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SYNTHESIS OF ORGANIC PHOSPHORUS COMPOUNDS CONTAINING A LINEAR P-B BOND CHAIN

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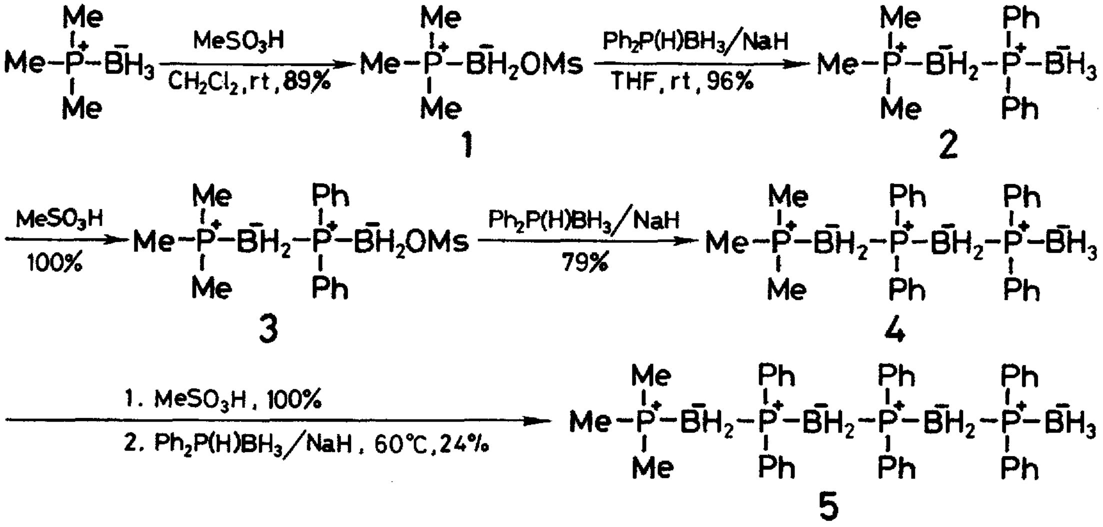
Summary: Organic phosphorus compounds containing a linear P-B bond chain are synthesized via methanesulfonate derivatives of phosphine-boranes.

Phosphine-boranes, adducts of phosphines with boranes, constitute a unique class of organic phosphorus compounds.[1,2] They exhibit characteristic chemical properties, and hence they can potentially be used both as reagents in organic synthesis and as precursors to useful organic phosphorus compounds.

We wish to report here a new kind of phosphine-borane that contains a linear P-B bond chain.[3,4] Some charge alternation (+-+-+-+-) may exist in these molecules, since phosphorus and boron atoms possess +1 and -1 formal charges, respectively. These charasteristic bond sequences might be responsible for peculiar properties of the compounds.

Our synthetic route is illustrated in the following scheme. It consists of substitution of a hydrogen atom of the boranato group by a methanesulfonate group and nucleophilic substitution reaction on the boron atom with secondary phosphine-borane.



Thus, the reaction of trimethylphosphine-borane with methanesulfonic acid in dichloromethane provided practically pure methanesulfonate derivative 1[5] in 89% yield. Subsequent reaction of 1 with diphenylphosphine-borane proceeded smoothly in the presence of NaH at room temperature.[6] The resulting phosphine-borane 2[7] having a P-B-P-B linkage was again treated with methanesulfonic acid to afford the corresponding sulfonate derivative 3[8] in 98% yield. Repetition of this procedure afforded 4[9] and 5[10] in moderate yields.

Many analogous compounds may be synthesized by this method, since various secondary phosphine-boranes including unsymmetrical ones can be readily prepared from dialkylchlorophosphines or secondary phosphine oxides. Synthesis and reactions of related compounds are currently being investigated in our laboratory.

References

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2) For recent representative work dealing with phosphine-boranes: (a) R. Köster, W. Schüssler, and L. Synoradzki, Chem. Ber., 120, 1105 (1987). (b) R. Köster, Y.-H. Tsay, and L. Synoradzki, Chem. Ber., 120, 1117 (1987). (c) H. J. Bestmann, and T. Röder, Angew. Chem. Int. Ed. Engl., 22, 782 (1983). (d) G. Müller, D. Neugebauer, W. Geike, F. H. Kohler, J. Pebler, and H. Schmidbauer, Organometallics, 2, 257 (1983). (e) H. Schmidbauer, E. Weiss, and W. Graf, Organometallics, 4, 1233 (1985). (f) T. Imamoto, T. Kusumoto, N. Suzuki, and K. Sato, J. Am. Chem. Soc., 107, 5301 (1985).
3) Schmidbauer et al. have extensively studied the synthesis and reactions of phosphine-boranes having $P^{+}-B^{-}-P^{+}$ unit. Ref. 1a and 2e and references cited therein.
4) Cyclic trimers and tetramers of phosphinoboranes (R_2PBH_2) were reported earlier. J. Emsley and D. Hall, "The Chemistry of Phosphorus", Harper & Row, New York, 1976, pp. 445-454.
5) Compound 1: mp 87-93 °C; IR (KBr) 3010, 2400, 1400, 1310 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (d, J=12 Hz, 9H), 2.81 (s, 3H); FABMS: m/e 183 (M-1). This compound was very sensitive to moisture, and further purification by recrystallization was difficult to achieve.
6) Substitution reaction of phosphine-monohaloborane with organic phosphorus compounds such as secondary phosphine oxides have been reported. See Ref. 2e.
7) Compound 2: mp 122-123 °C; IR (KBr) 3040, 2350, 1480, 1430, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, J=12 Hz, 9H), 6.90-7.90 (m, 10H); FABMS: m/e 287 (M^+); MS: m/e 274 ($M-BH_3$); Anal. Calcd for $C_{15}H_{24}B_2P_2$: C, 62.57; H, 8.40. Found: C, 62.30; H,8.37.
8) Compound 3: mp 82-85 °C; IR (KBr) 3000, 2400, 1440, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (d, J=12 Hz, 9H), 2.68 (s, 3H), 7.15-7.90 (m, 10H).
9) Compound 4: mp 143-144 °C; IR (KBr) 3040, 2320, 1480, 1430, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (d, J=12 Hz, 9H), 6.80-7.80 (m, 20H); MS: m/e 472 ($M-BH_3$); Anal. Calcd for $C_{27}H_{36}B_3P_3$: C, 66.74; H, 7.47. Found: C, 66.56; H,7.30.
10) Compound 5: mp 170-171 °C; IR (KBr) 3030, 2320, 1480, 1430, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (d, J=10 Hz, 9H), 6.00-7.60 (m, 30H); Anal. Calcd for $C_{39}H_{48}B_4P_4$: C, 68.49; H, 7.07. Found: C, 68.21; H, 6.88.

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