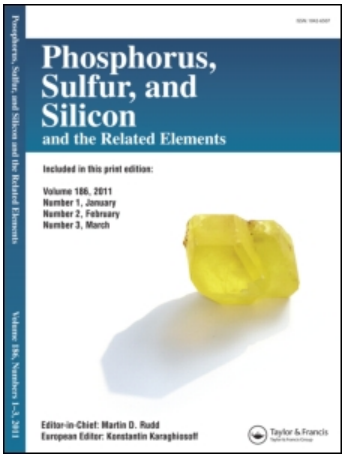

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Synthesis and Stereochemical Studies of 1-Phosphabicyclo[4.4.0]decane and 4-*t*-Butylphosphorinane Derivatives

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SYNTHESIS AND STEREOCHEMICAL STUDIES OF 1-PHOSPHABICYCLO (4.4.0)DECANE AND 4-t-BUTYLPHOSPHORINANE DERIVATIVES

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Abstract The title compounds and their derivatives have been prepared in good yield. Several of the synthetic steps are novel and have general applicability. Isomer assignments for these materials were based upon nmr and x-ray data. A two bond phosphorus-carbon coupling Karplus relation has been established for phosphines and applied to the systems under investigation. Extensive stereochemical studies were conducted. The conformational energy barrier in cis-"phosphadecalin" (2) was estimated to be 12.3-13.6 kcal/mol. Hydroxide ion attack on cis-phosphonium salt 5 went with retention at phosphorus, while cis or trans 4 proceeded with considerable inversion. Nucleophilic displacements on derivatives of phosphorinane generally went with inversion of configuration.

INTRODUCTION

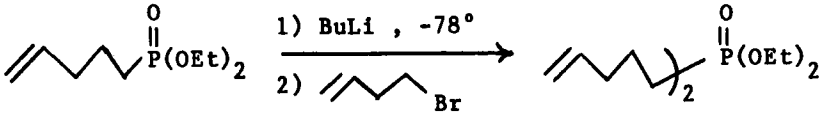
The stereochemical outcome of nucleophilic attack at phosphorus in phosphonium salts and in esters has been extensively investigated.[1] The results are dependent on the nucleophile, leaving group and substrate structure (acyclic and cyclic). Alkaline hydrolysis of methylethylphenylbenzyl phosphonium iodide goes with inversion[2], whereas benzyl substituted phosphetanium[3] and phospholanium[4] salts go with retention. Six-membered rings (benzyl leaving group) undergo less stereospecific hydrolysis.[5] Only a limited number of phosphinate esters have been subject to stereochemical study; acyclic esters proceed with inversion of configuration[6], whereas 4-membered heterocycles go with retention.[7] Five-and six ring phosphinate esters have not been studied.

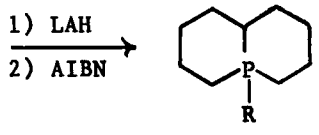
Herein we report results on the synthesis, configurational assignments, and stereochemical behavior of derivatives of the title compounds.

SYNTHESIS

The synthetic route to "phosphadecalin"(2) is shown(Scheme I). Alternate methods will be given including a convenient way of making secondary carbon to phosphorus bonds via tosylhydrazones.

Scheme I



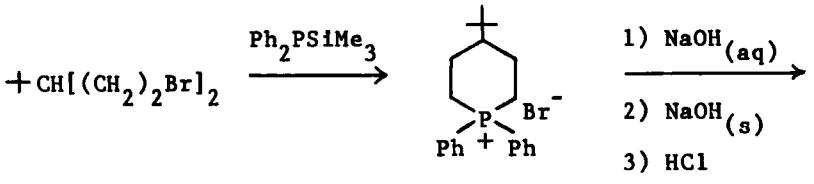


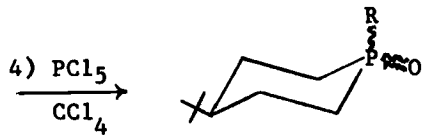
2) R = e⁻ pair 4) R = -OMe

3) R = =O 5) R = $-CH_2Ph$

The synthesis of acid chlorides 6a and 6b was achieved in high overall yield (Scheme II); these were converted to alkyl and arylphosphinate ester derivatives used for stereochemical studies.

Scheme II





6a	R = -Cl(cis)	80%
6b	R = -Cl(trans)	20%
7	R = -OMe	
8	R = -OPh	
9	R = -Ph	

10

ISOMER ASSIGNMENTS

Whereas trans-2 is in a locked conformation, cis-2 is conformationally mobile. The peak width of the ^{31}P peak (-45.2 ppm) of trans-2 was temperature invariant; that of cis-2(-30.4 ppm) broadened with decreasing temperature. A large body of ^{13}C nmr data was obtained for 2-5; assignments were made on the basis of symmetry, coupling constant size, and off-resonance experiments. Of special interest was the $^{2}JPCC$ coupling dependence on the dihedral angle. About sixty values were obtained from 18 isomeric sets (literature and this work) of various compounds; a Karplus relation was evident (maximum at 0-30°), and applied to cis and trans-2.

The isomer assignments for 6a and 6b were made using ^{13}C nmr shift values relative to 4-t-butyl-1-phenylphosphorinane 1-oxide (9) whose isomer assignment was made by x-ray.[8] The shifts of C-2 and C-4 in 6b and its derivatives are downfield relative to those in 6a; C-3 in 6b and its derivatives is more shielded than in 6a.

STEREOCHEMICAL RESULTS

Treatment of cis-4 with NaOH(MeOH/H_2O) gave 65-70% inversion. Base hydrolysis of various mixtures of cis and trans-4 was consistent with 100% inversion for the trans isomer. Isotopic studies (^{18}O) confirmed that P-O cleavage prevailed. The cis salt 5 gave predominent retention on treatment with NaOH/MeOH. A low-temp. nmr line shape analysis of cis-2 gave an activation energy barrier of about 12.3-13.6 kcal/mole.

In the acid chlorides 6a and 6b attack with CH_3O^-, PhO^-, and Ph^- went with inversion, as did transesterification reactions. In the methyl (7) or phenyl phosphinate (8) derivative of 6, equilibration of isomers could be attained:

$$\underset{30\%}{7(\text{trans})} \xrightleftharpoons{CH_3O^-} \underset{70\%}{7(\text{cis})} \qquad \underset{15\%}{8(\text{trans})} \xrightleftharpoons{PhO^-} \underset{85\%}{8(\text{cis})}$$

The axial preference of CH_3O or PhO is noteworthy. Also remarkable was the fact that 80:20 6a:6b gave only the cis-methyl phosphinate when treated with $AgNO_3$/MeOH.

The cis and trans isomers of 10 were prepared from the corresponding isomers of phenylphosphine oxide 9 by methylation with $(CH_3)_3O^+PF_6^-$. On treatment with water in acetonitrile both isomers gave retention of configuration at phosphorus. This contrasts with inversion of configuration on treatment with hydroxide ion.[9] In each case exclusive or predominant P-O bond cleavage occurred as supported by experiments using H_2O^{18}.

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