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N-PROPARGYLAMINOPHOSPHINES. A NOVEL REARRANGEMENT OF PROPARGYLHETEROATOM SUBSTITUTED TRIVALENT PHOSPHORUS COMPOUNDS

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Abstract. *N-Methyl-N-propargylaminodiethylphosphine rearranges spontaneously with P-N bond cleavage to N-methyl-Z-3-diethylphosphino-2-propenal imine; the corresponding aminodiphenylphosphine behaves similarly but trivalent propargylamino dialkoxy or diamino phosphorus compounds are stable.*

The rearrangement of trivalent propargyloxy phosphorus compounds to allenic products (eq. 1) is a well known reaction.[1-3] A similar rearrangement has been observed for a few thio analogues,[4,5] but two nitrogen analogues,

$$X_2P\text{-}O\text{-}CR^1R^2C{\equiv}CH \longrightarrow X_2P{\lesssim}^{O}_{CH=C=CR^1R^2} \qquad \text{(eq. 1)}$$

prepared from $(EtO)_2PCl$ and propargylamines, did not rearrange even at 100°.[1] We have investigated the reactions of various trivalent chloro phosphorus compounds with N-methylpropargylamine and present here evidence for a new rearrangement which occurs in certain cases.

A series of trivalent chloro phosphorus compounds (1a-e) was treated with N-methylpropargylamine in ether in the presence of triethylamine. The products (Scheme) were the trivalent propargylamino phosphorus compounds (2a-c) when phosphorus contained electronegative substituents (OR, NR_2), and these did not rearrange, in accordance with Mark's results.[1] Thus (2a) could be purified by vacuum distillation (30%, b.p. 45-46°/0.5 mm Hg, δ_P 143.6 δ_H 2.20 (≡CH, t, $^4J_{HH}$ 2.4 Hz), 2.76 (NCH_3, d, $^3J_{PH}$ 8.8 Hz) in $CDCl_3$). In the case of Et_2PCl (1d), the trivalent product (2d) could be observed by NMR (δ_P 67.6 in C_6D_6) and gave (3d) (δ_P 83.8 in C_6D_6) when trapped with S_8, but (2d) rearranged during a few hours at 25°. According to NMR the rearranged product was N-methyl-Z-3-diethylphosphino-2-propenal imine (4d).

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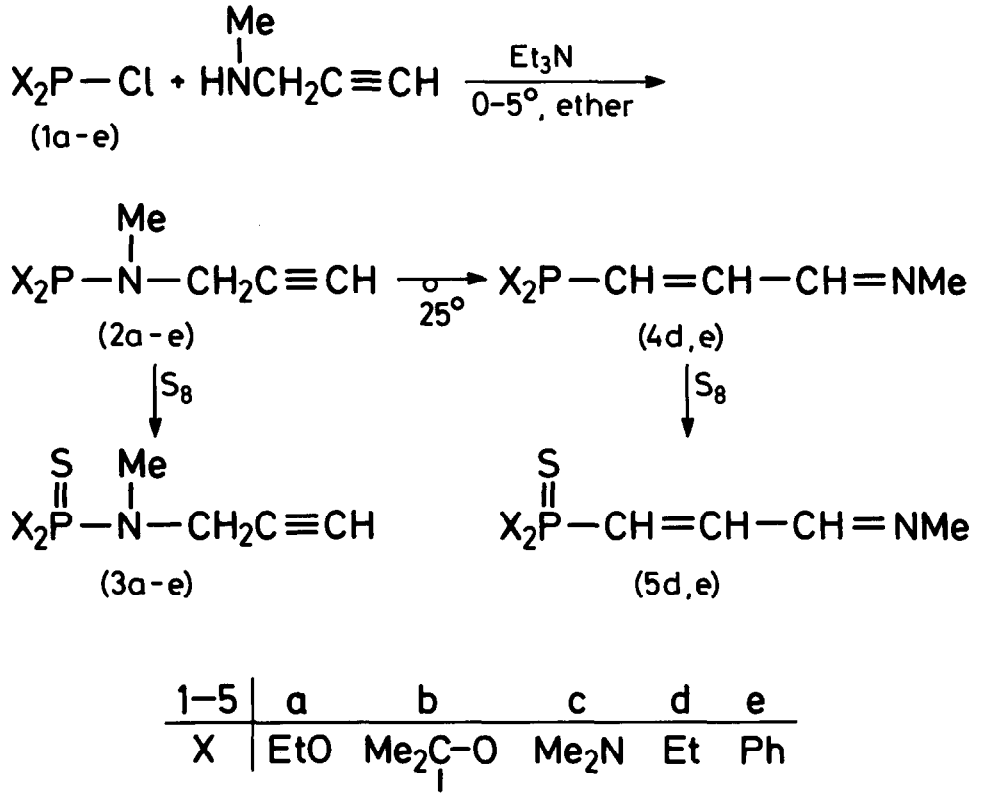


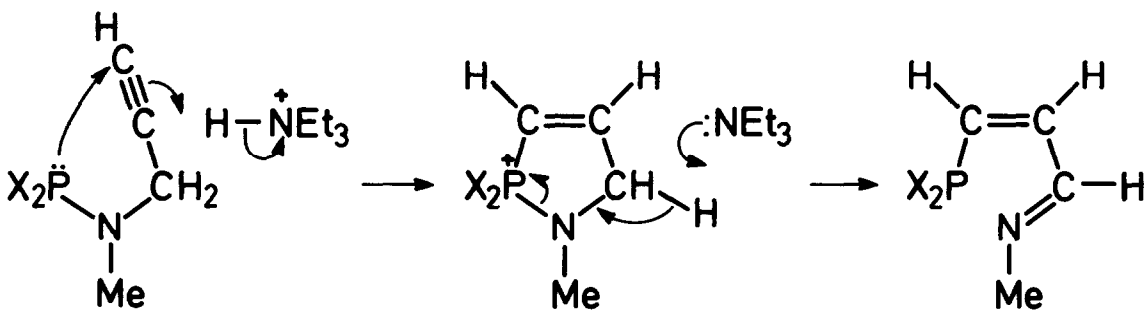
1–5	a	b	c	d	e
X	EtO	$Me_2C(-O)$	Me_2N	Et	Ph

Evidence for the structure of this unexpected rearrangement product (4d) is i) the high-field phosphorus chemical shift (δ_P -39.1 in C_6D_6) and the second order ^1H NMR ethyl signals are in accordance with a trialkylphosphine;[6,8] this is corroborated by the reaction of (4d) with S_8 to give (5d) (δ_P 45.4 in C_6D_6); ii) the NMR coupling between phosphorus and the N-methyl hydrogens is small ($^6J_{PH}$ 0.4 Hz) in contrast to that in (2a-e) ($^3J_{PH}$ 7-9 Hz) showing that the P-N bond of (2d) is absent in (4d); iii) three low-field one proton signals are seen, one of which (δ_H 8.78) in the characteristic low-field region of aldimines;[7] iv) the P-C=C-H coupling is large ($^3J_{PH}$ 19.3 Hz) corresponding to a trans coupling,[8] and the H-C=C-H coupling constant ($^3J_{HH}$ 11.8 Hz) agrees with a cis coupling;[8,9] v) the ^{13}C NMR spectrum (in C_6D_6) corroborates the proposed structure, showing three sp^2 carbon doublets (δ_C 161.3, 143.8 and 142.3 (ref. TMS), J_{PC} 22, 13 and 25 Hz, resp.), a N-CH_3 singlet (δ_C 48.2) and two doublets from P-Et (δ_C 20.9 and 9.9, J_{PC} 10 and 13 Hz, resp.).

Diphenylchlorophosphine (1e) reacted similarly with N-methylpropargylamine to give (2e) (δ_P 66.9 in ether) which quickly rearranged to (4e) (δ_P -28.3 in ether). The structural similarity of (4e) to (4d) is shown by the low-field

signal from an imine CH proton (δ_H 8.77) and the narrow N-CH_3 multiplet signal, but a full assignment of the ^{1}H NMR spectrum could not be made because the phenyl group signals partly covered the CH=CH signals. Addition of S_8 to (4e) gave (5e) (δ_P 69.8 in C_6D_6).

The rearrangement of (2d,e) to (4d,e) conceivably proceeds via addition of a proton and the phosphino group to the triple bond to give a cyclic phosphonium intermediate (I), followed by a base catalyzed elimination to give the product:



The weaker P-N bond, compared to a P-O bond,[10] could be the reason why the P-N bond i cleaved here, whereas the C-O bond is cleaved in the oxy analogues to give allenic products. Also, a P=O bond (in the allenic product) is stronger than a P=N bond (in a corresponding allenic product here).[10]

In accordance with the above mechanism only the more nucleophilic phosphines (2d,e) rearrange, and only Z-isomers (4d,e) are observed.

Work is in progress to establish the scope of this novel rearrangement and to find evidence for the postulated intermediate (I).

Experimental.

A solution of N-methylpropargylamine (10 mmol) in dry ether (2 ml) was added dropwise with stirring to a solution of the trivalent chloro phosphorus compound (1a-e) (10 mmol) and triethylamine (12 mmol) in ether (50 ml) at 0-5° under nitrogen. After 1 h the suspension was filtered and the solvent removed in vacuo to give the crude propargylamino product (2a-d) or the rearranged product (4e). Addition of S_8 to the ether solution and refluxing for 0.5 h followed by evaporation of the solvent gave crude (3a-d) or (5e) which in part was purified by vacuum distillation (3a,b) or recryst. from pentane (3c). (3a): 30% yield, b.p. 71-72°/0.5 mm Hg, δ_P 75.3, δ_H 2.81 (NCH_3, d, $^3J_{PH}$ 10.4 Hz), 2.26

(≡CH, t, $^4J_{HH}$ 2.4 Hz) in $CDCl_3$. (3b): 40% yield, b.p. 114-115°/0.5 mm Hg, δ_P 82.3, δ_H 4.05 (CH_2, dd, $^3J_{PH}$ 13.3, $^4J_{HH}$ 2.4 Hz), 2.88 (NCH_3, d, $^3J_{PH}$ 11.1 Hz), 2.32, (≡CH, t, $^4J_{HH}$ 2.4 Hz), 1.55 and 1.43 (CCH_3, s) in $CDCl_3$. (3c): 40% yield, m.p. 26.5-27°, δ_P 81.4, δ_H 3.96 (CH_2, dd, $^3J_{PH}$ 11.7, $^4J_{HH}$ 2.4 Hz), 2.78 (NCH_3, d, $^3J_{PH}$ 9.8 Hz), 2.65 (Me_2N, d, $^3J_{PH}$ 11.7 Hz), 2.27 (≡CH, t, $^4J_{HH}$ 2.4 Hz) in $CDCl_3$. In the case of (2d), the filtered ether solution was kept overnight at room temperature and then evaporated to give the crude, rearranged product (4d) which was purified by vacuum distillation (40% yield, b.p. 40-41°/0.5 mm Hg). Full ^1H NMR data for (4d): δ_H 8.78 (CH=N, dddq, $^4J_{PH}$ 3.7, $^4J_{HH}$ 0.9, $^3J_{HH}$ 8.9 and 1.7 Hz), 6.99 (C=CH-C, ddd, $^3J_{PH}$ 19.3, $^3J_{HH}$ 8.9 and 11.8 Hz), 6.05 (P-CH=C, dddq, $^2J_{PH}$ 5.1, $^6J_{HH}$ 0.6, $^4J_{HH}$ 0.9, $^3J_{HH}$ 11.8 Hz), 3.23 (NCH_3, ddd, $^6J_{PH}$ 0.4, $^6J_{HH}$ 0.6, $^4J_{HH}$ 1.7 Hz) in C_6D_6.

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