Surprising Reactivity of Very Crowded Phosphinic Derivatives

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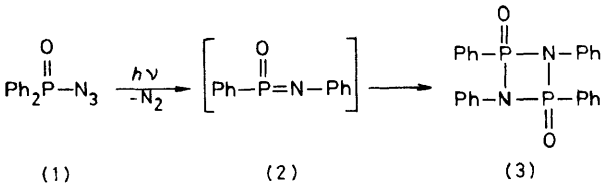
Summary An example of intramolecular cyclisation of a crowded phosphinic chloride *via* loss of hydrogen chloride and formation of a phosphorus–carbon bond is described; unexpected cleavage of an acyclic phosphorus–carbon bond is also reported.

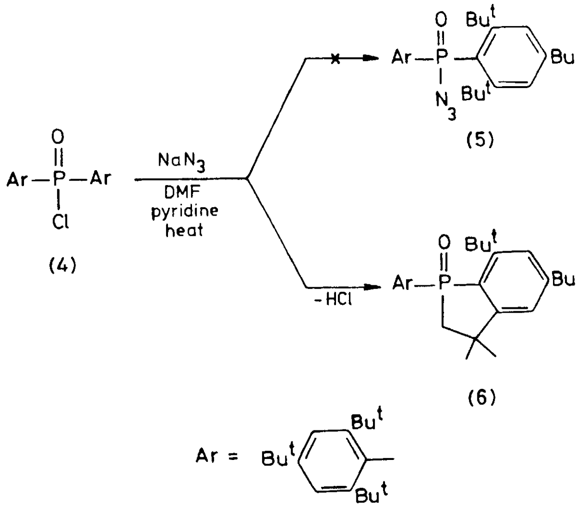
In a recent paper,[1] we reported the photolysis of the oxide of diphenylphosphinyl azide (**1**) which leads unequivocally to the iminophosphine oxide (**2**), a new three co-ordinate pentavalent organophophorus compound. However, this unusually hybridized phosphorus derivative had a very short lifetime and in the absence of trapping agent it gave diphosphadiazetidine (**3**) and polymers.

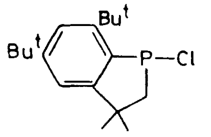

(1) (2) (3)

In order to prevent such a head-to-tail dimerization, we tried to synthesize a very crowded azide, bis(2,4,6-tri-t-butylphenyl)phosphinyl azide (**5**) from the corresponding chloride (**4**)[2,3] and sodium azide.

In pyridine–benzene solution, under reflux, no reaction occurred because of the large steric hindrance. In *NN*-

dimethylformamide-pyridine solvent, under reflux, the formation of the expected azide (**5**) was not observed either but, surprisingly, a cyclic phosphinic derivative (**6**) was obtained in 80% yield.[4]

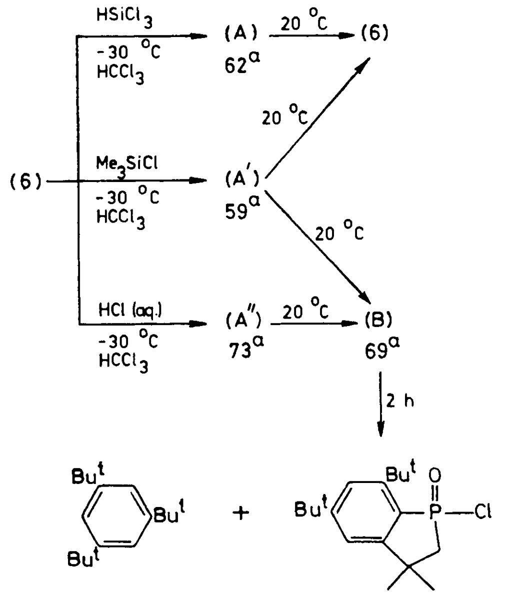




(**7′**) (see ref. 4)

Compound (**6**) (m.p. 171 °C) was purified by chromatography on silica gel and its structure was determined by spectroscopy: $\nu_{P=O}$ 1185 cm^{-1}; M^+ = 536; $\delta(^{31}P)$ + 54 p.p.m.; $\delta(^1H)$ (250 MHz) 0·82, 0·90, 1·36, 1·37, and 1·67 (5 × s, 5 Bu^t), 1·35 (d-like, CH_3) and 1·45 (d, CH_3, J_{P-H} 5 Hz), 2·80 (t-like, CH_2, A of H_AH_BP system, $J_{AB} = J_{AP} = 15$ Hz) and 3·14 (d of d, CH_2, B of H_AH_BP system, J_{BP} 8 Hz), and 7·5 (m, 4 arom-H); $\delta(^{13}C)$ (62·86 MHz) 31·02, 31·17, 31·80, 33·27, and 34·06 [5 × s, 5 C(CH$_3$)], 27·50 (d, CH_3, J_{P-C} 13 Hz) and 38·00 (s-like, CH_3), 44·01 (d, CH_2, J_{P-C} 68 Hz), 129·47 (d, *ipso*-C, J_{P-C} 64 Hz), 131·95 (d, *ipso*-C, J_{P-C} 55 Hz), and 157·25 (d, *meta*-arom-C, J_{P-C} 29 Hz).

If the reaction leading to (**6**) is surprising, the reactivity of this cyclic derivative is also unusual.



(**8**) (**7**)

a $\delta(^{31}P)$ value in p.p.m. measured in $CHCl_3$.

It seems that the addition of polarized chloride compounds to (**6**) gives rise to a complex (A). Depending on the nature of the reagent, this complex gives again the starting material or leads to a new derivative (B), not yet isolated. Finally, 2,4,6-tri-t-butylbenzene (**8**) and the cyclic phosphinic chloride (**7**) (m.p.: 223—225 °C) were isolated and identified by spectroscopy: (**7**) $\nu_{P=O}$ 1170 cm^{-1}; c.i.m.s. $M + 1 = 327$; $\delta(^{31}P)$ + 66 p.p.m.; $\delta(^1H)$ (250 MHz) 1·40 (s, Bu^t) and 1·65 (s, Bu^t), 1·52 (s-like, CH_3) and 1·56 (d, CH_3, J_{P-H} 2 Hz), 2·60 (t-like, CH_2, A of H_AH_BP system, $J_{AB} = J_{AP} = J_{BP} =$ 15 Hz) and 2·73 (t-like, CH_2, B of H_AH_BP system), and 7·6 (m, 2 arom-H); $\delta(^{13}C)$ (62·86 MHz) 31·12 [s, C(CH$_3$)] and 31·70 [s, C(CH_3)], 45·07 (d, CH_2, J_{P-C} 84 Hz) and 126·10 p.p.m. (d, *ipso*-C, J_{P-C} 110 Hz).

(*Received*, 18*th August* 1981; *Com.* 1008.)

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[1] G. Bertrand, J. P. Majoral, and A. Baceiredo, *Tetrahedron Lett.*, 1980, 5015.

[2] M. Yoshifuji, I. Shima, and N. Inamoto, *Tetrahedron Lett.*, 1979, 3963.

[3] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *Angew. Chem., Int. Ed. Engl.* 1980, **19**, 399.

[4] J. P. Majoral, G. Bertrand, A. Baceiredo, and P. Mazerolles, International Conference on Phosphorus Chemistry, Durham (North Carolina), 1—5 June 1981. An analogous intramolecular cyclisation from 2,4,6-tri-t-butyldichlorophosphine affording compound (**7′**) was described at the same congress by M. Yoshifuji, I. Shima, and N. Inamoto.