$^+NH_3$ cation and hence reduces the basicity of the amine group.

Experimental Section

The preparation of the 4-aminothianes **1a–f**, **2a–f**, and **3a,b** have been communicated.[2]

Kinetic Procedure. The pure aminothianes were dried in vacuo before use. The 2,4-dinitrochlorobenzene was also dried before use. Dioxane was purified as described in the literature[9] and 80% dioxane was used as the solvent.

The rate was followed conductometrically.[10] The concentration of the amine was maintained at twice the concentration of 2,4-dinitrochlorobenzene in order to trap the HCl formed during the reaction. The amine (0.4 mol) and the 2,4-dinitrochlorobenzene (0.2 mol) solutions were prepared and thermostated at 50 ± 0.01 °C. Equal volumes (2 mL) of the solutions were mixed in the conductance cell. Immediately after mixing, the conductance was measured. At appropriate time intervals, the conductance values of the reaction mixture were then recorded. The infinity readings were determined after keeping the reaction mixture in the conductance cell at 75 °C for 72 h. The rate constant k_2 is given by

$$k_2 = (1/2tb)[(C_t - C_0)/(C_\infty - C_t)]$$

where b = concentration of 2,4-dinitrochlorobenzene in moles/liter, C_0 = initial conductance, C_t = conductance at time t, and C_∞ = conductance at infinite time

Measurement of Dissociation Constants.[7] The pure amines were dried in vacuo before use. Methyl Cellosolve was purified by fractional distillation. Distilled water free from carbon dioxide was prepared and 80% methyl Cellosolve was used as the solvent.

The amine (about 15 mg) was dissolved in 80% methyl Cellosolve (25 ml). While the solution was stirred under nitrogen, 0.05 N hydrochloric acid was added dropwise from a burette that could be read to 0.005 mL. The pH values were measured in a pH meter, precalibrated with buffers at pH 4.0 and 9.2 with a glass electrode. All measurements were made at 27 ± 0.01 °C. The equivalence point was determined from a plot of pH against volume of HCl added. An average value (pK_a) of one-fourth, one-half, and three-fourth neutralizations was taken, and at least two independent titrations were carried out on each compound.

Preparation of Substituted *N*-(2,4-Dinitrophenyl)-4-aminothianes. A solution of the aminothiane (0.0019 mol) and 2,4-dinitrochlorobenzene (0.41 g, 0.002 mol) in 90% ethanol (25 mL) was boiled on a water bath for 6 h. When the solution cooled, the derivative crystallized out. It was filtered, washed with cold ethanol (10 mL), and recrystallized (ethanol). Other relevant data were given in Table II.

Registry No. **1a**, 69832-20-8; **1b**, 70095-68-0; **1c**, 78837-43-1; **1d**, 78837-44-2; **1e**, 78837-45-3; **1f**, 78837-46-4; **2a**, 69832-19-5; **2b**, 70071-36-2; **2c**, 78918-40-8; **2d**, 78918-41-9; **2e**, 78837-47-5; **2f**, 78837-48-6; **3a**, 21926-00-1; **3b**, 78837-49-7; **4a**, 78837-50-0; **4b**, 78837-51-1; **4c**, 78837-52-2; **4d**, 78837-53-3; **4e**, 78837-54-4; **4f**, 78837-55-5; **5a**, 78918-42-0; **5b**, 78918-43-1; **5c**, 78918-44-2; **5d**, 78918-45-3; **5e**, 78837-56-6; **5f**, 78837-57-7; 2,4-dinitrochlorobenzene, 97-00-7.

Supplementary Material Available: An expanded Table II showing combustion analytical data (1 page). Ordering information is given on any current masthead page.

(9) Weissburger, A.; Pros Kauer, E. S., Eds. "Organic Solvents"; Interscience: New York, 1955; p 371.
(10) Guggenheim, E. A.; Prue, J. F. "Physiocochemical Calculations"; North-Holland Publishing Co.: Amsterdam, 1959; p 445.

New Method for Building Carbon–Phosphorus Heterocycles

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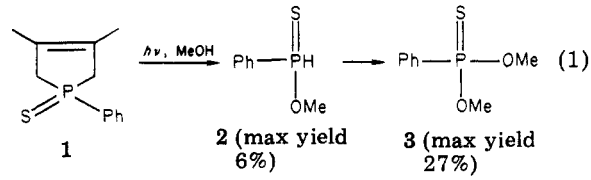
Received May 12, 1981

The photolysis of 1-substituted 3,4-dimethylphosphole sulfides–*N*-phenylmaleimide cycloadducts in alcohols (R'OH) has been found to proceed with high yields whatever the nature of the R substituent. It provides a ready access to the almost unknown phosphinothioates RP(S)(H)OR'. When R = $(CH_2)_nBr$ the phosphinothioates thus obtained are readily cyclized by NaH in THF. Five-, six-, and seven-membered rings have been obtained in this way.

Recently some efforts have been devoted to the devising of new general methods for building carbon–phosphorus heterocycles. Indeed, older classical methods were often plagued by low yields and/or limited practical applicability.[1] As far as monocyclic compounds are concerned, two new methods have appeared very recently in the literature. The first one was devised by Quin[2] and relied upon an ozone cleavage of the double bond at the junction of a bicyclic phospholene. Its main purpose was the synthesis of large-membered functional rings. On our side we described a method relying upon two successive Arbuzov rearrangements so as to convert two P–O–C bonds into two P–C bonds.[3] This method was satisfactory but was relatively complex. Thus we decided to carry on new research in order to devise a simpler method. The results of our work are described hereafter.

Results and Discussion

Our starting point was an observation of Tomioka[4] describing the cleavage of phospholene sulfide **1** under UV irradiation in alcohol (eq 1). The primary product **2** was



1 **2** (max yield 6%) **3** (max yield 27%)

obtained in very poor yield, and additional work[5a] on the

(1) For a very recent account, see: Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981.
(2) Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370.
(3) Mathey, F.; Mercier, F. *J. Chem. Soc., Chem. Commun.* **1980**, 191.
(4) Tomioka, H.; Takata, S.; Kato, Y.; Izawa, Y. *J. Chem. Soc. Perkin Trans. 2* **1980**, 1017.
(5) (a) Tomioka, H.; Nakamura, S.; Ohi, T.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3707. (b) The photolysis of the dimer of 1-phenylphosphole oxide (which contains a 7-phosphanorbornene skeleton) shows an enhancement of the rate of the photocleavage when compared to the photolysis of 1-phenyl-3-phospholene oxide; see: Tomioka, H.; Hirano, Y.; Izawa, Y. *Tetrahedron Lett.* **1974**, 1865, 4477.

0022-3263/81/1946-4386$01.25/0

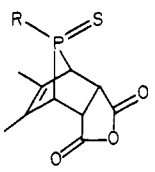
Table I. Photocleavage of 7-Phosphanorbornene Sulfides in Methanol

starting compd	R	irradn time,[a] h	yield, % 28	yield, % 29
4	Ph	3	80	
5	Bu	4.5	35	5
6	Ph	3	80	
7	Bu	3	65	
8	Bu	4.5	~0	
9	Bu	8	38	15
15	Br-$(CH_2)_4$-	3.5	70	
16	Br-$(CH_2)_5$-	3.5	75	
17	Br-$(CH_2)_6$-	3.5	65	

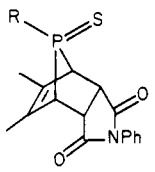
[a] Medium-pressure mercury lamp (125 W), room temperature, 2.5×10^{-2} mol/L solution of adduct in methanol/THF (50:50).

photocleavage of phospholene oxides showed that the reaction was restricted to the phenylphosphorus compounds.

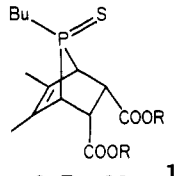
On the other hand, Kashman[6] has demonstrated that monomeric 1-phenyl-3,4-dimethylphosphole sulfide gave numerous Diels–Alder reactions with dienophiles thus producing easily 7-phosphanorbornene sulfides. Thus, in order to circumvent the yield and scope limitations of the reaction described by Tomioka, we decided to study the photocleavage of various 7-phosphanorbornene sulfides.[5b] We hoped that the very high strain existing in the 3-phospholene ring of these products (CPC ca. 87°[7] vs. 94°[8] for monocyclic phospholenes) would improve both the yield and the generality of this photocleavage. Indeed, 7-phosphanorbornene sulfides have been already shown to lose their R—P=S bridge upon heating.[6,9,10] Our preliminary photolysis experiments were performed with compounds **4–9**. Compounds **4** and **5** were prepared by reaction of the corresponding phosphole sulfides **10** and **11** with maleic anhydride as described by Kashman for **4**.[6]



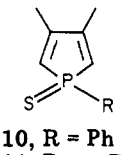
4, R = Ph
5, R = *n*-Bu



6, R = Ph
7, R = *n*-Bu



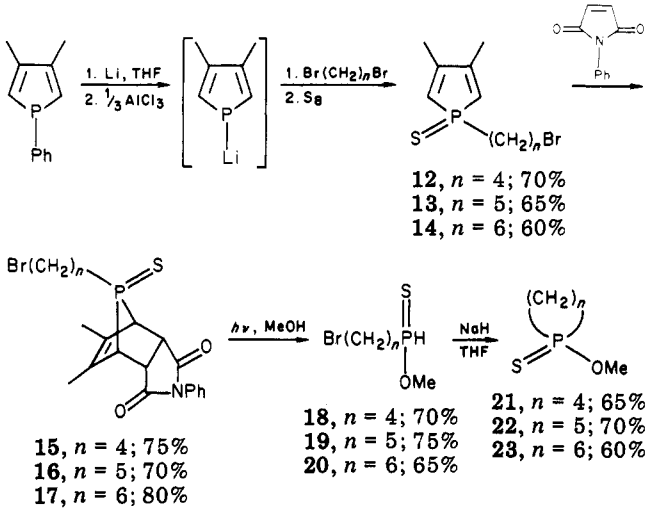
8, R = Me
9, R = H



10, R = Ph
11, R = *n*-Bu

Compounds **6** and **7** were similarly prepared by using *N*-phenylmaleimide. These sharp-melting solids were obtained in high yield, they were easily recrystallized, and their handling was very convenient. It must be noted that **6** is different from the product obtained by sulfuration of the 1-phenyl-3,4-dimethylphosphole–*N*-phenylmaleimide cycloadduct: in **6**, the phenyl group is syn to the double bond whereas it is anti in the cycloadduct.[11] Compounds **8** and **9** were simply obtained by methanolysis or hydrolysis of **5**. The results of the photocleavage experiments are collected in Table I. It appears immediately that **8** and **9** are rather poorly photocleaved in methanol. Since **5** is in part transformed into **8** during the photolysis, its rather deceiving results are not too surprising. On the contrary, the *N*-phenylmaleimide cycloadducts **6** and **7** are very efficiently photocleaved, and it is possible to avoid the oxidation of the P–H bond of the primary photoproducts.

Scheme I. Preparation of C-P Heterocycles by Photocleavage of 7-(ω-Bromoalkyl)phosphanorbornene Sulfides



12, *n* = 4; 70%
13, *n* = 5; 65%
14, *n* = 6; 60%

15, *n* = 4; 75%
16, *n* = 5; 70%
17, *n* = 6; 80%

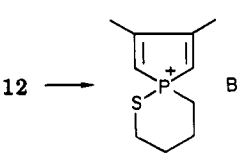
18, *n* = 4; 70%
19, *n* = 5; 75%
20, *n* = 6; 65%

21, *n* = 4; 65%
22, *n* = 5; 70%
23, *n* = 6; 60%

Having in hand now a general and efficient synthesis of the almost unknown RP(S)(H)(OR′) species, we used it to build a new route to carbon–phosphorus heterocycles. This route is depicted in Scheme I.

In four steps, from the readily available 1-phenyl-3,4-dimethylphosphole[12] and α,ω-dibromoalkanes we are able to prepare carbon–phosphorus heterocycles. This route offers the following advantages. (a) Since 3,4-dimethylphospholyllithium freed from phenyllithium is compatible with numerous functional groups,[13] it is very probably possible to prepare functional rings. (b) This route is not restricted to the synthesis of easily made five- and six-membered rings. (c) The exocyclic substituents on phosphorus can be easily changed; reduction to P^{III} compounds is possible.[3]

In the first step we take advantage of the preferential cleavage of the P–Ph bond of 1-phenylphospholes by lithium in THF.[14] Unpublished work in our laboratory[15] has proven (by ^{31}P NMR) that stoichiometric amounts of $AlCl_3$ reacted selectively with PhLi without destroying the phospholyllithium, thus allowing cleaner reactions of the P–Li derivative especially with functional alkyl halides. In this manner, the reaction with α,ω-dibromoalkanes affords the expected 1-(ω-bromoalkyl)phospholes in good yields. They are immediately reacted in situ with sulfur to avoid self-quaternization. It is interesting to note that sulfide **12** tends to undergo slowly an intramolecular S-alkylation to give the bicyclic phosphonium salt **24** (eq 2).



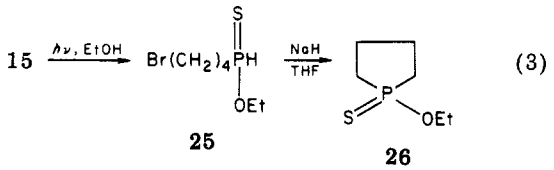
(2)

24

(6) Kashman, Y.; Wagenstein, I.; Rudi, A. *Tetrahedron* **1976**, *32*, 2427.
(7) Chiu, Y. Y. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1969**, *91*, 4150.
(8) McPhail, A. T.; Komson, R. C.; Engel, J. F.; Quin, L. D. *J. Chem. Soc., Dalton Trans.* **1972**, 874.
(9) Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1977**, *14*, 705.
(10) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.
(11) Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 319.
(12) Mathey, F.; Mankowski-Favelier, R. *Bull. Soc. Chim. Fr.* **1970**, 4433.
(13) Muller, G.; Bonnard, H.; Mathey, F.; *Phosphorus Sulfur* **1981**, *10*, 175.
(14) Braye, E. H.; Caplier, I.; Saussez, R. *Tetrahedron* **1971**, *27*, 5523.
(15) De Lauzon, G.; Mathey, F., unpublished work.

The reaction can be monitored by ^{31}P NMR (^{31}P(**12**), 48.7 ppm; ^{31}P(**24**), 40.8 ppm). In the IR spectrum of **24** (KBr) we note the disappearance of the 640-cm^{-1} peak associated with the P=S bond of 1-alkylphosphole sulfides and the appearance of a peak at 590 cm^{-1} associated with the P–S–C bond of the phosphonium salt.[16]

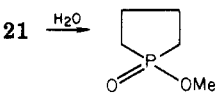
The second and third steps deserve no special comments. We have just performed one experiment in ethanol with $n = 4$. We have obtained the expected product **25** in 75% yield (eq 3).



(3)

25 **26**

The final cyclization takes place with NaH in refluxing THF. The cyclic products **21–23** and **26** have been completely characterized by their ^1H, ^{31}P, mass, and IR spectra and their elemental analyses. Upon being allowed to stand (1 month), **21** seems to undergo a very slow hydrolysis to give, probably, the corresponding oxide **27** (eq 4). Indeed,



(4)

27

a new peak appears in the ^{31}P NMR spectrum of **21** in the region normally associated with cyclic phosphinates: ^{31}P (**21**) 119.7 ppm; ^{31}P (**27**) 79.9 ppm. This suspected hydrolysis could be related to the cyclic strain effect demonstrated by Westheimer.[17]

Other uses of this type of photocleavage will be reported in due course.

Experimental Section

All reactions were performed under an argon atmosphere. ^1H NMR spectra were recorded on a R24 Perkin-Elmer spectrometer. ^{31}P spectra were run on a WP80 Bruker spectrometer; chemical shifts were externally referenced to 85% H_3PO_4 and are positive for downfield shifts. Unless otherwise stated, the NMR spectra were recorded in $CDCl_3$ solutions. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer; band positions are given in reciprocal centimeters.

1-(ω-Bromoalkyl)-3,4-dimethylphosphole Sulfides 12–14. To a solution of 4.15 g (0.022 mol) of 1-phenyl-3,4-dimethylphosphole in 60 mL of dry THF cooled by a water bath was added 0.4 g (0.057 mol) of small pieces of lithium. After being stirred for 4 h, the reaction mixture was filtered over glass wool, and 1.0 g (0.0075 mole) of anhydrous $AlCl_3$ was rapidly added at −10 °C. The mixture was allowed to stand 1 h at room temperature and then poured within 10 min into a solution of 0.1 mol of the dibromoalkane in 20 mL of THF kept at 0 °C. After 1 h at room temperature, the bromoalkylphosphole was sulfurized with 0.8 g (0.025 mol) of sulfur and stirred 2 h more. The reaction mixture was then acidified with dilute HCl at 0 °C, put in 300 mL of water, and worked up as usual with ether.

The crude phosphole sulfides thus obtained, and containing the excess of dibromoalkane, were directly used for the preparation of the 7-phosphanorbornenes **15–17**.

Purification of analytical samples were performed by vacuum distillation of the remaining dibromoalkane and chromatography of the residue through a silica gel column with CH_2Cl_2.

1-(4-Bromobutyl)-3,4-dimethylphosphole sulfide (**12**): yield 65–70%, ^1H NMR δ 1.85 (m) and 2.0 (d) (12 H, methyls and $(CH_2)_3P$), 3.30 (t, 2 H, CH_2Br), 5.85 (d, $^2J_{PH}$ = 31 Hz, 2 H ethylenic); ^{31}P NMR δ 48.7; mass spectrum (70 eV, 90 °C), m/e (relative intensity) 280 (2) and 278 (2, M), 199 (100, M − Br), 144 (50, M − C_4H_7Br), 143 (38, M − C_4H_8Br), 111 (16, M − C_4H_8BrS).

As a neat oil as well as in solution, phosphole sulfide **12** has undergone after 1 month a cyclization leading to phosphonium compound **24**: mp 186 °C (EtOH–Et_2O); ^1H NMR δ 2.23 and 2.65 (m, 12 H, methyls and $(CH_2)_3S$), 3.55 (m, 2 H, CH_2P), 7.05 (d, $^2J_{PH}$ = 35 Hz, 2 H, ethylenic); ^{31}P NMR 40.9; IR (Nujol) ν(PC) 1140, ν(PS) 590; mass spectrum (70 eV, 190 °C), m/e (relative intensity) 280 (1) and 278 (1, M), 199 (100, M − Br), 144 (40, M − C_4H_7Br), 143 (45, M − C_4H_8Br), 111 (27, M − C_4H_8BrS). Anal. Calcd for $C_{10}H_{16}BrPS$: C, 43.07; H, 5.77; P, 11.09. Found: C, 43.55; H, 5.29; P, 10.78.

1-(5-Bromopentyl)-3,4-dimethylphosphole sulfide (**13**): yield 65%; ^1H NMR δ 1.68 (m) and 2.0 (d) (14 H, methyls and $(CH_2)_4P$), 3.30 (t, 2 H, CH_2Br), 5.75 (d, $^2J_{PH}$ = 30 Hz, 2 H ethylenic); ^{31}P NMR δ 49.3; IR (neat) ν(PC) 1137, ν(PS) 640, ν(CBr) 665 and 560; mass spectrum (70 eV, 130 °C), m/e (relative intensity) 292 (7) and 280 (7, M), 213 (100, M − Br), 144 (45, M − C_5H_9Br), 143 (27, M − $C_5H_{10}Br$), 111 (11, M − $C_5H_{10}BrS$).

1-(6-Bromohexyl)-3,4-dimethylphosphole sulfide (**14**): yield 60%; ^1H NMR δ 1.35–1.75 (m) and 2.0 (d) (16 H, methyls and $(CH_2)_5P$), 3.33 (t, 2 H, CH_2Br), 5.80 (d, $^2J_{PH}$ = 30 Hz, 2 H ethylenic); ^{31}P NMR δ 49.0; IR (neat) ν(PC) 1137, ν(PS) 640, ν(CBr) 665 and 560; mass spectrum (70 eV, 130 °C), m/e (relative intensity) 308 (15) and 306 (15, M), 227 (62, M − Br), 144 (100, M − $C_6H_{11}Br$), 143 (34, M − $C_6H_{12}Br$), 111 (12, M − $C_6H_{12}BrS$).

Maleic Anhydride Adducts 4 and 5 and Derivatives 8 and 9. A solution of 0.01 mol of phosphole sulfide **10** or **11** and 0.012 mol of maleic anhydride in 10 mL of CH_2Cl_2 was allowed to stand overnight. Ethyl ether or hexane was then added and the precipitate collected and recrystallized in acetone–ether. 7-Phenyl-7-phosphanorbornene **4**, mp 157 °C (lit.[6] mp 157 °C). 7-Butyl-7-phosphanorbornene **5**: yield 60%; ^1H NMR δ 0.9–2.06 (m) and 1.7 (d) (15 H, methyls and C_4H_9P), 3.06 (m, 2 H, $(CH)_2P$), 4.5 (m, 2 H, 2CHCO); ^{31}P NMR δ 114.7; mp 201 °C.

3,4-Bis(carbomethoxy)-7-butyl-7-phosphanorbornene **8** was obtained by acidic methanolysis of anhydride **5**: yield 90%; mp 179 °C; ^1H NMR δ 0.9–2.03 (m) and 1.75 (d) (15 H, methyls and C_4H_9P), 2.75 (m, 2 H, $(CH)_2P$), 3.53 (s, 6 H, methyls), 4.03 (m, 2 H, 2CHCO); ^{31}P NMR (acetone) δ 102.0.

3,4-Dicarboxy-7-butyl-7-phosphanorbornene **9** was prepared by acidic hydrolysis of anhydride **5**: mp 183 °C; ^1H NMR (Me_2SO-d_6) δ 0.9–2.08 (m) and 1.75 (d) (15 H), 2.8 (m, 2 H) 3.78 (m, 2 H); ^{31}P NMR (Me_2SO-d_6) δ 103.9.

***N*-Phenylmaleimide Adducts.** These were prepared from phosphole sulfides and *N*-phenylmaleimide under the same conditions as for the anhydride adducts.

7-Phenylphosphanorbornene **6**: yield 90%; mp 273.5 °C; ^1H NMR δ 1.55 (d, $^4J_{PH}$ = 2 Hz, 6 H, methyls), 3.45 (m, $^2J_{PH}$ = 3.8 Hz, 2 H, $(CH)_2P$), 4.18 (m, $^3J_{PH}$ = 2.4 Hz, 2 H, 2CHCO), 6.80–7.56 (m, 10 H, phenyls); ^{31}P NMR δ 107.1. Anal. Calcd for $C_{22}H_{20}NO_2PS$: C, 67.16; H, 5.12; P, 7.87. Found: C, 67.15; H, 5.04; P, 7.67.

7-Butylphosphanorbornene **7**: yield 80%; mp 185.5 °C; ^1H NMR δ 0.9 (m, 3 H), 1.23–2.20 (m) and 1.75 (d) (12 H, methyls and $(CH_2)_3P$), 3.1 (m, 2 H, $(CH)_2P$), 4.05 (m, 2 H, 2CHCO), 6.8–7.35 (m, 5 H, phenyl); ^{31}P NMR δ 112.0. Anal. Calcd for $C_{20}H_{24}NO_2PS$: C, 64.32; H, 6.49; P, 8.29. Found: C, 64.41; H, 6.49; P, 8.32.

7-(4-Bromobutyl)-7-phosphanorbornene **15**: yield 75%; mp 165.5 °C (MeOH); ^1H NMR δ 1.77 (d) and 1.85–2.15 (m) (12 H, methyls and $(CH_2)_3P$), 3.15 (m) and 3.35 (t) (4 H, $(CH)_2P$ and CH_2Br), 4.08 (m, 2 H, 2CHCO), 6.85–7.37 (m, 5 H, phenyl); ^{31}P NMR δ 110.5. Anal. Calcd for $C_{20}H_{23}BrNO_2PS$: C, 53.10; H, 5.13; Br, 17.66; P, 6.85. Found: C, 53.16; H, 5.10; Br, 17.63; P, 6.79.

7-(5-Bromopentyl)-7-phosphanorbornene **16**: yield 70%; mp 169.5 °C; ^1H NMR δ 1.58–2.15 (m) and 1.75 (d) (14 H, methyls and $(CH_2)_4P$), 3.12 (m) and 3.31 (t) (4 H, $(CH)_2P$ and CH_2Br), 4.05 (m, 2 H, 2CHCO), 6.83–7.35 (m, 5 H, phenyl); ^{31}P NMR δ 111.1. Anal. Calcd for $C_{21}H_{25}BrNO_2PS$: C, 54.08; H, 5.40; P, 6.64. Found: C, 54.20; H, 5.46; P, 6.53.

7-(6-Bromohexyl)-7-phosphanorbornene **17**: yield 80%; mp 136 °C; ^1H NMR δ 1.46–2.10 (m) and 1.75 (d) (16 H, methyls and $(CH_2)_5P$), 3.13 (m) and 3.33 (t) (4 H, $(CH)_2P$ and CH_2Br), 4.03

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(17) Kluger, R.; Westheimer, F. H. *J. Am. Chem. Soc.* **1969**, *91*, 4143.

(m, 2 H, 2CHCO), 6.83–7.37 (m, 5 H, phenyl); ^{31}P NMR δ 111.0. Anal. Calcd for $C_{22}H_{27}BrNO_2PS$: C, 55.00; H, 5.67; Br, 16.63; P, 6.45. Found: C, 55.00; H, 5.70; Br, 16.67; P, 6.56.

Irradiation of the 7-Phosphanorbornenes. All the irradiations were conducted by using a 125-W medium-pressure mercury lamp and a water-cooled quartz immersion well. The irradiations were performed on 0.05 mol of the phosphanorbornene in 100 mL of THF and 100 mL of MeOH. After reaction, the solvents were removed under water-jet vacuum and the residue chromatographed through a deoxygenated silica gel column, with CH_2Cl_2, under argon. Irradiation times and yields are given in Table I. *O*-Methyl phenylphosphinothioate (**2**): ^{1}H NMR δ 3.70 (d, $^3J_{PH}$ = 12.5 Hz, 3 H, CH_3O), 7.45–8.15 (m, 5 H, phenyl), 8.26 (d, $^1J_{PH}$ = 540 Hz 1 H, PH). The spectrum is identical with that published by Tomioka and al.

O-Methyl Butylphosphinothioate (**28**, R = Bu) and Di-*O*-methyl Butylphosphonothioate (**29**, R = Bu). Irradiation of **7** gave the pure phosphinothioate: ^{1}H NMR δ 0.9–2.05 (m, 9 H, butyl), 3.48 (d, $^3J_{PH}$ = 13.5 Hz, 3 H, CH_3O), 7.3 (dq, $^1J_{PH}$ = 512 Hz, 1 H, PH); ^{31}P NMR δ 77.5; IR (neat) ν(PH) 2320; mass spectrum (70 eV, 70 °C), *m/e* (relative intensity) 152 (65, M).

Irradiation of compounds **5** and **9** gave a mixture of **28** and **29** (R = Bu), as indicated in Table I. The percentages have been estimated by integration of the methyl signals respectively at 3.23 and 3.35 ppm (d, $^3J_{PH}$ = 13.5 Hz) in C_6D_6 solution.

O-Methyl (4-bromobutyl)phosphinothioate (**18**): ^{1}H NMR δ 1.60–2.17 (m, 6 H, $(CH_2)_3P$), 3.38 (t, 2 H, CH_2Br), 3.60 (d, $^3J_{PH}$ = 14.2, 3 H, CH_3O), 7.51 (dm, $^1J_{PH}$ = 496 Hz, 1 H, PH); ^{31}P NMR δ 75.7; IR (neat) ν(PH) 2320.

O-Methyl (5-bromopentyl)phosphinothioate (**19**): ^{1}H NMR δ 1.40–2.15 (m, 8 H, $(CH_2)_4P$), 3.35 (t, 2 H, CH_2Br), 3.55 (d, $^3J_{PH}$ = 14.3, 3 H, CH_3O), 7.40 (dm, $^1J_{PH}$ = 492 Hz, 1 H, PH); ^{31}P NMR δ 76.5.

O-Methyl (6-bromohexyl)phosphinothioate (**20**): ^{1}H NMR δ 1.25–2.15 (m, 10 H, $(CH_2)_5P$), 3.33 (t, 2 H, CH_2Br) 3.60 (d, $^3J_{PH}$ = 14 Hz, 3 H, CH_3O), 7.40 (dm, $^1J_{PH}$ = 492 Hz, 1 H, PH).

O-Ethyl (4-bromobutyl)phosphinothioate (**25**): prepared under the same conditions as the O-methylated compound, but in ethyl alcohol: ^{1}H NMR δ 1.27 (t, 3 H, CH_3), 1.66–2.20 (m, 6 H, $(CH_2)_3P$), 3.28 (t, 2 H, CH_2Br), 3.70–4.20 (m, 2 H, CH_2O), 7.40 (dm, $^1J_{PH}$ = 514 Hz, 1 H, PH); ^{31}P NMR δ 71.4.

Cyclization of the Phosphinothioates 15–17. To a suspension of 1.2 g (0.05 mol) of NaH in 80 mL of THF at 50 °C was added dropwise a solution of 0.005 mol of ω-bromoalkyl phosphinothioate in 20 mL of THF. The mixture was stirred for 0.5 h at 50 °C, cooled at −10 °C and hydrolyzed with a saturated NH_4Cl aqueous solution. The organic layer was separated and the solvent removed. The residue was then worked up as usual with ether. After solvent removal, the oily residue was chromatographed through a silica gel column and then vacuum distilled (Kugelrohr).

1-Methoxyphospholane sulfide (**21**): bp 160 °C (3 mm); yield 65%; ^{1}H NMR δ 1.5–2.4 (m, 8 H, $(CH_2)_4$), 3.52 (d, $^3J_{PH}$ = 13.5 Hz, 3 H, CH_3O); ^{31}P NMR δ 119.7; IR (neat) ν(PC) 1110, ν(POC) 1025, ν(PS) 730 and 610; mass spectrum (70 eV, 70 °C), *m/e* (relative intensity) 150 (100, M), 122 (35, M − $(CH_2)_2$), 120 (77, M − OCH_2). Anal. Calcd for $C_5H_{11}OPS$: C, 39.99; H, 7.38. Found: C, 39.67; H, 7.41.

1-Ethoxyphospholane sulfide (**26**): bp 90 °C (0.3 mm); yield 67%; ^{1}H NMR δ 1.27 (t, $^3J_{HH}$ = 6, 8 Hz, 3 H, CH_3), 1.7–2.23 (m, 8 H, $(CH_2)_4P$), 3.7–4.2 (dq, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 9.6 Hz, 2 H, CH_2P); ^{31}P NMR δ 116.5.

1-Methoxyphosphorinane sulfide (**22**): bp 100 °C (0.4 mm); yield 70%; ^{1}H NMR δ 1.55–2.25 (m, 10 H, $(CH_2)_5$), 3.52 (d, $^3J_{PH}$ = 13.0 Hz, 3 H, CH_3O); ^{31}P NMR 91.5; IR (neat) ν(PC) 1120, ν(POC) 1020, ν(PS) 730 and 610; mass spectrum (70 eV, 80 °C), *m/e* (relative intensity) 164 (100, M), 136 (26, M − $(CH_2)_2$), 134 (62, M − OCH_2), 122 (37, M − $(CH_2)_3$). Anal. Calcd for $C_6H_{13}OPS$: C, 43.89; H, 7.98; P, 19.52. Found: C, 43.93; H, 8.05; P, 19.33.

1-Methoxyphosphepane sulfide (**23**): bp 150 °C (0.5 mm); yield 60%; ^{1}H NMR δ 1.45–2.30 (m, 12 H, $(CH_2)_6$), 3.49 (d, $^3J_{PH}$ = 13.0 Hz, 3 H, CH_3O); ^{31}P NMR δ 105.9; IR (neat) ν(PC) 1095, ν(POC) 1033, ν(PS) 690 and 590; mass spectrum (70 eV, 80 °C), *m/e* (relative intensity) 178 (50, M), 136 (22, M − $(CH_2)_3$), 122 (10, M − $(CH_2)_4$), 86 (100, C_6H_{14}), 84 (100, C_6H_{12}). Anal. Calcd for $C_7H_{15}OPS$: C, 47.17; H, 8.48. Found: C, 47.30; H, 8.52.

Registry No. **2**, 26855-55-0; **4**, 62241-64-9; **5**, 78870-58-3; **6**, 78961-93-0; **7**, 78870-59-4; **8**, 78870-60-7; **9**, 78870-61-8; **10**, 30540-37-5; **11**, 30540-40-0; **12**, 78870-62-9; **13**, 78870-63-0; **14**, 78939-72-7; **15**, 78870-64-1; **16**, 78870-65-2; **17**, 78870-66-3; **18**, 78870-67-4; **19**, 78870-68-5; **20**, 78870-69-6; **21**, 78870-70-9; **22**, 78870-71-0; **23**, 78870-72-1; **24**, 78870-73-2; **25**, 78870-74-3; **26**, 78870-75-4; **28** (R = Bu), 78870-76-5; **29** (R = Bu), 78870-77-6; 1-phenyl-3,4-dimethylphosphole, 30540-36-4; 1,4-dibromobutane, 110-52-1; 1,5-dibromopentane, 111-24-0; 1,6-dibromohexane, 629-03-8; maleic anhydride, 108-31-6; *N*-phenylmaleimide, 941-69-5.

A Highly Convergent and Efficient Total Synthesis of Prostaglandins (±)-PGA and (±)-PGB[1]

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The mixed cyanocuprate derived from *trans*-1-iodo-3-[(*tert*-butyldimethylsilyl)oxy]oct-1-ene was added regioselectively (1,4:1,2 = 15:1) to cyclopentadiene monoepoxide. The trans-1,4-adduct **4** was stereospecifically converted to epoxy alcohol **6** and then to the corresponding epoxy ketone **7** (97%). After the enol phosphate **8** was regiospecifically formed, a second 1,4-conjugate addition of the cyanocuprate derived from 1-lithio-7-[(trimethylsilyl)oxy]heptane was used to introduce the top chain of the prostaglandin nucleus. The resulting hydroxy enol phosphate **9** could be selectively transformed into either PGA or PGB under basic conditions. This new synthetic approach to prostaglandins provides a general route to new prostaglandin analogues in very few steps.

The total syntheses of various naturally occurring prostaglandins have been achieved with considerable success and creativity over the past decade.[2] Notwithstanding the elegant syntheses of the PG series using organocopper reagents,[3] there previously was absent an ap-

(1) A preliminary report on this synthetic strategy to prostaglandins was made at the 3rd IUPAC Meeting on Organic Synthesis, June 15–20, 1980, Madison, WI, and at the 2nd Chemical Congress of the North American Continent, August 25–29, 1980, Las Vegas, NV.

(2) For two comprehensive reviews on the syntheses of prostaglandins, see: Mitra, A., "The Synthesis of Prostaglandins"; Wiley: New York, 1977. Newton, R. F.; Roberts, S. M. *Tetrahedron* **1980**, *36*, 2163.

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