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Synthesis of 2-Iodo-4,5-dimethylphosphinine and Its Conversion to Organometallic Derivatives

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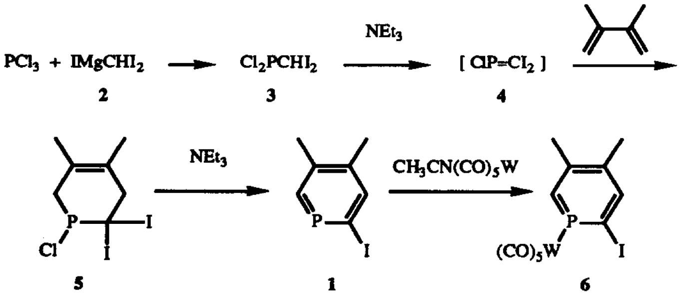
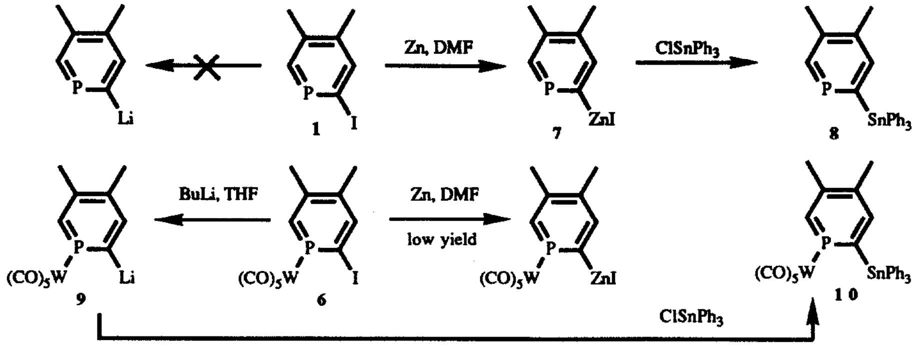
Abstract: *The synthesis of the title compound 1 via a halophosphaalkene/Diels Alder route is described. Conversion of 1 to the corresponding zinc derivative 7 as well as conversion of the tungsten complex 6 to the lithium compound 9 allows funtionalization of the phosphinine system at the 2-position.*

Although a number of functionalized phosphinines (or phosphabenzenes) are known[1], a general approach is still desirable. In principle, organometallic derivatives of phosphinines - if readily available from the corresponding halo derivatives - would furnish such a route. Recently, Mathey et al. have devised an elegant access to 2-chloro- and 2-bromo-substituted phosphinine; they turned out to be disappointingly unreactive in attempted direct derivatization[2a,b], but the 2-bromo derivative could be successfully converted to an organolithium derivative after transformation to its pentacarbonyltungsten complex[2c]. In view of the normally higher reactivity of aryl iodides, we hoped that iodophosphinines would be easier to derivatize. We here report the synthesis of 2-iodo-4,5-dimethylphosphinine (1) and its conversion to organometallic derivatives.

Our synthesis of 1 is essentially based on the strategy of Mathey[2]. Crude dichloro(diiodomethyl)phosphine (3)[3], obtained from the reaction of trichlorophosphine with carbenoid 2[4] at approximately -100 °C, was treated at 0 °C with an excess of triethylamine in 2,3-dimethyl-1,3-butadiene as solvent. Presumably[2], the reaction proceeded via 4 and 5 to give 1[3] which, after double distillation, was obtained in 33 % yield (relative to iodoform, the precursor of 2[4]). Treatment of 1 in THF with acetonitrile(pentacarbonyl)tungsten gave 6[3] (yield 67%).



As expected, **1** was quite reactive in attempted metalation reactions, e.g. with butyllithium or magnesium; however, the yields were low (magnesium) or zero (lithium). Fortunately, the conversion to the organozinc derivative **7** was easily achieved by a method recently described by Knochel et al.[5], i.e. treatment with activated zinc dust in DMF; **7** was characterized by its spectral data[3] (spectral yield 85 -90 %) and by derivatization with chlorotriphenyltin which gave **8**[3] in 37 % isolated yield. In contrast, **6** did not react in a clean fashion with zinc dust, but, with butyllithium in THF at - 90 °C, underwent selective conversion to the lithium reagent **9**[2c,3] ; **9** gave **10**[3] in 50 % yield on reaction with chlorotriphenyltin.



After **7** and **9** have become available and their usefulness in derivatization reactions (to **8** and **10**) has been illustrated, we are further investigating the scope of their application in preparing other 2-functionalized phosphinines.

References and Notes

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3 **1**: yellowish crystals, mp 30 °C; bp 76 °C/10^{-3}mbar. NMR (C_6D_6): δ(^{1}H) 1.69 (d, ^5J(PH)=3.6 Hz, 3H, 4-CH_3), 1.74 (s, 3H, 5-CH_3), 7.69 (d, ^2J(PH)=38.6 Hz, 1H, H6), 7.95 (d, ^3J(PH)=5.6 Hz, 1H, H3); δ(^{13}C{^{1}H}) 21.5 (d,^4J(PC)=1.9 Hz, 4-CH_3), 22.7 (d,^3J(PC)=3.4 Hz, 5-CH_3), 121.0 (d,^1J(PC)=71.4 Hz, C2), 141.4 (d,^3J(PC)=17.5 Hz, C4), 141.9 (d,^2J(PC)=14.8 Hz, C5), 145.7 (d,^2J(PC)=15.2 Hz, C3), 159.7 (d,^1J(PC)=56.9 Hz, C6); δ(^{31}P) 216.2. **6**: brown-yellow crystals dec. 126-7°C. NMR (C_6D_6): δ(^{1}H) 1.49 (s, 3H, 5-CH_3), 1.53 (d, ^5J(PH)=6.4 Hz, 3H, 4-CH_3), 7.54 (d, ^2J(PH)=25.6 Hz, 1H, H6), 7.73 (d, ^3J(PH)=17.3 Hz, 1H, H3); δ(^{31}P) 184.3. **7** :NMR (DMF$_{d7}$): δ(^{1}H) 2.32 (d, ^5J(PH)=3.3 Hz, 3H, 4-CH_3), 2.35 (s, 3H, 5-CH_3), 8.14 (d,^3J(PH)=18.8Hz, 1H, H3), 8.42(d, ^2J(PH)=31.6 Hz, 1H, H6); δ(^{31}P) 223. **8**: colourless crystals, mp 122-3 °C. NMR ($CDCl_3$): δ(^{1}H) 2.31 (d, ^5J(PH)=3.5 Hz, 3H, 4-CH_3), 2.43 (s, 3H, 5-CH_3), 7.3-7.5 (m, 9H, *m,p*-$SnPh_3$), 7.55-7.75 (m, 6H, *o*-$SnPh_3$), 7.99 (d, ^3J(PH)=12.4 Hz, ^3J(SnH)=70.5 Hz, 1H, H3) 8.62 (d, ^2J(PH)=35.7 Hz, ^4J(SnH)=26.6 Hz, 1H, H6); δ(^{31}P) 218 (^2J($P^{117}Sn$)=301 Hz, ^2J($P^{119}Sn$)=315 Hz). **9**: NMR (THF) δ(^{31}P) 163 (^1J(PW)=240Hz). **10**: yellow crystals, mp 144-5 °C. NMR (C_6D_6): δ(^{1}H) 1.67 (d, ^5J(PH)=6.2 Hz, 3H, 4-CH_3), 1.77 (s, 3H, 5-CH_3), 7.20-7.35 (m, 9H, *m,p*-$SnPh_3$), 7.60-7.75 (m, 6H, *o*-$SnPh_3$), 7.86 (d, ^2J(PH)=29.4 Hz, 1H, H6), 8.36 (d, ^3J(PH)=23.7 Hz, ^3J(SnH)=24 Hz, 1H, H3); δ(^{31}P) 180 (^2J($P^{117}Sn$)=187 Hz, ^2J($P^{119}Sn$)=196 Hz,^1J(PW)=266 Hz).

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