphorane	Yield	Characterisation [a]
1	(1; R = OPh)	catechol	(2; R = OPh)	80	Ref. 2
2	(1; R = OMe)	catechol	(2; R = OMe)	71	m.p. 80-81.5° ^{31}P[b] 32.9 τ 3.2 (s,4H),6.4 (d,3H), 8.7 (s,12H)
3	(1; R = OPh)	pinacol		89	m.p. 107-109° ^{31}P 44.2 τ 2.9 (s,5H), 8.75 (s,6H), 8.90 (s,6H).
4	(1; R = OPh)	$(HOCH_2)_2$	(3; R = H)	80	b.p. 120°/0.2 mmHg ^{31}P 37.2
5	(1; R = OPh)	$[HOC(CF_3)_2]_2$	(3; R = CF_3)	91	Ref. 2
6		$(HOCH_2)_2$		79	m.p. 36-38° Ref. 3
7		$[HOC(CF_3)_2]_2$		92	m.p. 113-113.5° ^{31}P 41.6 ^{19}F[c] 1.22, 2.97, 3.72, 6.59 (equal intensity)
8		$[HOC(CF_3)_2]_2$		88	m.p. 107-108° ^{31}P -2.7 ^{19}F 4.36 (3F), 5.31 (3F), 6.06 (6F)
9		$(HOCH_2)_2CMe_2$		56	m.p. 61.5-63° ^{31}P 46.2 τ 2.8 (s,5H), 6.45 (d,8H) 7.00 (d,2H), 9.15(s,12H)

[a] N.m.r. spectra at room temperature. [b] P.p.m. to high field of 85% H_3PO_4.

[c] P.p.m. to high field of internal $PhCF_3$.