

Novel Routes to t-Butoxy-compounds of Phosphorus

By GEORGE SOSNOVSKY, D. J. RAWLINSON, and E. H. ZARET

(Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616)

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 trivalent 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).



- a; R = Ph; d; R = PrⁱO;
b; R = MeO; e; R = BuⁿO;
c; R = EtO;

TABLE

t-Butoxy-compounds of phosphorus*

Product	Method	Boiling point or melting point °C	—CH ₂ O—	n.m.r. (δ) CH—O—	Me ₃ CO—
(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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¹ V. Mark and J. R. Van Wazer, *J. Org. Chem.*, 1964, **29**, 1006, and references therein; J. Fertig, W. Gerrard, and H. Herbst, *J. Chem. Soc.*, 1957, 1488; W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith, and P. L. Wyvill, *ibid.*, 1953, 1920; E. Cherbuliez, C. Gandillon, A. de Picciotto, and J. Rabinowitz, *Helv. Chim. Acta*, 1959, **42**, 2277; F. W. Hoffmann, R. J. Ess, and R. P. Usinger, *J. Amer. Chem. Soc.*, 1956, **78**, 5817.

² R. Burgada, G. Martin, and G. Mavel, *Bull. Soc. chim. France*, 1963, 2154; G. Olah and A. Oswald, *J. Org. Chem.*, 1960, **25**, 603; F. Cramer, W. Rittersdorf, and W. Bohm, *Annalen*, 1962, **654**, 180; J. A. Maynard and J. M. Swan, *Austral. J. Chem.*, 1963, **16**, 596; J. Cheymol, P. Chabrier, M. Selim, and P. Leduc, *Compt. rend.*, 1958, **247**, 1014; J. F. Allen, S. K. Reed, O. H. Johnson, and N. J. Brunsvold, *J. Amer. Chem. Soc.*, 1956, **78**, 3715; J. Michalski and A. Zwierzak, *Roczniki Chem.*, 1961, **35**, 619.

³ G. Sosnovsky and E. H. Zaret, *Chem. and Ind.*, 1966, 628.