

ISOPHOSPHINDOLE P-OXIDE, A REACTIVE INTERMEDIATE

T. H. Chan* and K. T. Nwe

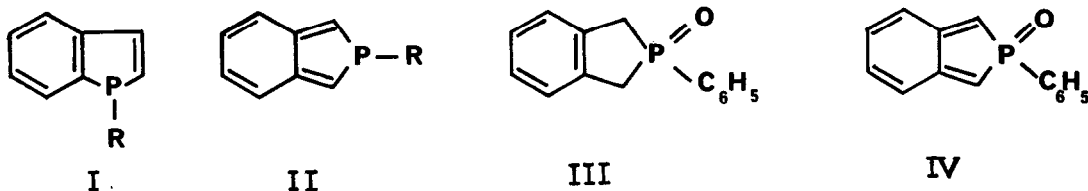
Department of Chemistry

McGill University,

Montreal, Canada.

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A comparison of the chemistry of phosphindole (I) with the isoconjugated isomer isophosphindole (II) is of interest. Recent work on the phosphindole system indicated¹ that there is considerable p_{π} - p_{π} overlap between the phosphorus lone pair and the unsaturated system. The energy barrier to the phosphorus pyramidal inversion was found to be much lower than normal phosphines.² There is however virtually nothing known about the iso-phosphindole system.³ Our recent synthesis of 2-phenylisophosphindoline 2-oxide (III)⁴ led us to consider the conversion of III into the corresponding isophosphindole (IV).



Bromination of III⁴ with N-bromosuccinimide (1 mole) and catalytic amount of benzoyl peroxide in refluxing benzene for 12 h gave stereospecifically r-1-bromo-t-2-phenylisophosphindoline 2-oxide (V) as the only mono-brominated product (50% yield) after preparative layer chromatography (silica gel). Also isolated as minor products were 1,1-dibromo- (VI), trans-1,3-dibromo- (VII) as well as r-1,c-3-dibromo-t-2-phenyliso-phosphindoline 2-oxide (VIII). Structural determination was facilitated

greatly by mass spectrometry and nmr spectroscopy. Careful examination of the nmr spectra allowed the stereochemistry of V and VIII to be assigned. The assignment is based on two considerations. First, there is the shielding effect of the phenyl ring.⁵ Secondly, the magnitude of the geminal $^2J(\text{P-C-H})$ coupling constants depends on the orientation of the phosphoryl group in the same manner as its dependence on the phosphorus lone pair orientation.^{6,7} This leads to the consistent observation that the hydrogen cis to the phenyl ring is always at a higher field and has a smaller $^2J(\text{P-C-H})$ coupling constant (Table I).

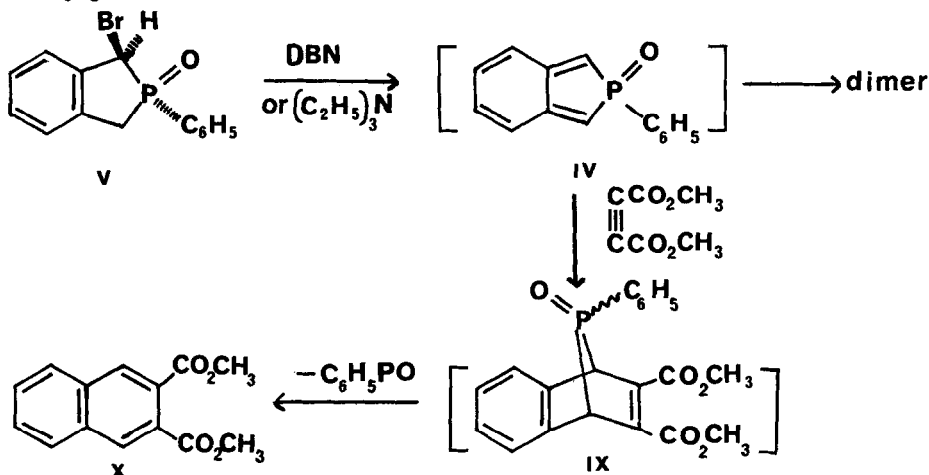
	III	VI	V	VII	VIII
δ_{H_a} ($^2J(\text{P-C-H}_a)$)	3.51 (16)	3.59 (17)	3.59 (17)		
δ_{H_b} ($^2J(\text{P-C-H}_b)$)	3.35 (9)	3.36 (9)	3.36 (9)		
$\delta_{\text{H}_{a'}}$ ($^2J(\text{P-C-H}_{a'})$)				5.6 (10)	
$\delta_{\text{H}_{b'}}$ ($^2J(\text{P-C-H}_{b'})$)			5.2 (2)	5.3 (2.5)	5.2 (2)

Table I: The chemical shifts (δ , in ppm) and geminal coupling constants (in hertz) of benzylic protons of some isophosphindolines.

Treatment of V with either 1,5-diazabicyclo[3.4.0]nonene-5 (DBN) or triethylamine in refluxing benzene for several hours led to dehydrobromination and the formation of IV which however dimerized rapidly. The dimeric product was isolated as a hygroscopic colorless solid of m.p. 216-220° (decomp) in 62% yield.⁸

Support for the formation of IV was gained by trapping it with a

dienophile. Thus, when the dehydrobromination of V by triethylamine was carried out in the presence of dimethyl acetylenedicarboxylate, the major product obtained was found to be dimethyl 2,3-naphthalenedicarboxylate (X).⁹ The formation of X can only arise from the Diels-Alder adduct IX by extrusion of the C_6H_5PO moiety, a process which has been well documented.¹⁰⁻¹²



The reactivity of IV should be contrasted with that of P-oxide of I (R=phenyl) which has been characterised as a stable solid.¹ The chemical pattern is therefore in analogy with the indene-isoindene system.¹³

References and Notes

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3. A. Rauk, J. D. Andose, W. G. Frick, R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6507 (1971).
4. T. H. Chan and K. T. Nwe, *Phosphorus*, in press.
5. L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970).
6. J.-P. Albrand, D. Gagnaire, M. Picard and J.-B. Robert, *Tetrahedron Letters*, 4593 (1970); also *Chem. Comm.*, 1469 (1968).
7. Similar dependence of geminal $^2J_{C-C-H}$ coupling constants on the orientation of a polar group on carbon has been observed, J. A. Schwarcz and A. S. Perlin, *Can. J. Chem.*, **50**, 3667 (1972).
8. Spectroscopic data for the dimer: IR (KBr): 1210 cm^{-1} ($\nu_{P=O}$);

Nmr (CDCl₃): 7.0-7.8 (m, 14 H, Ar-H), 6.3 (m, 4 H, =C-H),
 5.3 (d or ³d, 1 H, J_{P-C-H}=22 hz), 3.8-4.2 (m, 2H), 3.4 (m, 1 H);
 mass spectrum: m/e=452⁺(M), 228 (C₁₄H₁₃PO);

Analysis: Found: C, 70.87; H, 5.12;
 Calcd: C, 71.48; H, 5.14 for C₂₈H₂₂P₂O₂·H₂O.

The nmr spectrum ruled out a symmetric structure for the dimer.

9. Spectroscopic data of X are identical with that of authentic sample obtained from the esterification of 2,3-naphthalenedicarboxylic acid.

Nmr (CDCl₃): δ 8.2 (s, 2 H); δ 7.7-8.0 (m, 2 H); δ 7.4-7.7 (m, 2 H);
 δ 3.98 (s, 6 H)

IR: ν_{C=O}=1720 cm⁻¹

10. E. H. Braye, W. Hubel and I. Caplier, J. Amer. Chem. Soc., 83, 4406 (1961).
11. F. B. Clarke III and F. H. Westheimer, ibid, 93, 4541 (1971).
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13. Isoindene has been postulated as a reactive intermediate and has been trapped as Diels-Alder adduct. See J. A. Berson and G. B. Asperin, Tetrahedron, 20, 2697 (1964).

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