

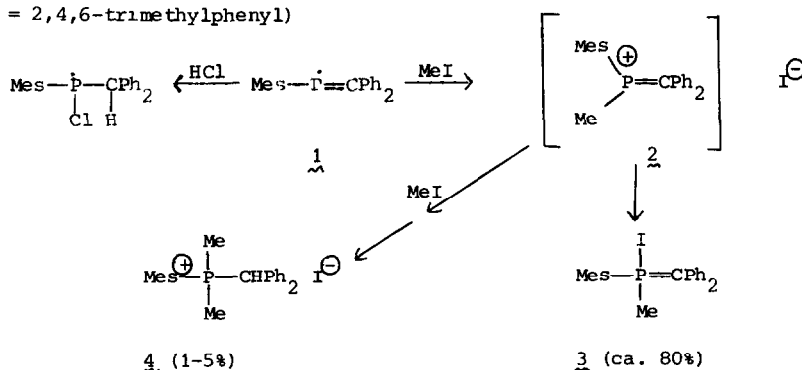
A NUCLEOPHILIC REACTION OF A PHOSPHAALKENE
 THE METHYLATION OF MESITYLDIPHENYLMETHYLENEPHOSPHINE

Th.A. van der Knaap and F. Bickelhaupt*
 Vakgroep Organische Chemie, Vrije Universiteit
 De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract The reaction of the title compound (1) with methyl iodide gives the ylide 3 and the phosphonium salt 4. The intermediate formation of the phosphoniaalkene 2 is postulated

Tertiary phosphines are, as a rule, good nucleophiles¹. In contrast, derivatives of two-coordinate trivalent phosphorus have a rather low basicity and nucleophilicity. Thus, attempts to protonate or alkylate derivatives of phosphabenzene have met with failure². Phosphaalkenes³⁻⁵ form metal σ -complexes involving the lone pair at phosphorus^{3b,4a}; phosphabenzenes⁶ and benzazaphospholes⁷ behave similarly. However, hydrogen chloride adds to mesityldiphenylmethylenephosphine (1) in such a fashion that the proton becomes attached to carbon and not to phosphorus^{3a} (Scheme 1). We now report what we believe to be the first case of nucleophilic alkylation at phosphorus of a phosphaalkene which does not bear heteroatoms at the double bond (Scheme 1).

Scheme 1 (Mes = 2,4,6-trimethylphenyl)

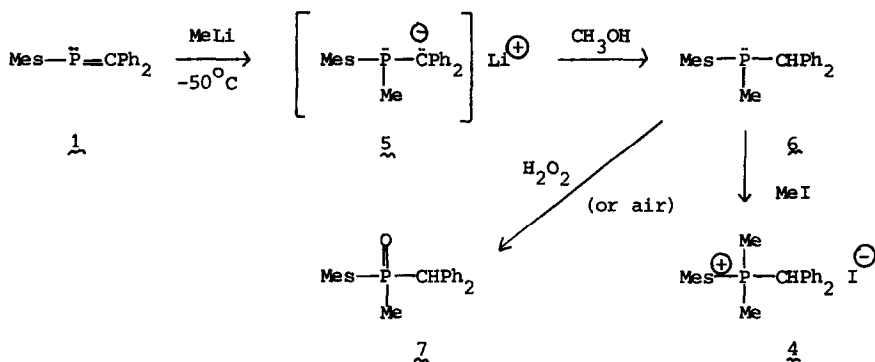


The reaction was performed by heating a solution of 1 (650 mg; 2.06 mmol) in methyl iodide (4 ml) in a sealed vessel for 24 h at 50°C in the dark. Colourless crystals of 4 (1-5%) deposited and were separated by decantation of the mother liquor. To the latter, hexane (10 ml) was added. This solution was evaporated to half its volume, whereupon a red viscous oil separated, according to its NMR spectrum, it contained ca. 80% of 3. It was purified by decantation of the supernatant liquid followed by 4 extractions with hexane (which was distilled back onto the residue for the following extraction). From the extracts red crystals of 3 were obtained (25% isolated yield), mp. 98-130°C. The structure assignment of 3 is based on the elemental analysis and the spectral data⁸. 3 is unique as an ylide bearing iodine on phosphorus. The influence of iodine is reflected in the physical and chemical properties. In comparison to ordinary

phosphorus ylides⁹, many NMR signals are strongly shifted downfield: $\delta^{31}\text{P}=44.4$ ppm (cf. $\delta^{31}\text{P}=8$ ppm in $\text{Ph}_3\text{P}=\text{CPh}_2$ ¹⁰), $\delta^1\text{H}$ ($\text{P}-\text{CH}_3$)=3.02 ppm (cf. $\delta^1\text{H}=1.70$ ppm in $[\text{Ph}_2\text{CH}_3\text{P}=\text{C}(\text{COR})-\text{C}]_2$ ($\text{R}=\text{p-tol}$)¹¹ and $\delta^{13}\text{C}$ ($\text{P}=\text{C}$)=112.8 ppm (cf. $\delta^{13}\text{C}=42.5$ ppm in $\text{Ph}_3\text{P}=\text{CPh}_2$ ¹⁰).

The structure of 4 follows from its spectral data¹⁷, moreover, 4 was identical with a sample synthesized by an independent route (Scheme 2). The reaction of 1 with methyllithium in diethyl ether at -50°C gave the expected addition of the nucleophile to phosphorus^{3a,13} under formation of the red anion 5 which afforded 6 with methanol; 6 was characterized by oxidation to 7¹⁵, and on reaction with methyl iodide gave 4¹² (mp. $230\text{--}233^\circ\text{C}$, dec.).

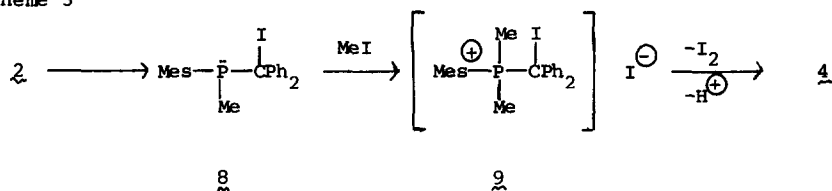
Scheme 2



The formation of 3 and 4 can best be explained by nucleophilic attack of the phosphorus atom of 1 on methyl iodide under formation of the reactive intermediate phosphoniaalkene 2 (Scheme 1). A radical pathway as postulated by Niecke and Bitter¹⁶ for the reaction of an aminoiminophosphine with organic halides is unlikely, as, contrary to Niecke's results, the reaction of 1 is accelerated by heat but not by irradiation (2 hrs., 350 nm).

Surprising is the ambident reactivity of 2 which adds the iodide anion at two different sites. Addition of iodide to phosphorus is the major pathway, leading directly to 3; this step is irreversible as heating of 3 in methyl iodide did not yield 4. The formation of 4 is rationalized by assuming addition of iodide to carbon; the intermediate 8 is quaternized by methyl iodide to give 9, which is reduced by iodide and protonated (possibly by traces of moisture) (Scheme 3)

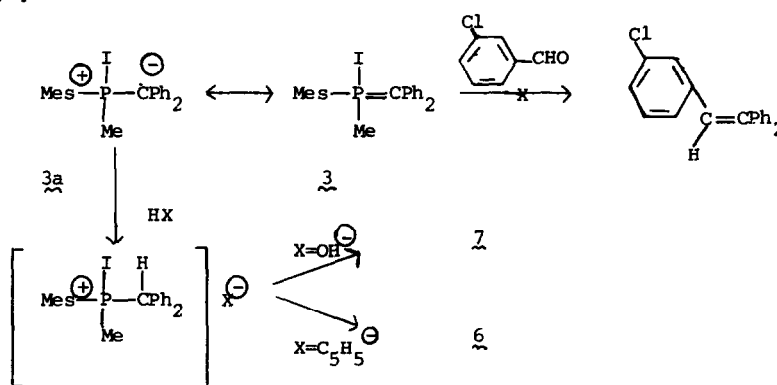
Scheme 3



The regioselectivity of the addition reactions of 1 deserves some comment. Theoretical calculations¹⁷ on $\text{HP}=\text{CH}_2$, $\text{PhP}=\text{CH}_2$ and $\text{HP}=\text{CHPh}$ as simple models for 1 indicate that the HOMO is essentially the lone pair at phosphorus. This implies that the reactions of 1 with soft electrophiles of low polarity ($\text{Cr}(\text{CO})_5\text{L}$ ^{3b,4a}, MeI) are frontier orbital controlled. The higher reactivity of phosphaaalkenes relative to phosphabenzenes under these conditions is not unexpected, as in the $\text{Cr}(\text{CO})_5$ complexes, 1 is a better electron donor than 2,4,6-triphenylphosphabenzene^{3b}. However, with charged or highly polar reactants (H^+ , RO^- , RLi), Coulombic interactions prevail and lead to the opposite regioselectivity^{3a}, as electronegativity considerations and theoretical calculations¹⁷ assign (more) negative charge to carbon in the polarized $\text{P}=\text{C}$ bond.

A preliminary investigation of the chemical properties of 3 confirmed the abnormal properties as an ylide which were already deduced from the NMR spectra. In particular, the low chemical shift of the ylidic carbon atom (vide supra) may in part be an indication of reduced negative charge, and consequently of a stronger contribution from the ylene structure 3 as compared to the normally more important ylide structure 3a (Scheme 4).

Scheme 4



Accordingly, the nucleophilic reactivity of 3 is strongly reduced. It reacts neither with methyl iodide (it survives the formation conditions!) nor with m-chlorobenzaldehyde (no Wittig reaction). Hydrolysis with water gives 7. On reaction with cyclopentadiene, 3 showed no Diels-Alder-reactivity, but gave 6 in low yield, presumably via protonation by cyclopentadiene followed by reduction.

References and Notes

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 8. Elemental analysis of $\underline{3}$: $C_{23}H_{24}IP$ (458.29); calc. C 60.27, H 5.28, I 27.69, P 6.76; found C 59.74, H 5.48, I 26.82, P 6.61. 1H NMR (THF- d_6): δ = 2.31 (br.s, 9H, aryl- CH_3), 3.02 (d, $^2J_{PH}$ = 18 Hz, 3H, P- CH_3), 6.73-7.15 (m, 6H, aryl-H), 7.15-7.44 (m, 4H, aryl-H), 7.55-7.80 ppm (m, 2H, aryl-H). ^{13}C NMR (THF- d_6): δ = 21.3 (p- CH_3), 24.7 (d, $^3J_{PC}$ = 4.4 Hz, o- CH_3), 30.0 (d, $^1J_{PC}$ = 89.3 Hz, P- CH_3), 112.8 (d, $^1J_{PC}$ = 102.7 Hz, ylidic C), 122.8 (d, $^1J_{PC}$ = 96.8, Mes-C(1)), 126.5-138.8 (m, aryl-C), 143.0-144.4 ppm (m, aryl-C). ^{31}P NMR (THF- d_6): δ = 44.4 ppm. UV (CDCl₃) λ_{max} = 360 nm (log ϵ = 3.9). Mass spectrum, m/z (%) 348 (25) [M^+ - HI + H₂O = $\underline{7}^+$] (probably formed when introducing the sample into the spectrometer), 332 (13) [M^+ - I + H = 6^+] 181 (30), 167 (100) [Ph_2CH^+], 127 (10); $C_{23}H_{25}P$: calc. m/z = 332.1693, found m/z = 332.1688.
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 13. n-Butyllithium adds in an analogous fashion to the P=C bond, the nucleophile attacking phosphorus¹⁴.
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 15. mp 159-163°C (from hexane). 1H NMR (C₆D₆): δ = 1.47 (d, $^2J_{PH}$ = 12 Hz, 3H, P- CH_3), 1.92 (s, 3H, p- CH_3), 2.36 (s, 6H, o- CH_3), 4.32 (d, $^2J_{PH}$ = 8 Hz, 1H, CHPh₂), 6.53 (d, $^4J_{PH}$ = 4 Hz, 2H, mesityl-H), 6.62-7.44 (m, 8H, Ph-H), 7.71-7.90 ppm (m, 2H, Ph-H). ^{31}P NMR (CDCl₃): δ = 42.3 ppm. Mass spectrum, m/z (%). 348 [M^+ - CHPh₂], 167 (100) [CHPh₂]⁺, $C_{23}H_{24}OP$ calc. 348.1643, found 348.1640.
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