Quinquecovalent Adducts from Ethylene Phosphonothioites and from Dimethyl t-Butylphosphonite

By A. P. STEWART and S. TRIPPETT*

(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary Quinquecovalent adducts from ethylene phosphonothioites readily eliminate ethylene sulphide to give phosphoryl compounds; the low-temperature ^{1}H n.m.r. spectrum of the adduct of dimethyl t-butylphosphonite with methylenedeoxybenzoin shows that the t-butyl group preferentially occupies an *equatorial* position.

ETHYLENE phosphonothioites (1; R = Ph or Bu^t) form stable 1 : 1-adducts with diacetyl, benzylideneacetylacetone, phenanthraquinone, *etc.*, which on warming readily eliminate ethylene sulphide to give the corresponding phosphonate or phosphinate esters.[2] Thus the t-butylphosphonothioite (I; R = Bu^t), b.p. 48—50° at 0·9 mm Hg, ^{31}P n.m.r. -174 p.p.m., with diacetyl at room temperature gave the adduct (2), τ 8·63 (9H, d, $J_{P,H}$ 20 Hz), 8·25 (3H, s), 8·14 (3H, s), 7·2br (2H, m), and 6·25 and 5·6br (2H, 2m), ^{31}P -24 p.p.m., which slowly at room temperature and rapidly at 100° gave ethylene sulphide (86%) and the phosphonate (3) (80%), m.p. 79—80°. The benzylideneacetylacetone adduct of (1; R = Bu^t) contained the two isomers (4a) and (4b)† as shown by the presence of two t-butyl signals at τ 8·71 (J 11 Hz) and 9·04 (J 11 Hz);

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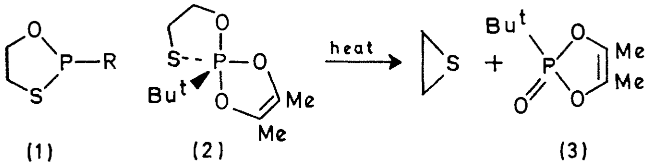
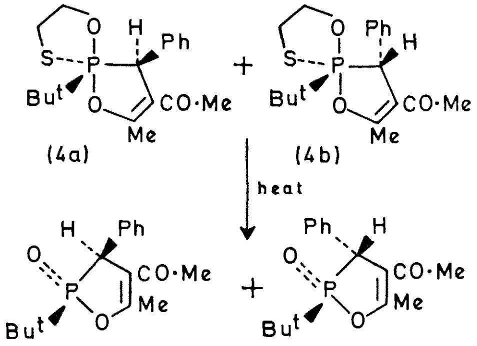
† These isomers are not interconvertable by pseudorotation processes.

elimination of ethylene sulphide at 100° gave the isomeric phosphinates (5), m.ps. 148—152° and 173—175°.

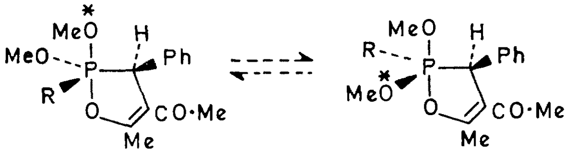
Dimethyl t-butylphosphonite (6), b.p. 100—105° at 230 mm Hg, obtained (60%) from t-butyldichlorophosphine and sodium methoxide in ether,[2] with benzylideneacetylacetone formed a 1 : 1-adduct whose n.m.r. spectrum, τ 8·85 (9H, d, J 18·8 Hz), 8·13 (3H, s), 7·5 (3H, s), 6·86 (3H, d, J 8 Hz), 6·34 (3H, d, J 12 Hz), and 5·77 (2H, d, J 13 Hz), was unchanged from −90 to +150°. This contrasts with the corresponding dimethyl phenylphosphonite (7) adduct,[3,4] in which pseudorotation to equilibrate the isomers (8a; R = Ph) and (8b; R = Ph) was inhibited at −20°, and could be due either to extremely rapid pseudorotation between (8a; R = Bu^t) and (8b; R = Bu^t) or to the presence in the t-butylphosphonite adduct of only one detectable isomer,§ presumably (8b; R = Bu^t), because of steric effects. That the latter is the correct explanation was shown by the low-temperature n.m.r. spectra of the 1 : 1-adducts (9; R = Bu^t and Ph), from treatment of (6) and (7) with methylenedeoxybenzoin where geometrical isomerism is not possible. In the spectra of both adducts, the single doublet at 35° due to the equivalent methoxyls split into two doublets below −10° because of slow pseudorotation between (9a) and (9b), *e.g.* for the t-butyl adduct the doublet at τ 6·43 ($J_{P,H}$ 11 Hz) became two doublets at τ 6·27 ($J_{P,H}$ 13·5 Hz) and 6·58 (J_{PH} 8·5 Hz).



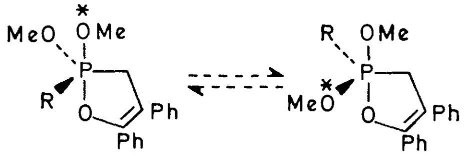
(1) (2) (3)



(5)



(7a) (7b)



(9a) (9b)

These results demonstrate that, whatever its kinetic preference,[5] the t-butyl group is thermodynamically more stable in the *equatorial* position of a trigonal bipyramidal phosphorane when in competition with methoxyl. We have so far been unable to obtain quinquecovalent phosphorus compounds having two t-butyl groups attached to phosphorus.

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§ By analogy with the formation of the adducts (4), both isomers of (8; R = Bu^t) would be formed initially.

[1] A similar elimination has been postulated in a five-co-ordinate intermediate; N. K. Hamer, *Chem. Comm.*, 1968, 1399.

[2] See P. C. Crofts and D. M. Parker, *J. Chem. Soc.* (*C*), 1970, 332 for a previous attempt to prepare this compound.

[3] D. Gorenstein and F. H. Westheimer, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **58**, 1747; F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

[4] F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.* ,1968, **90**, 1275.

[5] W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 577.