(35) Commercial copper(I) iodide (Ventron) was recrystallized from aqueous potassium iodide and then extracted with THF in a Soxhlet extractor for several hours. Copper iodide which was not purified in this way gave erratic results in this reaction. For preparation of lithium dimethylcuprate, commercial copper iodide was used with no purification.

(36) L. S. Minckler, A. S. Hussey, and R. H. Baker, *J. Am. Chem. Soc.*, **78**, 1009 (1956).
(37) L. A. Paquette and N. A. Nelson, *J. Org. Chem.*, **27**, 2272 (1962).
(38) For an explanation of this nomenclature, see J. A. Marshall and P. C. Johnson, *J. Org. Chem.*, **35**, 192 (1970).

Carbon–Phosphorus Heterocycles. A One-Step Synthesis of Phosphindolines and Phosphinolines. Cyclization of Diphenylalkenylphosphine Oxides with Polyphosphoric Acid[1]

M. El-Deek,[2] G. D. Macdonell, S. D. Venkataramu, and K. Darrell Berlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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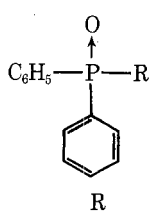
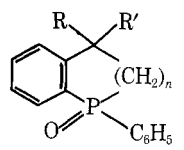
A convenient method of wide scope for the synthesis of phosphindoline and phosphinoline derivatives has been developed from the readily available starting materials. Cyclization of diphenylalkenylphosphine oxides occurred in the presence of 115% polyphosphoric acid (PPA) at 180 °C for 4 h to give C–P heterocyclic systems in modest to good yield (40–70%). Work-up of the reaction mixtures simply involved addition to ice–water. The resulting homogeneous solution was extracted with chloroform and dried; the solvent was evaporated under reduced pressure to yield the respective phosphindoline or phosphinoline. ^{1}H NMR, ^{31}P NMR, elemental, infrared, and mass spectral analyses supported the structure of these phosphorus analogues of the corresponding indole and tetrahydroquinoline heterocycles. This method of synthesis of phosphindoline and phosphinoline offers not only the merit of being simple and inexpensive but also a one-step and rapid process from appropriately substituted alkenyl (aryl) phosphine oxides.

In our studies directed toward the development of simple, new synthetic methods for the production of carbon–phosphorus heterocyclic compounds, we have investigated the possibility of cyclization of diphenylalkenylphosphine oxides in the presence of 115% polyphosphoric acid (PPA) as cyclizing agent. At present, reported pathways leading to the synthesis of phosphindoline or phosphinoline systems involve cyclization by intramolecular quaternization[3,4] and cyclization by cycloaddition of trivalent phosphorus compounds with a diene or diyne derivative.[5–7] Both methods usually employ very uncommon starting materials and long overall reaction times. The rare intermediates needed for the synthesis also limit their versatility. The ready availability of diphenylalkenylphosphine oxides **1a–g** encouraged us to investigate the possibility of their cyclization in the presence of PPA as the cyclizing agent. Certain oxides of **1** possess the correct functionality and geometry for cyclizations to give the corresponding phosphindoline and/or phosphinoline **2**. 3-Methyl-1-phenylphosphindoline 1-oxide (**2a**), which has been prepared from *o*-bromobenzoic acid through a long series of reactions (12 steps),[8] can be synthesized by the cyclization of diphenylallylphosphine oxide (**1a**) with PPA in one step.



R

	R
1a	$CH_2CH{=}CH_2$
b	$CH_2CH{=}CHCH_3$
c	$CH_2CH_2CH{=}CH_2$
d	$CH_2C(CH_3){=}CH_2$
e	$CH_2CH{=}C(CH_3)_2$
f	$CH(CH_3)CH{=}CH_2$
g	$CH(C_6H_5)CH{=}CH_2$



	R	R′	*n*
2a	H	CH_3	1
b	H	CH_3	2
c	CH_3	CH_3	1
d	CH_3	CH_3	2

Diphenylallylphosphine oxide can be obtained from chlorodiphenylphosphine and allyl alcohol in the presence of pyridine without the isolation of allyl diphenylphosphinite (**3**). The latter can be converted into oxide **1a** by heating

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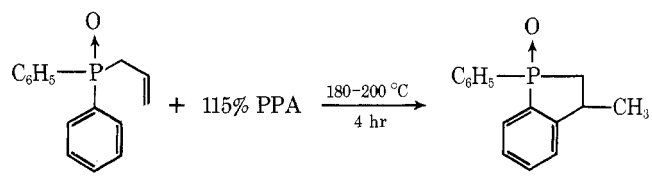
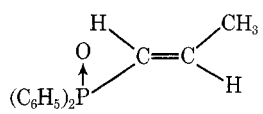
in situ at 140 °C.[9,10] In the presence of 115% PPA[11] at 180–200 °C for 4 h, the phosphine oxide **1a** underwent ring closure to 3-methyl-1-phenylphosphindoline 1-oxide (**2a**) in moderate yield (37%) along with a polymer. After 4 h,



1a **2a**

the reaction mixture was slowly poured into ice–water with stirring to give a homogeneous solution. Normal work-up gave a viscous yellow oil, which on distillation yielded pure **2a**. Oxide **2a** could be crystallized only with difficulty. In our attempts to optimize the reaction conditions, decreasing the reaction temperature to 120–150 °C gave the starting material *trans*-propenyldiphenylphosphine oxide[12] (**4**) and a polymeric product.



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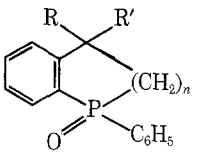
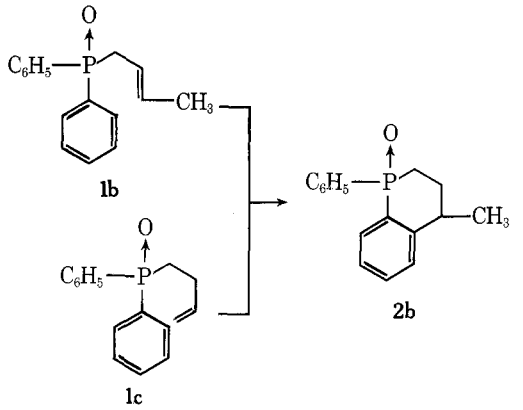
Interestingly, the phosphine oxides **1b** and **1c** also underwent ring closure to produce 1,2,3,4-tetrahydro-4-methyl-1-phenylphosphinoline 1-oxide (**2b**). Tentatively, one could assume that protonation had occurred at the β carbon in **1b** and at the δ carbon in **1c** to create a secondary cation. The second step could reasonably involve an elec-

Table I



Compd	R	R′	n	Mp, °C	Yield, %	Molecular formula	Anal, %		
							C	H	P
2a[a]	H	CH_3	1		37	$C_{15}H_{15}OP$			
2b	H	CH_3	2	105–115	70	$C_{16}H_{17}OP$	Calcd		12.1
							Found		12.08
2c	CH_3	CH_3	1	114–115	50	$C_{16}H_{17}OP$	Calcd 74.98	6.68	12.08
							Found 74.86	6.65	12.03
2d	CH_3	CH_3	2	99–101	40	$C_{17}H_{19}OP$	Calcd 75.53	7.08	11.45
							Found 75.39	6.90	11.45

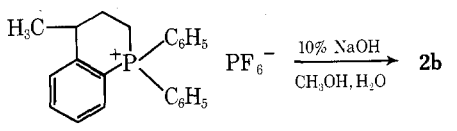
[a] This compound was previously reported in ref 8.



1c

trophilic attack on the benzene ring, followed by a proton loss to regenerate the aromatic ring. This postulated reaction mechanism has been recently supported by other work[13,14] which concerned the extensive study of the mechanism of alkenyl-substituted phosphonium salts by PPA. It was found that the reaction proceeded through a mechanism reminiscent of a cation alkylation process to give phosphinolinium systems and/or an isophosphinolinium salt, respectively.

Surprisingly, oxide **2b** could also be prepared in high yield from a base-cleavage reaction of 1,2,3,4-tetrahydro-4-methyl-1,1-diphenylphosphinolinium hexafluorophosphate (**5**).[14] This served as proof of structure for **2b.** Under



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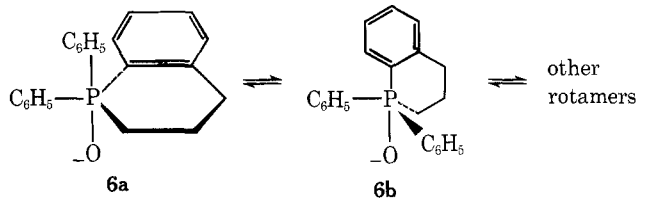
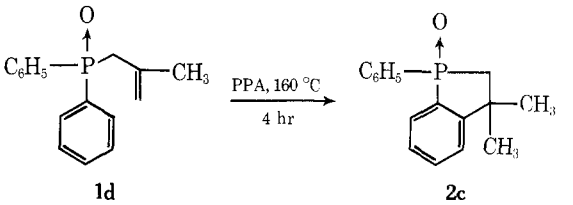
the conditions of cleavage employed, the phenyl group was lost, presumably expelled from the apical position of the postulated intermediate **6a** with no C–P ring opening ob-



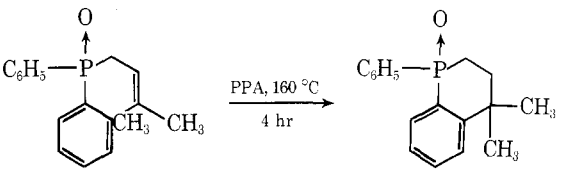
6a 6b

served. Marsi has suggested that an intermediate phosphorane generated from attack of a nucleophile on a system possessing a phosphorinane unit could have the CPC ring bonds diequatorially positioned.[15] The high yield of the ring-containing **2b** could result from a precursor rotamer like **6a** present in high concentration in an equilibrating system.

Similar cyclizations were performed with 2-methylallyldiphenylphosphine oxide (**1d**) and 3-methylbut-2-enyldiphenylphosphine oxide (**1e**) to give 3,3-dimethyl-1-phenylphosphindoline 1-oxide (**2c**) and 1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinoline 1-oxide (**2d**), respectively.

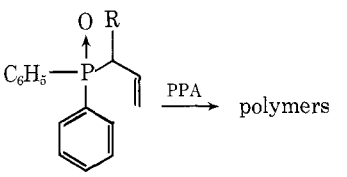


1d 2c



1e 2d

Again, cation stability may be one controlling factor in determining the ring size. Changing the position of the branch on the alkenyl group proved determinal. From 50 to 200 °C in the presence of 115% PPA, 1-methylallyldiphenylphosphine oxide (**1f**) and 1-phenylallyldiphenylphosphine oxide (**1g**) gave only polymeric compounds. Possibly,



1f, R = CH_3
g, R = C_6H_5

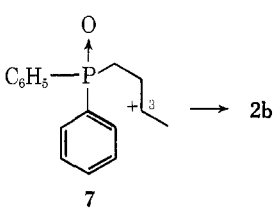
a steric factor involving an intermediate cation associated with $OPPA^{n-}$ may greatly decrease the rate of ring closure[13] but this must await a mechanistic study.

Structural identification of members of the phosphindoline and phosphinoline ring systems rests on elemental, infrared, mass spectral, and NMR analyses given in Tables I and II. The ^1H NMR spectrum of **2b** showed the methyl protons as two doublets (δ 1.32, 1.42 ppm, total 3 H). The observation of two doublets for the methyl proton signals almost assuredly arises from methyl groups in geometric isomers that form from attack of the ring from either face of the cation at C-3 in intermediate **7**. Thus, cis, trans iso-

Table II. NMR Spectral Data for the Starting Phosphine Oxides 1 and Reaction Products

Compd	Ir absorption spectra in KBr,[a] selected bands, cm^{-1}	^1H NMR spectral assignments, chemical shifts, δ [b]	^{31}P NMR, δ [c]
2b	1428 (s), 1176 (vs), 1114 (s), 904 (s), 809 (s), 727 (s), 704 (m)	1.32 [d (J_{HCCH} = OHz), trans CH_3] 1.42 [d (J_{HCCH} = OHz), cis CH_3] cis 45% and trans 55%, 3 H 1.62–2.84 [m, CH_2CH_2, 4 H] 2.88–3.40 [m, CH, 1 H] 7.05–7.84 [m, ArH, 9 H]	−23.54
2c	1428 (s), 1183 (vs), 1104 (s), 813 (vs), 769 (s), 740 (s), 680 (s)	1.44 [s, CH_3, 3 H] 1.56 [s, CH_3, 3 H] 2.04–2.60 [m, P-CH_2, 2 H] 7.20–7.80 [m, ArH, 9 H]	−46.68
2d	1428 (s), 1176 (vs), 1111 (s), 909 (s), 877 (s), 800 (vs), 769 (s)	1.38 [s, CH_3, 3 H] 1.42 [s, CH_3, 3 H] 1.80–2.60 [m, PCH_2CH_2, 4 H] 7.10–8.00 [m, ArH, 9 H]	−24.64
1b	1432 (s), 1183 (vs), 1122 (s), 1104 (s), 972 (vs), 738 (s), 719 (s), 693 (s)	1.40–1.72 [m, CH_3, 3 H] 3.06 [dd (J_{HCCH} = 6, J_{PCH} = 14 Hz, PCH_2, 2 H] 5.3–5.7 [m, CHCH, 2 H] 7.26–7.94 [m, $(C_6H_5)_2P$, 10 H]	−28.65
1c	1428 (s), 1164 (vs), 1113 (s), 1098 (s) 990 (s), 910 (m), 784 (s), 735 (s)	2.12–2.60 [m, PCH_2CH_2, 4 H] 4.86–5.19 [m, CH=CH_2, 2 H] 5.62–6.06 [m, CH=CH_2, 1 H] 7.30–7.69 [m, $(C_6H_5)_2P$, 10 H]	−30.35
1d	1626 (w), 1428 (s), 1183 (vs), 1136 (s), 900 (vs), 704 (s)	1.60–1.94 [m, CH_3, 3 H] 3.11 [d (J_{PCH} = 14 Hz), 2 H]; 4.60–4.94 [m, C=CH_2, 2 H] 7.26–7.98 [m, $(C_6H_5)_2P$, 10 H]	−27.59
1e	1666 (w), 1428 (s), 1219 (m), 1176 (vs), 1123 (s), 1031 (s), 740 (vs), 694 (vs)	1.45 [d (J_{HCCCH} = 3 Hz, trans CH_3, 3 H] 1.64 [d (J_{HCCCH} = 5 Hz, cis CH_3, 3 H] 3.09 [dd (J_{HCCH} = 7 Hz, J_{PCCH} = 14 Hz), PCH_2 4 H] 5.06–5.40 [m, CH=C, 1 H] 7.20–8.00 [m, $(C_6H_5)_2P$, 10 H]	−30.69
1f	1639 (w), 1428 (s), 1176 (vs), 1129 (s), 749 (s), 722 (vs), 699 (vs)	1.32 [dd (J_{HCCH} = 7, J_{PCCH} = 14 Hz, CH_3, 3 H] 2.90–3.50 [m, PCH, 1 H] 4.92–5.25 [m, CH=CH_2, 2 H] 5.62–6.12 [m, CH=CH_2, 1 H] 7.26–8.00 [m, $(C_6H_5)_2P$, 10 H]	−33.09

[a] The spectra were obtained on samples (4 mg) with KBr (400 mg) pellets. All compounds displayed strong absorption in the regions 1429–1432 and 1104–1129 cm^{-1} which has often been assigned to the C_6H_5–P bond. Many examples are reported to support the assignment ranges. See L. C. Thomas, "Interpretation of the Infrared Spectra of Organophosphorus Compounds", Heyden, London, 1974, Chapter 15. [b] Spectra obtained on $DCCl_3$ solution of each compound with Me_4Si as internal standard; peak positions quoted in the case of doublets are measured from the approximate center. [c] ^{31}P resonance is relative to 85% H_3PO_4. ^1H NMR spectra of **1a** was previously reported in ref 10, 18.



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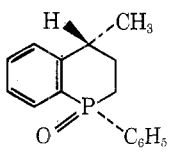
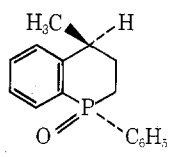
mers involving the methyl group with respect to the phosphoryl function could exist which would yield ^1H signals for two magnetically different methyl functions. In trans-



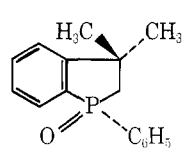
cis-**2b**



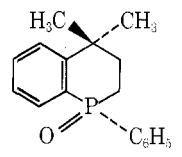
trans-**2d**

2b, the methyl protons might be expected to experience a deshielding effect due to the proximity of the oxygen atom of the phosphoryl group and hence could have a greater downfield chemical shift.[15] The relative intensities of the two signals indicate that about 45% of the cis form and 55% of the trans form were present in the $DCCl_3$ solution. There was also observed a J_{H_3CCH} of 7.0 Hz. The two methylene groups appear as a broad complex multiplet at δ 1.62–2.84 with apparently some long-range P–H coupling. Such NMR results are in accord with numerous studies available concerning the conformation of six-membered ring heterocyclic compounds containing phosphorus[16] or sulfur.[17]

The ^1H NMR spectrum of **2c** and **2d** showed the methyl protons as two singlets in each case. Conceivably, the deshielding effect of the oxygen of the phosphoryl group could cause the cis methyl group in **2c** to resonate at the lower field (δ 1.56 vs. 1.44) in **2d,** the signals are at δ 1.42 vs. 1.38.



2c

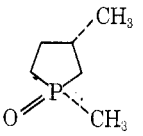


2d

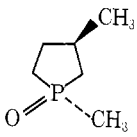
The negative ^{31}P chemical shift values for the open-chain phosphine oxides listed in Table II compare very well with those of many acyclic phosphine oxides.[18] For the 3-methylphosphindoline **2a,** two ^{31}P chemical shifts occur at −48.5 and −49.7 ppm. Substitution of the β proton by a methyl group as in **2c** also led to a deshielding effect (−46.7 ppm) at the phosphorus nucleus. Possibly, this extra deshielding could be attributed to steric crowding on the β carbon, which could result in modified bond angles about

the phosphorus. The phosphinolines **2b** and **2d** show the same effect but the difference is very small.

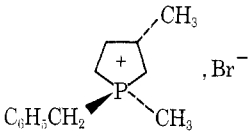
Some very recent work bears on this problem.[19,21] The identification of cis, trans isomers of 1,3-dimethylphospholane 1-oxide (**8**) included ^{31}P NMR values of −62.6 and −63.3 ppm (in C_6H_6).[19] Interestingly, the related salts **9** were reported to have identical values of −51.8 ppm.[19a] A mixture of phosphines **10a** and **10b** (precursors of **8a** and **8b**) has been reported[21] to display two signals (no proton decoupling) at +33.4 and 34.4 ppm but the assignment[19] of structure for each signal has not yet been accomplished. Recently, two isomers of **11** were separated[8] but ^{31}P NMR data were not included. ^1H NMR analysis revealed signals for CCH_3 protons centered at δ 1.45 and 1.53 but again individual structure assignments could not be made.



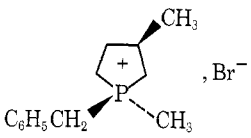
8a, mp 72–73.5 °C
(−62.6 ppm)



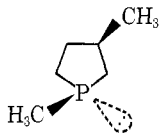
8b, mp 22 °C
(−63.3 ppm)



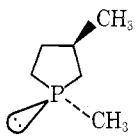
9a, mp 180–180.5 °C
(−51.8 ppm)



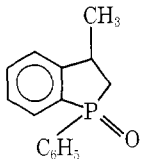
9b, mp 168.5–169.5 °C
(−51.8 ppm)



10a (bp 138.5°)

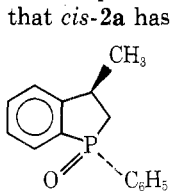


10b (bp 141°)

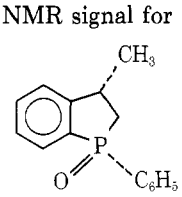


11

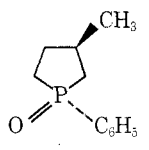
On the basis of proven structures **8a** and **8b**,[19b] we might conclude that *cis*-**2a** has the ^1H NMR signal for CH_3 protons that occur at δ 1.54 and *trans*-**2a** has the value at δ 1.45.[8] This would be in agreement with ^1H NMR and x-ray data on **12a** and **12b** in which a cis (**12a**) and trans (**12b**) relationship are present between the P=O and C–CH_3 groups.[19b,20] In $DCCl_3$ and C_6H_6, the ^1H NMR signal for the methyl group at C-3 was more deshielding when the P=O group was in a cis arrangement.[21] Interestingly, the ^{31}P NMR signal for *cis*-**2a** is at −48.5 ppm and that of *trans*-**2a** at −49.8 ppm. Unfortunately, similar data for **12a** and **12b** are not available at the moment. Our data appear to show that assignment of structure based on a correlation of ^{31}P NMR shift with shielding of C–CH_3 groups at a C-3 position in phospholane oxides (or as in **2a**) must be treated with care. Unless there is a severe steric parameter in *cis*-**2a** and *trans*-**2a**, we tentatively suggest that in the assignments of ^1H NMR signals, the P=O deshields the CH_3 group more than the C_6H_5 group.



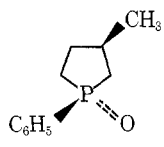
cis-**2a**



trans-**2a**



12a



12b

Experimental Section

General Data. Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5A unit as KBr pellets. ^1H NMR and ^{31}P NMR spectra were recorded with an XL-100(15) Varian spectrometer and obtained in $DCCl_3$ with tetramethylsilane as an internal standard unless otherwise indicated. Mass spectral analyses were performed on a CEC Model 21 HR unit and are available upon request. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Anhydrous solvents such as ether and benzene were dried over sodium and filtered prior to use.

Diphenylalkenylphosphine Oxides 1a–g. The key starting diphenylalkenylphosphine oxides for all heterocyclic compounds synthesized in this study were obtained by three different approaches.

A. Thermal Isomerization of Diphenylalkenylphosphinites at 140 °C.[9,10] By modification of a known method, it was possible to prepare diphenylallylphosphine oxide (**1a**) and diphenyl-2-methallylphosphine oxide (**1d**). The latter was obtained as follows. A solution of 7.2 g (0.1 mol) of 2-methyl-2-propen-1-ol (methallyl alcohol) in 100 ml of anhydrous ether containing 7.9 g (0.1 mol) of pyridine was cooled to 0 °C. Addition of 22.05 g (0.1 mol) of diphenylphosphinous chloride in 50 ml of anhydrous ether caused immediate reaction and the precipitation of pyridine hydrochloride. After the addition was completed (1 h), the reaction mixture was stirred for 2 h at room temperature. The mixture was filtered and the solvent was evaporated from the filtrate to yield 25 g (97%) of an oil. The oil was heated at 140 °C for 2 h, with stirring, to give a slightly yellow oil which crystallized on cooling to a colorless solid. This solid was chromatographed on alumina (Merck neutral) using benzene as eluent to give colorless crystals. Recrystallization (benzene–hexane) gave **1d**, mp 143–145 °C.

Anal. Calcd for $C_{16}H_{17}PO$: P, 12.08. Found: P, 12.17.

Diphenylallylphosphine oxide (**1a**) was prepared by the same procedure and gave the same physical data as reported in the literature.[9,10]

B. From Methyl Diphenylphosphinite with Alkyl Halide. The reaction vessel consisted of a 500-ml round-bottom flask equipped with a stirrer, N_2 inlet tube, dropping funnel, and a condenser. A solution of crotyl bromide (13.5 g, 0.1 mol) and methyl diphenylphosphinite (21.6 g, 0.1 mol, freshly prepared) in 200 ml of benzene was boiled for 24 h under conditions to allow the escape of methyl bromide. Evaporation of the solvent under reduced pressure gave a solid residue which was chromatographed on alumina (Merck neutral) using benzene as eluent. Colorless crystals of **1b** were obtained, mp 114–116 °C (lit.[20] mp 84–86 °C). Because the melting point difference was great, the sample was analyzed.

Anal. Calcd for $C_{16}H_{17}PO$: P, 12.08. Found P, 12.22.

C. Alkaline Hydrolysis of Alkenyltriphenylphosphonium Salts. 3-Butenyltriphenylphosphonium bromide[20] was converted to **1c** by a known method.[20] Oxide **1c** (91%, mp 102–103 °C) was identified with that described in the literature.

Ring Closures to Produce Phosphindoline and Phosphinoline. A typical experiment was performed as follows.

3-Methyl-1-phenylphosphindoline 1-Oxide (2a). In a 300-ml beaker was placed 200 ml of 115% PPA, which was then heated to 180 °C. To this was slowly added 4.0 g (16.5 mmol) of diphenylallylphosphine oxide (**1a**) over a 1-h period followed by 4 h of stirring. Upon completion of the addition, the solution became dark brown. Following the reaction period, the solution was cooled to 120 °C and slowly poured into ice–water (1000 ml) which produced a homogeneous solution upon stirring for 6 h with the separation of a sticky black resin. The solution was filtered, and the filtrate was extracted with $HCCl_3$ (five times with 100-ml portions). The combined organic layers, after washing with water, saturated sodium carbonate solution, and water, were dried ($CaCl_2$) and concentrated in vacuo. The resulting slightly yellow oil (1.5 g, 37%) was

distilled under vacuum (Kugelrohr), bp 160–170 °C (0.002 mm). Separation of the diastereomers of **2a** was effected by careful chromatography on a silica gel column using benzene with an increasing amount of chloroform. The oxide **2a** was identical in all respects with that reported in the literature.[8] A series of experiments were performed in which the ratio of PPA to **1a** was reduced from 50 ml:1 g to 40 ml:1 g to 30 ml:1 g to give **2a** but this procedure only resulted in decreasing yield of **2a.** Lowering the temperature of cyclization gave *trans*-1-(1-propenyl)diphenylphosphine oxide (**4**) which was identical in all respects with that prepared earlier,[12] along with the starting **1a** and a polymeric product.

1,2,3,4-Tetrahydro-4-methyl-1-phenylphosphinoline 1-Oxide (2b). Method A. The phosphine oxide (**1b** or **1c,** 2 g, 7.81 mmol) was slowly added to 100 ml of 115% PPA at 180 °C and, when the addition was complete, a stirring period of 4 h followed. When cooled to 110 °C, the solution was poured into 500 ml of ice–water and stirring produced a homogeneous solution. Extraction ($HCCl_3$, five times with 60-ml portions) gave a clear organic solution which was dried ($CaCl_2$). The chloroform was evaporated under vacuum to give a viscous oil which, upon scratching, solidified. This solid **2b** was twice sublimed at 100 °C (0.005 mm) to give a pure crystalline compound (Table I).

Method B. Base Hydrolysis of 1,2,3,4-Tetrahydro-4-methyl-1,1-diphenylphosphinolinium Hexafluorophosphate. The phosphonium compound **6** (1 g, 2.2 mmol) was boiled for 12 h in 100 ml of methanol–water (4:1) containing 10 g of NaOH. The mixture was cooled and 150 ml of water was added. The water layer was extracted ($HCCl_3$) and, after drying ($CaCl_2$), the solvent was evaporated to give solid **2b** (0.5 g, 90%) which was sublimed. It was identical in all respects with that prepared by method A.

3,3-Dimethyl-1-phenylphosphindoline 1-Oxide (2c). In a procedure directly analogous to the preceding one, the reaction of phosphine oxide **1d** (2 g, 7.81 mmol) and 100 ml of PPA at 180 °C gave **2c** in a yield of 1.0 g (50%). Sublimation was carried out at 100 °C (0.005 mm) (Table I).

1,2,3,4-Tetrahydro-4-4-dimethyl-1-phenylphosphindoline 1-Oxide (2d). Reaction of the phosphine oxide **1e** (2 g, 7.4 mmol) and 100 ml of PPA at 160 °C gave **2d** in good yield, 0.8 g (40%) (Table I).

Registry No.—**1a,** 4141-48-4; **1b,** 16540-56-0; **1c,** 16958-43-3; **1d,** 4455-75-8; **1e,** 13303-61-2; **1f,** 13303-58-7; **1g,** 13303-57-6; *cis*-**2a,** 58191-09-6; *trans*-**2a,** 58191-10-9; *cis*-**2b,** 58191-11-0; *trans*-**2b,** 58191-12-1; **2c,** 58191-13-2; **2d,** 58191-14-3; **5,** 54230-12-5; 2-methyl-2-propen-1-ol, 513-42-8; diphenylphosphinous chloride, 1079-66-9; crotyl bromide, 4784-77-4; methyl diphenylphosphinite, 4020-99-9; 3-butenylphosphonium bromide, 16958-42-2.

References and Notes

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(21) K. L. Marsi, F. R. Burns, and R. T. Clark, *J. Org. Chem.*, **37,** 238 (1972). A private communication from Dr. Marsi has indicated that **12a** has the following properties: bp 120 °C (0.01 mm); ^1H NMR ($DCCl_3$) δ 1.23 (C–CH_3) and (in C_6H_6) δ 0.853 (C–CH_3). Isomer **12b** has mp 60–61 °C; ^1H NMR ($DCCl_3$) δ 0.776 (C–CH_3) and (in C_6H_6) δ 1.19 (C–CH_3).

Direct Synthesis of Fluorinated Peroxides. IV. Addition of Pentafluorosulfur Peroxyhypochlorite to Alkenes

Michale J. Hopkinson, Nyal S. Walker, and Darryl D. DesMarteau*[1]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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Pentafluorosulfur peroxyhypochlorite, SF_5OOCl, undergoes addition reactions with alkenes forming pentafluorosulfurperoxy derivatives in good yield. The additions are predominantly unidirectional and proceed by an electrophilic mechanism. Reactions with C_2H_4, C_2F_4, C_2F_3Cl, CF_2CCl_2, CF_2CH_2, and *cis*-CFHCFH occur readily below 0 °C, whereas C_3F_6, 2-C_4F_6, and c-C_5F_8 were unreactive under all conditions. With *cis*-CFHCFH the addition was stereospecific. The new peroxides are stable at 22 °C and have been characterized by their physical properties and ir and NMR spectra. Comparison of SF_5OOCl reactions with those of the related compound CF_3OOCl are discussed.

The systematic synthesis of fluorocarbon peroxides and the resultant change in their classification from isolated laboratory curiosities to a well-established class of compounds was made possible by the reagents CF_3OOH,[2] CF_3OOCl,[3] CF_3OOF,[4] and CF_3OOOCF_3.[5] It has been shown that the only available route at present to a variety of peroxides is their direct synthesis via reactions in which the CF_3OO group is added to suitable substrates. In order to expand this interesting area of chemistry, the development of other reagents of the type R_FOOX has been a