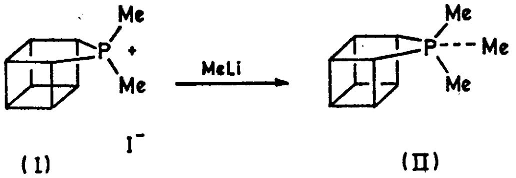
Angular Dependence of Phosphorane and Ylide Formation

By E. Wayne Turnblom and Thomas J. Katz*
(*Department of Chemistry, Columbia University, New York, New York* 10027)

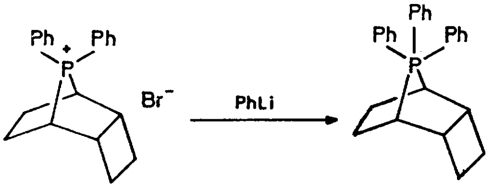
Summary If there is a critical angle at phosphorus below which phosphonium salts and phenyl-lithium form pentavalent phosphoranes and above which they form ylides, the angle is bracketed by that in (III) and (Va).

THE first penta-alkylphosphorane (II) was synthesized recently by treating the dimethylphosphonium salt (I) with methyl-lithium.[1] Although organolithium reagents react with other phosphonium salts to give ylides, the success of this and related reactions was attributed to the relief of angle strain around the phosphorus atom.[1,2] Among quaternary phosphonium salts whose substituents are similar but constrained at different angles, there should be a critical angle below which pentavalent phosphoranes form, and above which ylides form. We have bracketted that angle by constructing salts (III) and (Va), which differ by only one bond, and by showing that the former—the bicyclo[2,2,1]heptane—with phenyl-lithium gives the one kind of product (equation 1) and the latter—the bicyclo-[4,2,1]nonane—the other (equation 2).

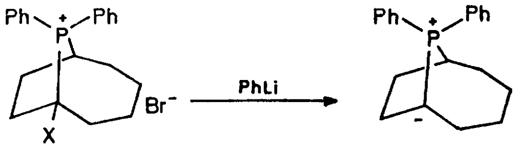


(I) (II)

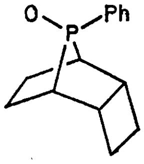
Salt (III) in tetrahydrofuran (THF), like diphenylphosphoniahomocubane bromide [(I) with Ph in place of Me],[2] reacts with phenyl-lithium (in 70:30 benzene–ether at room temperature to give a pentavalent phosphorane, in this case (IV) (65% yield, m.p. 118—119°). In contrast, salt (Va) in THF or in ether gives not the pentavalent phosphorane but the ylide (VI). When the reaction mixture [run 1: 0·53 mmol (Va), 2·3 mmol PhLi, 15 ml ether, 0·5 h; run 2: 0·53 mmol (Va), 1·1 mmol PhLi, 5 ml THF, 10 min; run 3: 0·16 mmol (Va), 0·33 mmol PhLi, 1 ml THF, 10 min] is quenched with DBr in D_2O and extracted with ether, no pentavalent phosphorane (or triphenylphosphine) is found after removal of the ether. However, when the aqueous solution is extracted with chloroform, the chloroform removed, and the product crystallized from methanol, the phosphonium salt (Vb) is isolated in *ca.* 32% yield. The presence of one bridgehead deuterium is shown by the intensity of the bridgehead proton's n.m.r. resonance at τ 5·25 being 1 compared to 22 for the sum of the intensities of the remaining resonances (found: run 1, 0·89; run 2, 1·0; run 3, 1·1).



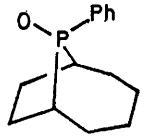
(III) (IV) (1)



(V)a; X = H
b; X = D
(VI) (2)



(VII)



(VIII)

The salt (III), m.p. 264—265°, was prepared in 53% yield by treating the phenylphosphine oxide (VII)[3] in THF at −78° with phenyl-lithium and then adding aqueous HBr, a procedure for making phosphonium salts that should work only with angle-strained phosphine oxides.[2] In contrast attempts to prepare the salt (Va) in this way failed, corresponding to the failure of reaction 2 to give the pentasubstituted phosphorus derivative. The salt (Va), m.p. 244—246°, had to be prepared instead by reducing (VIII)[4] with Si_2Cl_6 in benzene[5] to the phosphine and then quaternizing with bromobenzene and nickel bromide (180° for 3 h).[6]

The pentavalent phosphorane (IV), although stable at room temperature, fragments upon heating in the same way as (II),[1,2] giving cyclo-octa-1,5-diene and triphenylphosphine.† Its half-life in benzene at 75° is 36 min.

For (III), (IV), (Va), (VII), and (VIII) the following were in agreement with the structures assigned: analyses for C,H,P, and, when present, halide; ^{1}H n.m.r. spectra; and, except for the salts, parent peaks in the mass spectra.

Compound (VI) is the only bridgehead phosphorus ylide known and one of the few stable bridgehead ylides of any kind.[8]

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† No *cis*-divinylcyclobutane could be detected by n.m.r. Its Cope rearrangement is sufficiently slow ($t_{\frac{1}{2}}$ 2·75 h at 75°) that if present, it should have been observed.[7]

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[2] T. J. Katz and E. W. Turnblom, *J. Amer. Chem. Soc.*, 1970, **92**, 6701.

[3] Prepared by hydrogenating (PtO_2, MeOH) compound V reported by T. J. Katz, J. C. Carnahan, jun., G. M. Clarke, and N. Acton, *J. Amer. Chem. Soc.*, 1970, **92**, 734 (m.p. 152—154°).

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