Unusual Properties of Chloro- and Amino-phosphines in the 7-Phosphanorbornene Series

Louis D. Quin* and Jerzy Szewczyk

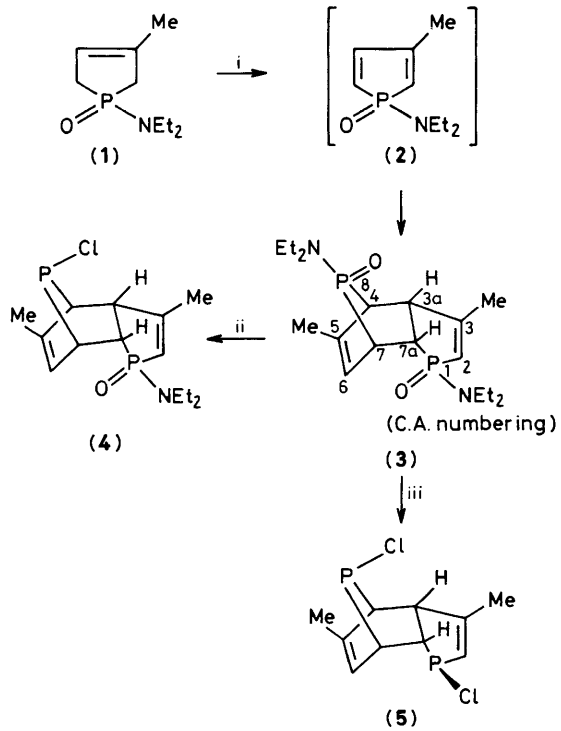
Duke University, Department of Chemistry, Durham, North Carolina 27706, U.S.A.

Phosphinamides based on the 7-phosphanorbornene framework can be reduced with $HSiCl_3$–C_5H_5N to give phosphinous chlorides which have remarkable chemical and ^{31}P n.m.r. properties and a strong preference for an *anti*-configuration of chlorine.

The first phosphanorbornenes with a *P*-chloro substituent (phosphinous chlorides) have been prepared by a new method and found to have quite unexpected properties. These are derived from the presence of severe bond angle contraction at P, along with the forced proximity of non-bonding orbitals; together these effects can be of considerable importance in phosphorus chemistry, as has been documented recently for tertiary phosphines.[1]

Dimers of phosphole oxides represent the most readily accessible compounds with the 7-phosphanorbornene structure. We have used the single dimer (**3**) from the phosphole derivative (**2**) [from (**1**), Scheme 1] as a precursor of a phosphinous chloride, employing the one-step reaction with trichlorosilane that we are reporting elsewhere.[2] The reaction with (**3**) was specific at the 7-phosphanobornene position (P-8), and gave only one diastereoisomer (**4**) that was isolated as a solid in 55—60% yield. With twice the amount of trichlorosilane and pyridine, conversion was complete into the bis(phosphinous chloride) (**5**).

Compound (**4**) is remarkable in its resistance to hydrolysis; it is not immediately affected on placement in water and survives chromatography on alumina. It gave satisfactory C, H, and P analyses and exact mass (M^+, *m/z* calc. 317.0866; found 317.0864). Remarkable also is the resistance to oxygen (no change after 5 days' exposure to air) and sulphur (in benzene, 5 days).



Scheme 1. *Reagents:* i, Br_2, Et_3N; ii, $HSiCl_3$ (1 equiv.), C_5H_5N (3 equiv.), C_6H_6, reflux; iii, $HSiCl_3$ (2 equiv.), C_5H_5N (6 equiv.), heat.

We have assigned the *anti*-configuration (*syn* and *anti* refer to the relation to the 5,6 double bond) to (**4**) because the ^{31}P n.m.r. spectrum has the expected two signals for the two ^{31}P nuclei, but shows *no coupling*. In tertiary phosphines in this series, $^3J_{PP}$ is sizeable (25 Hz) for the phosphine with *syn*-configuration but negligible (1—2 Hz) for the *anti*-isomer.[1] However, we have not yet found a way to prepare the other (*syn*) isomer of (**4**) to confirm that it has a large value for $^3J_{PP}$. Stereospecific ^{13}C n.m.r. features support the assignment; the couplings of P-8 to C-5 (δ 138.9) and C-6 (δ 126.5) are quite large (25.2 and 24.2 Hz, respectively) and consistent with the general observation[3] that $^2J_{PC}$ in phosphorus(III) forms is large when the lone pair is close to the carbon, and may be negligible when remote.[1]

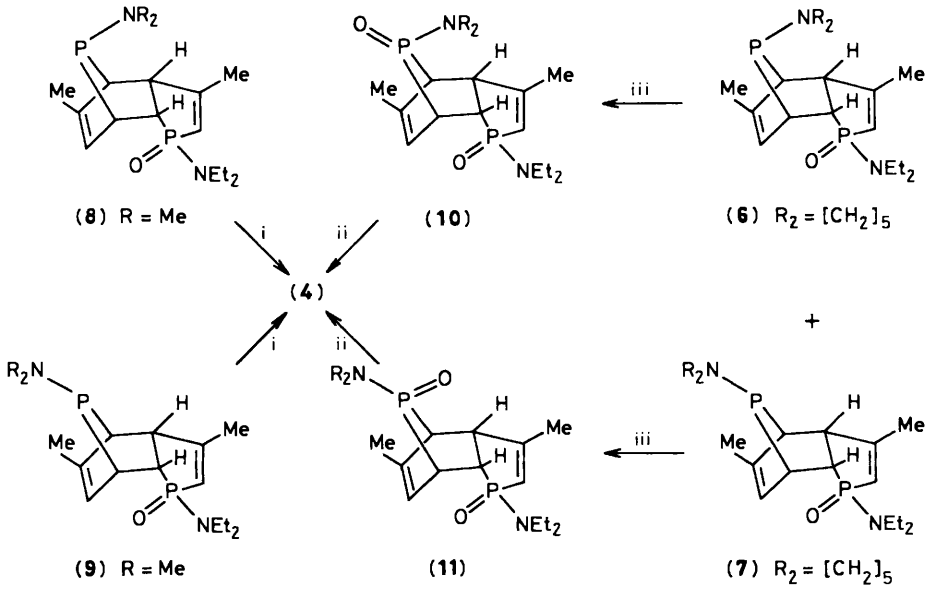
The bis(phosphinous chloride) (**5**) is less stable and not readily purified. Its n.m.r. properties support the *anti*-structure at P-8. At P-1 the configuration shown is suggested by the ^2J(P-1, C) value for C-7; as in the related phosphines of known geometry, the value is quite large (either 31.9 or 28.6 Hz in a d of d, δ 47.1) from proximity of the lone pair.[1] If the stereochemical structures of the amide (**3**) and its products are correct as shown,[4] then the reduction at P-8 is suggested to occur specifically with *inversion*, and that at P-1 specifically with *retention*.

The reactions of Scheme 2 reveal further peculiarities. The displacement of chlorine from (**4**) with secondary amines occurred largely with retention [e.g., piperidine in benzene, 25 °C, 2 days, gave 80% of (**7**) and 20% of (**6**) as determined by ^{31}P n.m.r. spectra of the crude product; sulphides gave satisfactory C, H, and P analyses]; inversion had been expected since this was the result of benzylamine attack on a 1-chlorophosphetane.[5] Both aminophosphines (**8**) and (**9**) reacted with anhydrous HCl to give only (**4**), which was also the sole product (as seen by ^{31}P n.m.r.) when the $HSiCl_3$–C_5H_5N reduction was applied to either phosphinamide (**10**) or (**11**).

Table 1. ^{31}P N.m.r. spectra.[a]

Compound	δ(P-8)	δ(P-1)	$^3J_{PP}$/Hz
(**3**)	82.5	62.0	41.5
(**4**)	43.6	57.1	~0
(**5**)	54.5	124.3	7.3
(**6**)	87.4	54.9	5.0
(**7**)	159.0	65.6	48.9
(**8**)	88.9	61.2	3.9
(**9**)	163.0	65.0	48.8
(**10**)	80.5	62.2	36.6
(**11**)	79.7	61.2	41.5

[a] Proton decoupled, Fourier transform mode on a JEOL FX-90Q spectrometer, in $CDCl_3$. All shifts are positive and downfield of 85% H_3PO_4.



Scheme 2. *Reagents:* i, dry HCl, 0 °C; ii, $HSiCl_3$ (1 equiv.), C_5H_5N (3 equiv.), C_6H_6, reflux; iii, Bu^tOOH, $CHCl_3$, 0—5 °C for (**6**)—(**7**) mixture, fractional crystallization.

The ^{31}P n.m.r. features of the aminophosphines [*e.g.*, (**6**) and (**7**), Table 1] are remarkable and resemble those of the related tertiary phosphines, where only the *syn*-isomer shows strong three-bond coupling and has a shift some 70 p.p.m. downfield of the *anti*-isomer, into a region in which other members of the family do not show resonances. The *anti*-isomers are also deshielded relative to other phosphines, but not as strongly. The phosphinous chlorides (**4**) and (**5**), however, give the opposite result of having ^{31}P shifts for P-8 (Table 1) that are some 70—80 p.p.m. *upfield* of monocyclic models [*cf.* $\delta(^{31}P)$ +125.5 p.p.m. for 1-chloro-3-methyl-1,5-dihydro-3-phosphole[2]]. The lone-pair repulsion with the π-electrons[1a] may be involved in this effect, but the electrophilic character at P-8, introduced with the chlorine substituent, may permit an interaction with the π-electrons that transfers electron density into the d-orbitals, providing a shielding effect. Such an explanation is attractive in accounting for the reduced reactivity to nucleophiles and oxidizing agents, and the remarkable driving force to attain the *anti*-stereochemistry. There is a resemblance to homoallylic participation in *anti*-norbornen-7-yl derivatives in this suggestion, except that we deal with a ground state.

We thank the U.S. Army Research Office for support of this work.

Received, 6th July, 1984; Com. 969

References

1 (a) K. C. Caster and L. D. Quin, *Tetrahedron Lett.*, 1983, **24**, 5831; (b) L. D. Quin, K. C. Caster, and J. C. Kisalus, *Phosphorus Sulfur*, 1983, **18**, 105.
2 L. D. Quin and J. Szewczyk, *Phosphorus Sulfur*, in the press.
3 L. D. Quin, 'The Heterocyclic Chemistry of Phosphorus,' Wiley-Interscience, New York, 1981, ch. 6.
4 The structure of (**3**) is based on the *X*-ray analysis for the single dimer formed from the *P*-ethoxy analogue of (**2**): Y.-Y. H. Chiu and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1969, **91**, 4150. *X*-Ray analysis of (**4**) has been attempted, but the crystals proved to be unsatisfactory for this purpose.
5 J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 1972, 713; see also O. Dahl, *Phosphorus Sulfur*, 1983, **18**, 201.