Tetrahedron Letters No.55, pp. 5799-5802, 1968. Pergamon Press. Printed in Great Britain.

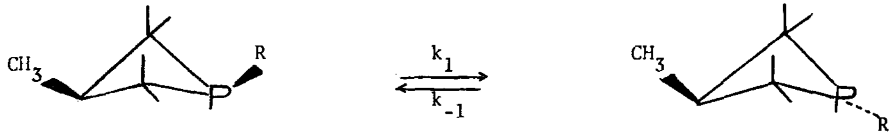
PYRAMIDAL INVERSION IN SUBSTITUTED PHOSPHETANES

Sheldon E. Cremer, Robert J. Chorvat, C. H. Chang, and Donald W. Davis
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616

(Received in USA 11 April; received in UK for publication 15 October 1968)

Although the rate of inversion about nitrogen in tertiary amines is generally rapid and must be studied by low temperature nmr techniques (1), corresponding inversion about phosphorus is comparatively slow (2); indeed, optically active phosphines have been prepared and are stable to racemization at room temperature (2b-d). However, at elevated temperatures stereomutation in phosphorus compounds has been observed and some limited quantitative studies carried out. One such study was reported by Horner (2a) on methyl-n-propylphenylphosphine; at 130° (decalin) the halflife was 5 hr. and the activation energy 28.6 kcal/mole. A second study on a diphosphine was recently disclosed by Lambert (3) who found the inversion barrier to be about 26 kcal/mole.

We now wish to report the quantitative results (Table I) for inversion in 1-phenyl-2,2,3,4,4-pentamethylphosphetane (I) (4) and 1-t-butyl-2,2,3,4,4-pentamethylphosphetane (II) (5). That thermal interconversion occurred at all was initially surprising in view of the stability exhibited by 1-methyl-4-ethyl-4-phosphorinanol (6a) and substituted 1,3,2-dioxaphospholanes (6b) and the fact that constraint by a small ring increases the barrier in aziridine (1b) and azetidine (1c) relative to their 5- or 6-membered homologues.



Ia (cis); R = Ph
IIa (cis); R = t-C_4H_9
IIIa (cis); R = CH_3

Ib (trans); R = Ph
IIb (trans); R = t-C_4H_9
IIIb (trans); R = CH_3

TABLE I

Compound I[a]			Compound II[b]		
T(°C)	$k_1 \times 10^6$ sec^{-1}	k_1/k_{-1}	T(°C)	$k_1 \times 10^5$ sec^{-1}	k_1/k_{-1}
112.0	1.65 ± .11	1.51	118.8	2.65 ± .03	1.31
143.2	41.2 ± .17	1.49	131.6	9.83 ± .01	1.30
165.4	2.66×10^2 ± .15	1.48	145.0	27.6 ± .22	1.29
190.2	1.66×10^3 ± .06	1.40	157.0	75.1 ± .12	1.23

(a) $I_a \rightarrow I_b$: $\Delta H^{\ddagger} = 29.8 \pm .1$ kcal/mole, $\Delta S^{\ddagger} = -8$ e.u.

(b) $II_a \rightarrow II_b$: $\Delta H^{\ddagger} = 28.2 \pm .9$ kcal/mole, $\Delta S^{\ddagger} = -8$ e.u.

In contrast to the facile inversion observed for II, the 1-methyl derivative, III, showed no measurable amount of inversion even after 4 days at 162°. Hence, a clear steric factor seems to be operative in the t-butyl derivative due to nonbonded interactions with the adjacent methyl groups in the ring. A similar steric effect has been observed in the case of 1-t-butylaziridine (1a).

The explanation for pyramidal inversion in I is more complex and several factors may be involved. Indeed, Anet has considered the importance of steric, inductive, conjugative, and electrostatic (or electron repulsion) effects upon the rate of nitrogen inversion (7). In the case of the 1-phenyl derivative the possibility of either p_π-p_π or d_π-p_π overlap in the transition state may serve to lower the energy barrier for interconversion of the isomers. Basicity measurements, ultraviolet data, and dipole moment studies (8) indicate the former type of bonding to be present in aromatic phosphines; the amount of delocalization, however, is much less than in the nitrogen counterpart. The latter type of bonding has been invoked to explain the stereomutation in diphosphines (3). Recently, Schiemenz has provided experimental evidence for both the donor (p_π-p_π) and acceptor (d_π-p_π) properties of trivalent phosphorus (9).

Although the above bonding possibilities may account for the process Ia $\rightleftarrows$ Ib, a definitive explanation must await further experimental work.

Acknowledgment. - The authors are grateful to the National Cancer Institute for Public Health Service Grant CA-07806, which supported this investigation.

REFERENCES

1. (a) S. J. Brois, J. Am. Chem. Soc., **89**, 4242 (1967) and references cited therein; for exceptions to rapid inversion see S. J. Brois, ibid., **90**, 508 (1968) and R. S. Atkinson, Chem. Commun., 676 (1968); (b) A. T. Bottini and J. D. Roberts, J. Am. Chem. Soc., **80**, 5203 (1958); (c) J. M.Lehn and J. Wagner, Chem. Commun., 148 (1968).
2. (a) L. Horner and H. Winkler, Tetrahedron Letters, 461 (1964); (b) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, ibid., 161 (1961); (c) W. E. McEwen, "Topics in Phosphorus Chemistry", Vol. 2, M. Grayson and E. J. Griffith, Ed., J. Wiley and Sons, New York, N.Y., 1965, pp 17-23; (d) L. Horner, Pure and Applied Chem., **9**, 225 (1964).
3. J. B. Lambert and D. C. Mueller, J. Am. Chem. Soc., **88**, 3669 (1966).
4. For the synthesis and tentative stereochemical assignment of this system see S. E. Cremer and R. J. Chorvat, J. Org. Chem., **32**, 4066 (1967). The cis geometry of Ia was recently substantiated by preliminary X-ray work carried out by Prof. L. M. Trefonas on the methyl bromide salt. It is assumed that quaternization goes with retention of configuration (2b). The distinct separation of the ring protons in the nmr of Ia and Ib was used to follow their relative proportion in the equilibrium and rate studies; the isomers are not interconvertible at 25°. The kinetic measurements were carried out on neat samples of I and II in evacuated glass tubes.

5. The preparation of II was achieved by treatment of the phosphinic acid chloride (J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962)) with *t*-butyllithium at 0° followed by trichlorosilane reduction of the resultant oxide. The stereochemical assignment is tentative and was made on the basis of nmr analogy to the splitting pattern and chemical shift of Ia and Ib.

6. (a) L. D. Quin and H. E. Shook, Jr., *Tetrahedron Letters*, 2193 (1965); see also, H. E. Shook, Jr., and L. D. Quin, *J. Am. Chem. Soc.*, **89**, 1841 (1967); (b) B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966).

7. F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 357 (1967); for calculations of inversion barriers in pyramidal species see G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967).

8. R. F. Hudson, "Organo-Phosphorus Chemistry", Academic Press, London and New York, 1965, Chapter 2; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier Publishing Co., Amsterdam, London, and New York, 1967, Chapter 1.

9. G. P. Schiemenz, *Angew. Chem. internat. edit.*, **4**, 603 and 1093 (1965).