

Novel Routes to t-Butoxy-compounds of Phosphorus

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In the past¹ difficulties have been experienced in the preparation of t-butoxy-derivatives of phosphorus compounds, and to date, only a few well-defined mono-t-butoxy-products have been reported.² Recently, we described an unusual transformation of di-n-butyl t-butyl peroxyphosphate into the di-n-butyl t-butyl phosphate (Ie).³

Now we report two more generally applicable routes for the preparation of t-butoxy-derivatives (Ia—d) (Table). Method A involves the reaction of an ethereal solution of equimolar quantities of a dialkyl t-butyl peroxyphosphate² with triphenylphosphine at 25—35°. Method B involves the reaction of a monochloro-derivative of

a tervalent phosphorus compound with t-butyl hydroperoxide in the presence of pyridine, e.g., the reaction of a mixture of dimethyl phosphorochloridite, $(\text{MeO})_2\text{PCl}$ (0·1 mole), t-butyl hydroperoxide (0·11 mole), and pyridine (0·11 mole) in petroleum at 10—15° yielded 56% of (Ib).

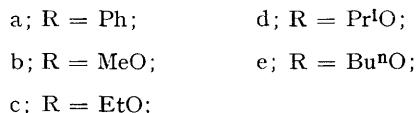


TABLE
t-Butoxy-compounds of phosphorus*

Product	Method	Boiling point or melting point °C		n.m.r. (δ)
(Ia)	B	111—112	$-\text{CH}_2\text{O}-$	$\text{Me}_3\text{CO}-$
(Ib)	A, B	37/0·05 mm.		1·50
(Ic)	A	64/1·0 mm.	3·79—4·25	1·47
(Id)	A	54/0·1 mm.		1·50
			4·25—4·80	1·45

* Satisfactory elemental analyses were obtained for these compounds.

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