

Selectivity in reactions of tricyclic phosphatranes : pseudo-equatorial nucleophilic attack on the trigonal bipyramidal configuration of phosphorus : X-ray crystal structure of [EtSP(OCH₂CH₂)₃]⁺BF₄⁻

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Selectivity in Reactions of Tricyclic Phosphatranes. Pseudo-equatorial Nucleophilic Attack on the Trigonal Bipyramidal Configuration of Phosphorus. X-Ray Crystal Structure of [EtSP(OCH₂CH₂)₃N]⁺BF₄⁻

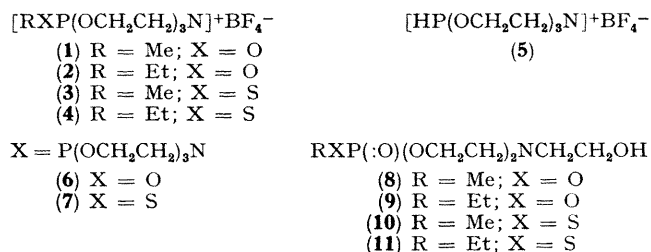
By D. VAN AKEN,* I. I. MERKELBACH, A. S. KOSTER, and H. M. BUCK

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Summary Reactions of tricyclic phosphatranes [RXP(OCH₂CH₂)₃N]⁺BF₄⁻; X = O, S and R = Me, Et, in which a transannular N → P bond brings phosphorus in a trigonal bipyramidal configuration, with nucleophiles (*e.g.* OH⁻) result exclusively in a nucleophilic attack on a pseudo-equatorial carbon atom, irrespective of the nature of the carbon atom in the apical ligand (XR).

FIVE-CO-ORDINATED phosphorus compounds are known to adopt the trigonal bipyramidal (TBP) configuration in which the apical positions are preferred by electron-withdrawing groups, whereas electron-donating groups are situated in equatorial positions.¹ In addition, the apical bonds are longer and weaker than the equatorial bonds causing apical entry and departure of groups.² Until now, little attention has been paid to reactions in which external nucleophiles discriminate between pseudo-equatorial and pseudo-apical carbon atoms in a TBP configuration. The observation of such selective reactions is hampered by the occurrence of pseudo-rotation which brings about ligand exchange in the trigonal bipyramid.³ In order to obtain a definite answer with respect to equatorial *vs.* apical reactivity for nucleophiles, we have synthesized the rigid tricyclic phosphatranes (1)–(4) in which a transannular N → P bond brings phosphorus in a TBP configuration. Previously, the characterization and molecular structure of the related

compound (5) was published by Verkade *et al.*^{4a} The molecular constraint which precludes intramolecular ligand exchange unambiguously ensures that the tricyclic compounds undergo nucleophilic attack exclusively at the pseudo-equatorial carbon atom, irrespective of the nature of the carbon atom situated in the apical ligand of the trigonal bipyramid (*vide infra*).



The compounds (1)–(4) were obtained by alkylation of the chalcogen atom of the corresponding bicyclic (thio)phosphate, (6) and (7), with trialkyloxonium tetrafluoroborate at -78 °C.⁵ All experimental evidence indicates that the structure of the O(S) alkylated compounds is a tricyclic cage (*N*-alkylation only is observed using alkyl iodide at higher temperature)^{4b}. In solution various n.m.r. methods confirm the presence of a P ← N bond.^{4b} The ³¹P

n m r shifts of (1)—(4) are considerably more upfield with respect to (6) and (7), in spite of the introduction of a positively charged group. This observation is a strong indication of the increase in co-ordination number of phosphorus. In the ^1H n m r spectra the signals of the exocyclic group are split into doublets owing to ^{31}P coupling, confirming the O(S) alkylation. Furthermore, ^{31}P coupling is observed for the CH_2N protons. This coupling is absent in the corresponding bicyclic analogues (6) and (7). Correspondingly, the CN signal in the ^{13}C n m r spectrum is also a singlet for the bicyclic compounds and a doublet for the tricyclic compounds. To verify the geometry, the structure of (4) was determined crystallographically.

Crystal data monoclinic, space group $P2_1/n$, $a = 8.457(9)$, $b = 18.268(13)$, $c = 9.358(5)$ Å, $\beta = 93.08(8)^\circ$, $D_m = 1.48$ g cm $^{-3}$, $D_c = 1.49$ g cm $^{-3}$, $Z = 4$. The structure was solved by direct methods using the MULTAN⁶ program. A computer drawing⁷ is given in the Figure. The configuration of phosphorus is indeed TBP with O—P—O angles near 120° , O—P—N angles of 85 — 87° , and O—P—S angles of 94 — 95° .

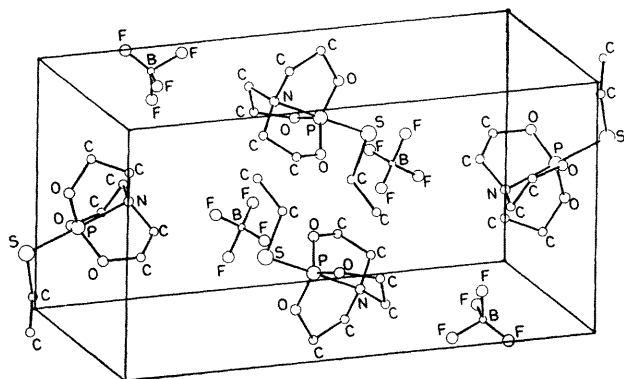


FIGURE ORTEP drawing of $[\text{EtSP}(\text{OCH}_2\text{CH}_2)_3\text{N}]^+\text{BF}_4^-$

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The S—P—N angle is 178° . The P—N bond length is 2.05 Å which is only slightly longer than the corresponding distance of 1.99 Å found in (5).^{4†}

With aqueous OH^- , compounds (1)—(4) react exclusively at the pseudo-equatorial carbon atom leading to the monocyclic products (8)—(11). In all products the ^{31}P couplings show that the bond of the exocyclic group linked to phosphorus is preserved [in (8), $J(\text{POCH}_2) = 11$ Hz and in (10), $J(\text{PSCH}_3) = 16$ Hz]. In addition, the resonances of the cage atoms are drastically changed. According to ^{31}P n m r spectroscopy, (8) and (9) are phosphates (δ ca 0 p p m), whereas (10) and (11) are thiophosphates (δ ca $+30$ p p m). Furthermore, the ^{13}C n m r spectra reveal that in the ring structure only two (equivalent) C(O) atoms show ^{31}P coupling [e.g. in (9) $\delta(\text{POCH}_2, \text{ring})$ 64.2 p p m, $J(\text{POCH}_2, \text{ring})$ 6 Hz, $\delta(\text{POCH}_2, \text{exo})$ 70.3 p p m, $J(\text{POCH}_2, \text{exo})$ 7 Hz]. In our opinion, the preference for pseudo-equatorial nucleophilic attack is an intrinsic property of the electronic configuration of the trigonal bipyramid. The dp π -bond (P=O) which is formed in the reaction is already developed to some extent for the equatorial oxygen atoms in the trigonal bipyramid owing to back-donation.¹ As a result, some electron density is transferred from the pseudo-equatorial carbon atoms to phosphorus rendering them more susceptible to nucleophilic attack. Since five-co-ordination is very widespread for group 4 and 5 elements as well as for transition metals, our model for pseudo-equatorial attack of nucleophiles might have a more generalized feature.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ E. L. Muetterties and R. A. Schunn, *Quart. Rev. Chem. Soc.*, 1966, **20**, 245, for a review, see R. Luckenbach, 'Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements,' G. Thieme, Stuttgart, 1973.

² D. Marquarding, F. Ramirez, I. Ugi, and P. Gillespie, *Angew. Chem.*, 1973, **85**, 99.

³ I. Ugi and F. Ramirez, *Chem. Ber.*, 1972, **8**, 198, J. I. Musher, *J. Chem. Educ.*, 1974, **51**, 94.

⁴ (a) J. C. Clardy, D. S. Milbrath, J. P. Springer, and J. G. Verkade, *J. Am. Chem. Soc.*, 1976, **98**, 623, (b) D. S. Milbrath and J. G. Verkade, *ibid.*, 1977, **99**, 6607.

⁵ M. Murray, R. Schmutzler, E. Grundemann, and H. Teichmann, *J. Chem. Soc. (B)*, 1971, 1714.

⁶ P. Main, S. E. Hull, L. Lessinger, G. German, J. P. De Clerq, and M. M. Woolson, MULTAN 78, Dept. of Physics, University of York, York, England.

⁷ C. Johnson, 'ORTEP, a Fortran Thermal-Ellipsoid Plot Program,' U.S. Atomic Energy Commission Report, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.