Novel Routes to t-Butoxy-compounds of Phosphorus

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IN the past[1] 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 peroxyphosphate[2] 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, $(MeO)_2PCl$ (0·1 mole), t-butyl hydroperoxide (0·11 mole), and pyridine (0·11 mole) in petroleum at 10—15° yielded 56% of (Ib).

$$R_2P(O)OCMe_3 \qquad (I)$$

a; R = Ph; d; R = Pr^iO;

b; R = MeO; e; R = Bu^nO;

c; R = EtO;

TABLE

*t-Butoxy-compounds of phosphorus**

Product	Method	Boiling point or melting point °c	n.m.r. (δ) $-CH_2O-$	n.m.r. (δ) CH–O–	n.m.r. (δ) Me_3CO-
(Ia)	B	111—112			1·50
(Ib)	A, B	37/0·05 mm.			1·47
(Ic)	A	64/1·0 mm.	3·79—4·25		1·50
(Id)	A	54/0·1 mm.		4·25—4·80	1·45

* Satisfactory elemental analyses were obtained for these compounds.

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