Polylithiumorganic Compounds, XIII[1]

"Phospha[3]radialenes" – Reactive Intermediates in the Synthesis of "Phospha[6]radialenes"

Adalbert Maercker* and Walter Brieden [+]

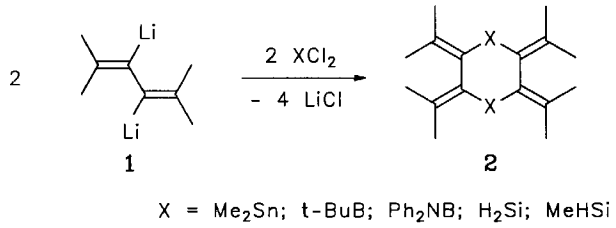
Institut für Organische Chemie der Universität Siegen,
Adolf-Reichwein-Straße, D-5900 Siegen (FRG)

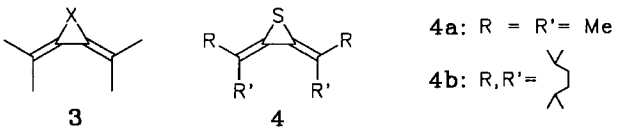
Received September 24, 1990

Key Words: Phospha[3]radialenes / Alkenylidenephosphiranes, tautomerism of / Phosphiranes, quaternization of / Phosphiranes, ring opening to bis(alkylchlorophosphino)butadienes / Phospha[6]radialenes

The reaction of the dilithiobutadiene **1** with various dichloroorganylphosphanes in diethyl ether at −80°C leads to the formation of the novel phosphiranes **5a−e** and **6a, 6c−e** in up to 86% yield. A thermal isomerization of the alkenylidenephosphiranes **6** leads to the complete formation of the corresponding "phospha[3]radialenes" **5**. Quaternization of the latter gives the cyclic phosphonium salts **8b−d**, on addition of iodomethane, while methylation of **5a** leads to the acyclic **9a**. The phosphiranes **5c−e** and **6c−e** are converted into the bis(alkylchlorophosphino)butadienes **10c−e** by addition of the corresponding dichloroorganylphosphane at room temperature, whereas **5a,b** and **6a** are quite unreactive. The interaction of **10e** with **1** gives the "phospha[6]radialene" **12e**, a formal dimer of **5e**. The isolated 1,4-diphosphorinane **12e** exists in a rigid trans-chair conformation as revealed by its NMR spectra.

Previously we have described the syntheses and structures of a number of "hetero[6]radialenes" **2**[2,3,4]. They have been prepared by treating a diethyl ether solution of 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (**1**)[5,6] with dichloro derivatives of tin[2], boron[3], and silicon[4].





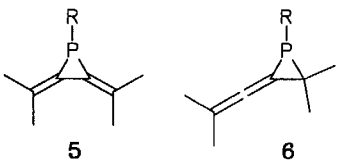
However, the reaction of **1** with dichlorostannanes, -boranes, or -silanes did not result in the formation of the "hetero[3]radialenes" **3**, conceivable intermediates in the reaction of **1** with the above electrophiles. In this article we describe the formation of the three-membered ring products **3**. Besides **4**, no further "hetero[3]radialenes" **3** have so far been prepared. **4a** has been obtained in a multistep synthesis[7], **4b** by alkenylidenecarbene addition to the corresponding thioketone[8,9].

[+] Present address: Department of Chemistry, Stanford University, Stanford, California 94305 (USA).

Results

The reaction of **1** with dichlorophosphanes in diethyl ether at −80°C leads to the formation of the novel three-membered ring compounds **5** in 58 to 86% yield after workup by distillation. The "phospha[3]radialene" structure is indicated by the mass spectrum and by the presence of PH and PC couplings with only *one* phosphorus atom in the ^{1}H- and ^{13}C-NMR spectra. Furthermore, the assignment to the phosphirane structure follows from the typical high-field ^{31}P-NMR shifts[10] in the range from $\delta = -149.3$ (**5b**) to −195.4 (**5e**).

Surprisingly, besides the signals of **5** the ^{1}H- and ^{13}C-NMR spectra of the crude products show an additional set of signals which indicates the formation of the allenic phosphiranes **6**. The molecular structure of **6** is determined from the ^{13}C-NMR resonance ($\delta \approx 190$, $^2J_{PC} \approx 5$ Hz) of the sp-hybridized carbon atom in the allene moiety[11] and the characteristic[12] IR absorption of the allenic carbon-carbon stretching frequency at 1970 cm^{-1}.

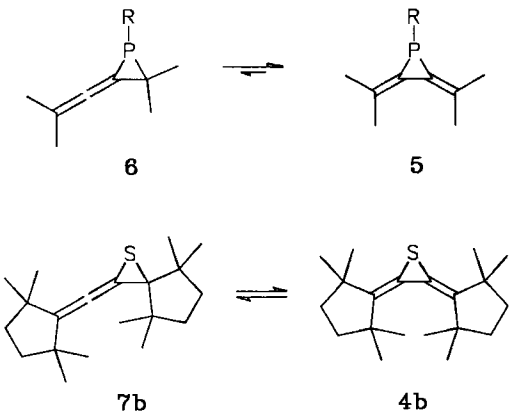


a: R = Ph (86%)
b: R = t-Bu (74%)
c: R = i-Pr (82%)
d: R = Et (64%)
e: R = Me (58%)

The air-sensitive phosphiranes **5** and **6** are obtained in a ratio of 1:1 when the reaction is carried out at −80°C, except with R = *t*Bu; here only **5b** is formed. Obviously the presence of a bulky *tert*-butyl substituent at the phosphorus hinders the formation of **6b**. The mixture of the isomeric

  0009−2940/91/0404−0933 $ 3.50+.25/0

phosphiranes **5** and **6** could not be separated by vacuum distillation. Distillation at standard pressure leads to a valence isomerization of the allenes **6** into the thermodynamically more stable "phospha[3]radialenes" **5**.



In contrast to the tautomerism of the butatriene episulfides **4b** and **7b**, the thermally equilibrated mixture of **5** and **6** exhibits only the presence of the "phospha[3]radialenes" **5**. In a similar thermal equilibration of **4b** and **7b** within the temperature range 90 to 120°C, the ratio of **4b** to **7b** becomes smaller at the higher temperature [**4b**/**7b**, 1.52 (90°C) and 1.16 (120°C)][8]. This relative instability of **4b** is due to the steric repulsion of the inner methyl groups in the hexadiene unit of **4b**. Our complete thermal conversion of **6** into **5** by heating to 150°C exhibits the intrinsic stability of the "hetero[3]radialenes" **3** relative to the corresponding isomeric allenes. For the corresponding carbocyclic rearrangement of alkenylidenecyclopropanes into dimethylenecyclopropanes temperatures of at least 360°C are necessary[13].

A. NMR Assignments in the "Phospha[3]radialenes" 5

The ^{1}H- and ^{13}C-NMR resonance lines of the substituent at the phosphorus in the "phospha[3]radialenes" **5** are assigned on the basis of the relative intensities in combination with the corresponding coupling constants. The different PC couplings ($^1J_{PC} \approx 35$ and $^2J_{PC} \approx 2$ Hz) to the phosphorus allow unequivocal assignment of the ^{13}C-NMR signals of the olefinic carbon atoms of the butadiene unit. In order to determine the assignment of the resonances of the two different allylic methyl groups in **5**, nuclear Overhauser experiments with **5b** are undertaken at 80 MHz in deuteriochloroform. Saturation of the singlet at $\delta = 2.01$ gave rise to an NOE at the doublet of the *tert*-butyl group ($\delta = 0.94$); the former signal therefore corresponds to the outer allylic methyl groups a. When the low-field doublet at $\delta = 2.15$ is saturated no enhancement at $\delta = 0.94$ occurs. Thus, it is indicated by NOE experiments that the *trans* $^4J_{PH}$ coupling constant of the inner methyl groups b in **5** is larger than the corresponding *cis* $^4J_{PH}$ (Figure 1).

The NOE experiments are a prerequisite for the assignment of the allylic methyl groups on the butadiene unit in the ^{13}C-NMR spectrum of **5b**. The C,H-connectivity is established by a two-dimensional carbon proton shift correlation. It is found that the carbon atoms at $\delta = 26.2$ and 24.8 are correlated with the protons at $\delta = 2.01$ and 2.15 and that the *cis* $^3J_{PC}$ coupling constant in **5b** is larger than the corresponding *trans* $^3J_{PC}$.

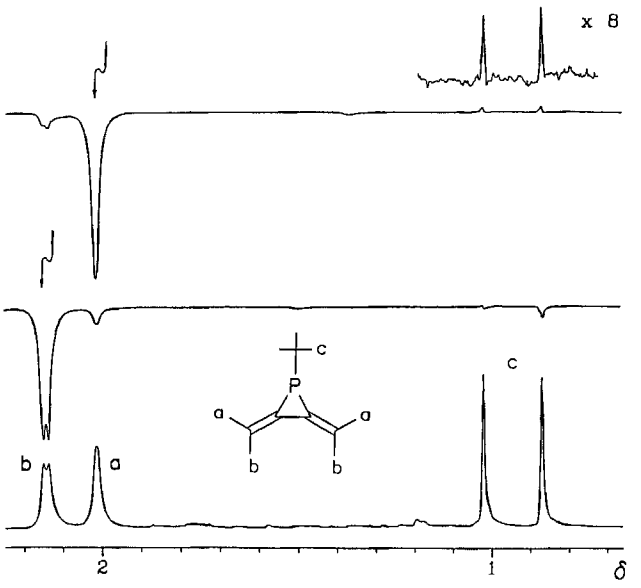


Figure 1. ^{1}H-NOE difference spectrum of **5b** at room temperature (80 MHz, $CDCl_3$)

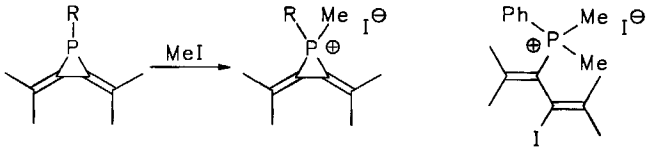
B. Reactions of the "Phospha[3]radialenes" 5

This section deals with the chemical properties of our novel phosphiranes. In an attempt to synthesize a "phospha[3]radialene" with tetracoordinate phosphorus a solution of **5a** in deuteriochloroform has been treated with dry oxygen. After 15 minutes only polymeric material could be obtained. The reaction has been carried out with ^{1}H- and ^{31}P-NMR control. When oxygen is passed through the solution of **5a** two additional sharp ^{1}H-NMR signals arise at $\delta = 2.16$ and 1.87 and one signal at $\delta = -49.3$ in the ^{31}P-NMR spectrum, which presumably indicates the formation of the corresponding "phospha[3]radialene" oxide. Furthermore, broad signals of polymeric compounds are detected during the reaction. After the disappearance of the signals of **5a** only the broad signals are present. The oxidation of the unsubstituted phosphirane (C_2H_5P) yields the unstable phosphirane 1-oxide[14], with ring-substituted phosphiranes only one method[15] gives stable phosphirane oxides. It involves cyclization by a 1,3-elimination of hydrogen halide from acyclic phosphane oxides containing an α-halogen and an α-hydrogen atom in two different substituents.

However, the quaternization of **5** with iodomethane is successful and leads to the formation of the desired phosphiranium salts **8**.

The formation of the moisture-sensitive quaternary phosphonium salts **8** is dependent on the substituent at the phosphorus atom **8b**, **8c**, and **8d** are obtained in 78 to 88% yield, whereas **8a** and **8e** could not be isolated. On the one hand, with excess iodomethane **5a** gives the acyclic phosphonium

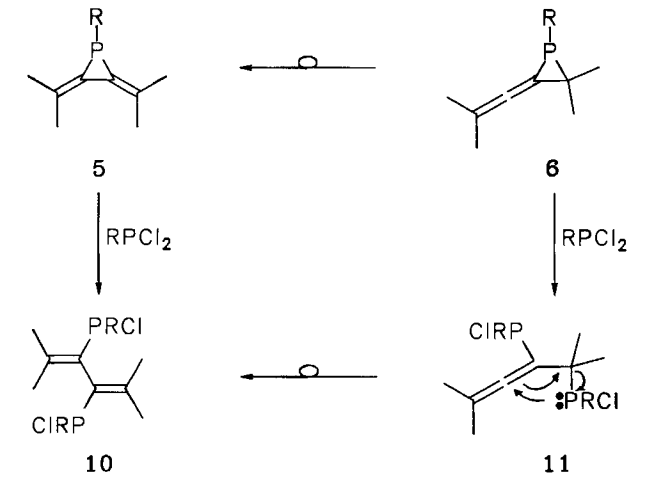
salt **9a** – probably via **8a** – while **5e**, when treated with iodomethane, yields only polymeric material.



5 **8** **9a**

A fascinating ring opening of **5** to the acyclic bis(chlorophosphino)butadiene derivatives **10** (100% yield) occurs upon treatment with dichloroorganophosphanes at room temperature. Under these mild conditions only **5c, 5d,** and **5e** react with the corresponding dichlorophosphane. The chirality of the two three-coordinate phosphorus atoms in **10** gives rise to a pair of diastereoisomers (*meso* and *d/l*). We did not, however, discover different sets of NMR signals of the expected diastereoisomers, so the relative configuration at the phosphorus of **10** could not be clarified.

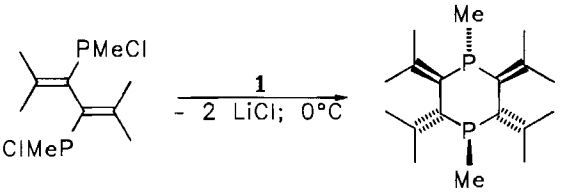
Scheme 1



10 **11**

Treatment of the mixture of the phosphiranes **5** and **6** with dichlorophosphane leads to the formation of only one acyclic bis(chlorophosphino)butadiene **10**. The allenic derivative **11** could not be detected by ^{1}H-NMR spectroscopy during the reaction. It is conceivable that **11** undergoes a rapid rearrangement to the butadiene derivative **10**. Interestingly, the interaction of the dichlorophosphane with the thermodynamically more stable phosphirane **5** is faster than with the allene **6**. This difference in reactivity makes it possible to isolate the pure allene **6**. Addition of dichlorophosphane to the mixture of **5** and **6** until **5** could not be observed any more by ^{1}H-NMR spectroscopy yields a mixture of **6** and **10** from which the allene **6** could be isolated by vacuum distillation.

10 represents a particularly interesting butadiene derivative since it is a promising precursor in the synthesis of a "1,4-diphospha[6]radialene". We have proven this assumption to be true in one example. The reaction of the dilithiobutadiene **1** with **10e** at 0°C in diethyl ether leads to the "1,4-diphospha[6]radialene" **12e** in 12% isolated yield. The 1,4-diphosphorinane **12e** exists in the rigid *trans*-chair conformation as revealed by its ^{1}H-NMR spectrum (C_{2h} symmetry). According to our results on the "1,4-disila[6]radialenes"[4] the NMR spectrum of **12e** displays two signals for the allylic methyl groups and one resonance for the methyl group at phosphorus, presumably in an axial position, both indicating the rigid *trans*-chair conformation. In principle a variety of 1,4-diphosphorinanes **12** in the interaction of **1** and **10** is expected. We have not been looking for configurational and conformational isomers of **12e**.



10e **12e**

Conclusion

The reaction of **1** with dichlorophosphanes at –80°C predominantly gives the phosphiranes **5** and **6**, which are stable towards an excess of the dilithiobutadiene derivative **1**. When phenyl- or *tert*-butyldichlorophosphane is added to a solution of **1**, or vice versa, only the phosphiranes **5a,b** and **6a** are obtained. Thus, the "1,4-diphospha[6]radialenes" **12a** and **12b** with a phenyl or *tert*-butyl group at the phosphorus cannot be prepared by our method, according to the lack of formation of the corresponding bis(chlorophosphino)butadiene derivatives **10a** and **10b**. The lack of formation of **10a** and **10b** even by the inverse addition of **1** to the corresponding dichlorophosphane shows that the simple diphosphorylation of **1** does not occur, since the monophosphorylated intermediate with one carbanionic centre immediately cyclizes to **5** or **6**. On the other hand the "1,4-diphospha[6]radialene" **12e** can be prepared in a one-pot synthesis: the dilithiobutadiene **1**, however, must be added at 0°C to a solution of dichloromethylphosphane in diethyl ether and not vice versa. In this case we consider also the phosphiranes **5** and **6** as intermediates in the formation of **12e**, as indicated by the complete formation of **10e** after addition of half an equivalent of **1**.

We thank the *Stiftung Volkswagenwerk* and the *Fonds der Chemischen Industrie* for their generous support.

Experimental

IR: Perkin Elmer (PE 580) and Beckman Acculab 4. – NMR: Bruker WP-80 and WH-400; solvent $CDCl_3$. Chemical shifts are given in values relative to TMS for protons, $CDCl_3$ for carbon atoms, and orthophosphoric acid (85%) for phosphorus atoms; coupling constants *J* in Hz. – MS: Varian MAT 112. – Melting points: Büchi SMP-20, uncorrected. – Combustion analyses: Mikroanalytisches Laboratorium Beller (Göttingen). – All reactions were performed in oven-dried (120°C) glassware under dry argon. – Dichlorophenylphosphane[16], *tert*-butyldichlorophos-

phane[17], dichloroisopropyl-, dichloroethyl-, and dichloromethylphosphane[18] were prepared by described methods.

General Procedure for the Preparation of the Phosphiranes **5** *and* **6**: A solution of dichlorophosphane (50.0 mmol) in diethyl ether (100 ml) was added dropwise over 2 h to a stirred 1.0 M solution of **1** (50 ml, 50 mmol)[5,6] in diethyl ether (diluted with 200 ml of diethyl ether) at −80°C. After warming up to room temp. the suspension (lithium chloride) was filtered. Removal of diethyl ether and heating (10 min) of the residue at 150°C gave the pure phosphiranes **5** after distillation. The mixture of the phosphiranes **5** and **6** (1:1) was obtained after removal of the volatile compounds in vacuo (0.01 Torr) at room temperature.

2,3-Diisopropylidene-1-phenylphosphirane (**5a**): Yield 9.30 g (86%), b.p. 84−85°C/0.02 Torr. − ^{1}H NMR (80 MHz): δ = 2.02 (d, J_{PH} = 0.7, CH_3-a), 2.17 (d, J_{PH} = 1.4, CH_3-b), 7.44−7.13 (m, C_6H_5). − ^{13}C NMR (100 MHz): δ = 24.9 (d, J_{PC} = 2.9, CH_3-b), 25.5 (d, J_{PC} = 3.9, CH_3-a), 119.2 (d, J_{PC} = 33.2, P*C*=C), 128.0 (s, C-*p*), 128.1 (d, J_{PC} = 6.0, C-*m*), 128.8 (d, J_{PC} = 7.0, PC=*C*), 131.5 (d, J_{PC} = 19.1, C-*o*), 140.2 (d, J_{PC} = 50.3, C-*i*). − ^{13}P NMR (32.4 MHz, C_6D_6): δ = −183.4. − IR (KBr, film): $\tilde{\nu}$ = 1730 cm^{-1} s, 740 s, 695 s. − MS: *m/z* (%) = 216 (70) [M^+], 201 (60) [M^+ − Me], 174 (36), 142 (30), 119 (50), 107 (46), 91 (100), 77 (40), 41 (41).

$C_{14}H_{17}P$ (216.3)
Calcd. C 77.76 H 7.92 P 14.32
Found C 77.65 H 7.99 P 14.40

1-tert-Butyl-2,3-diisopropylidenephosphirane (**5b**): Yield 7.25 g (74%), b.p. 64−65°C/0.01 Torr, m.p. 39−41°C. − ^{1}H NMR (80 MHz): δ = 0.94 [d, J_{PH} = 12.2, $C(CH_3)_3$], 2.01 (s, CH_3-a), 2.15 (d, J_{PH} = 1.0, CH_3-b). − ^{13}C NMR (100 MHz): δ = 24.8 (d, J_{PC} = 1.3, CH_3-b), 26.2 (d, J_{PC} = 3.5, CH_3-a), 28.9 [d, J_{PC} = 14.9, $C(CH_3)_3$], 31.4 [d, J_{PC} = 37.5, $C(CH_3)_3$], 118.2 (d, J_{PC} = 36.2, P*C*=C), 128.4 (d, J_{PC} = 6.8, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −149.3. − IR (KBr, film): $\tilde{\nu}$ = 1620 cm^{-1} s, 1365 s, 820 m. − MS: *m/z* (%) = 196 (59) [M^+], 181 (7) [M^+ − Me], 140 (31), 139 (29), 125 (67), 109 (42), 108 (30), 86 (26), 57 (100).

$C_{12}H_{21}P$ (196.3)
Calcd. C 73.44 H 10.78 P 15.78
Found C 73.02 H 10.72 P 15.50

1-Isopropyl-2,3-diisopropylidenephosphirane (**5c**): Yield 7.46 g (82%), b.p. 56−58°C/0.01 Torr. − ^{1}H NMR (400 MHz): δ = 0.99 [dd, J_{PH} = 13.8, J_{HH} = 7.1, $CH(CH_3)_2$], 1.30 [dsept, J_{PH} = 2.3, J_{HH} = 7.1, $CH(CH_3)_2$], 2.03 (s, CH_3-a), 2.14 (d, J_{PH} = 0.9, CH_3-b). − ^{13}C NMR (100 MHz): δ = 20.7 [d, J_{PC} = 12.9, $CH(CH_3)_2$], 24.6 (d, J_{PC} = 1.8, CH_3-b), 25.8 (d, J_{PC} = 3.5, CH_3-a), 29.7 [d, J_{PC} = 36.6, $CH(CH_3)_2$], 118.9 (d, J_{PC} = 35.3, P*C*=C), 127.9 (d, J_{PC} = 6.3, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −162.8. − IR (KBr, film): $\tilde{\nu}$ = 1600 cm^{-1} m, 1440 s, 1360 s. − MS: *m/z* (%) = 182 (100) [M^+], 167 (17) [M^+ − Me], 139 (74) [M^+ − Pr], 108 (43), 97 (41), 91 (52), 85 (82), 43 (52), 41 (87).

$C_{11}H_{19}P$ (182.25)
Calcd. C 72.50 H 10.51 P 16.99
Found C 72.60 H 10.26 P 17.03

1-Ethyl-2,3-diisopropylidenephosphirane (**5d**): 5.40 g (64%), b.p. 46−47°C/0.01 Torr. − ^{1}H NMR (400 MHz): δ = 0.94 (dt, J_{PH} = 13.2, J_{HH} = 7.6, CH_3), 1.17 (dq, J_{PH} = 5.2, J_{HH} = 7.6, CH_2), 2.03 (s, CH_3-a), 2.13 (d, J_{PH} = 1.2, CH_3-b). − ^{13}C NMR (20 MHz): δ = 10.4 (d, J_{PC} = 8.0, CH_3), 22.4 (d, J_{PC} = 39.2, CH_2), 24.4 (d, J_{PC} = 1.9, CH_3-b), 25.3 (d, J_{PC} = 3.8, CH_3-a), 119.1 (d, J_{PC} = 34.2, P*C*=C), 127.6 (d, J_{PC} = 7.8, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −177.7. − IR (KBr, film): $\tilde{\nu}$ = 1600 cm^{-1} m, 1440 s, 1360 s. − MS: *m/z* (%) = 168 (100) [M^+], 153 (16) [M^+ − Me], 139 (49) [M^+ − Et], 97 (42), 91 (54), 85 (53), 53 (43), 43 (52), 41 (58).

$C_{10}H_{17}P$ (168.2)
Calcd. C 71.40 H 10.19 P 18.41
Found C 71.22 H 10.14 P 18.42

2,3-Diisopropylidene-1-methylphosphirane (**5e**): Yield 4.50 g (58%), b.p. 35−37°C/0.01 Torr. − ^{1}H NMR (80 MHz): δ = 0.83 (d, J_{PH} = 4.2, CH_3), 2.03 (d, J_{PH} = 0.8, CH_3-a), 2.13 (d, J_{PH} = 1.4, CH_3-b). − ^{13}C NMR (20 MHz): δ = 13.8 (d, J_{PC} = 42.6, CH_3), 24.6 (d, J_{PC} = 1.7, CH_3-b), 25.1 (d, J_{PC} = 4.1, CH_3-a), 121.0 (d, J_{PC} = 34.2, P*C*=C), 127.6 (d, J_{PC} = 7.8, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −195.4. − IR (KBr, film): $\tilde{\nu}$ = 1605 cm^{-1} m, 1435 s, 1360 s. − MS: *m/z* (%) = 154 (100) [M^+], 139 (48) [M^+ − Me], 107 (21), 97 (26), 91 (51), 85 (36), 57 (38), 41 (55), 39 (32).

$C_9H_{15}P$ (154.2)
Calcd. C 70.11 H 9.80 P 20.09
Found C 70.00 H 9.66 P 19.98

2,2-Dimethyl-3-(2-methyl-1-propenylidene)-1-phenylphosphirane (**6a**), *Obtained from a Mixture of* **5a** *and* **6a**: ^{1}H NMR (80 MHz): δ = 1.08 (d, J_{PH} = 4.9, CCH_3-*syn*), 1.44 (d, J_{PH} = 15.2, CCH_3-*anti*), 1.84 (d, J_{PH} = 1.5, C=CCH_3), 1.90 (d, J_{PH} = 1.7, C=CCH_3), 7.20−7.50 (m, C_6H_5). − ^{13}C NMR (100 MHz): δ = 21.0 (s, CH_3), 21.6 (s, CH_3), 21.8 (s, CH_3), 27.3 (d, J_{PC} = 21.8, 2-CH_3-*anti*), 30.2 [d, J_{PC} = 28.7, $C(CH_3)_2$], 91.9 (d, J_{PC} = 42.2, P*C*=C=C), 98.2 (s, PC=C=*C*), 127.8 (d, J_{PC} = 6.0, C-*m*), 128.0 (s, C-*p*), 133.2 (d, J_{PC} = 17.1, C-*o*), 137.1 (d, J_{PC} = 46.3, C-*i*), 193.1 (d, J_{PC} = 6.0, C=*C*=C). − ^{31}P NMR (162 MHz): δ = −139.8. − IR (KBr, film): $\tilde{\nu}$ = 1970 cm^{-1} m.

1-Isopropyl-2,2-dimethyl-3-(2-methyl-1-propenylidene)phosphirane (**6c**): The mixture of **5c** and **6c** (1:1) from the reaction of dichloroisopropylphosphane (50.0 mmol) with **1** was treated with 3.05 g (21.0 mmol) of dichloroisopropylphosphane. Distillation gave pure **6c** (3.21 g, 35%), b.p. 28−30°C/0.002 Torr. − ^{1}H NMR (400 MHz): δ = 1.05−1.11 [8 signals, $CH(CH_3)_2$], 1.30 (d, J_{PH} = 14.8, CCH_3-*anti*), 1.38 [oct, J_{HH} = 7.1, J_{PH} = 7.1, $CH(CH_3)_2$], 1.48 (d, J_{PH} = 4.5, CCH_3-*syn*), 1.76 [br s, C=$C(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = 20.8 (s, CH_3), 21.1 (d, J_{PC} = 14.1, CH_3), 21.4 (s, CH_3), 21.5 (s, CH_3), 21.5 (d, J_{PC} = 24.7, CH_3), 26.6 [d, J_{PC} = 29.0, $C(CH_3)_2$], 26.9 [d, J_{PC} = 34.0, $CH(CH_3)_2$], 27.9 (d, J_{PC} = 21.1, 2-CH_3-*anti*), 93.2 (d, J_{PC} = 43.3, P*C*=C=C), 96.8 (s, PC=C=*C*), 190.2 (d, J_{PC} = 5.0, C=*C*=C). − ^{31}P NMR (32.4 MHz): δ = −124.5. − IR (KBr, film): $\tilde{\nu}$ = 1970 cm^{-1} m.

1-Ethyl-2,2-dimethyl-3-(2-methyl-1-propenylidene)phosphirane (**6d**), *Obtained from a Mixture of* **5d** *and* **6d**: ^{1}H NMR (80 MHz): δ = 0.85−1.40 (m, C_2H_5), 1.32 (d, J_{PH} = 13.8, CCH_3-*anti*), 1.46 (d, J_{PH} = 4.6, CCH_3-*syn*), 1.76 [d, J_{PH} = 1.4, C=$C(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = 11.5 (d, J_{PC} = 13.8, CH_2CH_3), 18.4 (d, J_{PC} = 38.6, CH_2CH_3), 20.7 (s, CH_3), 21.1 (s, CH_3), 21.3 (s, CH_3), 25.7 [d, J_{PC} = 28.3, $C(CH_3)_2$], 27.6 (d, J_{PC} = 22.7, 2-CH_3-*anti*), 93.3 (d, J_{PC} = 44.7, P*C*=C=C), 96.5 (s, PC=C=*C*), 190.5 (d, J_{PC} = 5.1, C=*C*=C). − ^{31}P NMR (162 MHz): δ = −137.2. − IR (KBr, film): $\tilde{\nu}$ = 1970 cm^{-1} m.

1,2,2-Trimethyl-3-(2-methyl-1-propenylidene)phosphirane (**6e**), *Obtained from a Mixture of* **5e** *and* **6e**: ^{1}H NMR (80 MHz): δ = 0.94 (d, J_{PH} = 5.1, PCH_3), 1.33 (d, J_{PH} = 15.5, CCH_3-*anti*), 1.46 (d, J_{PH} = 5.0, CCH_3-*syn*), 1.77 [d, J_{PH} = 1.5, C=$C(CH_3)_2$]. − ^{13}C NMR (20 MHz): δ = 9.3 (d, J_{PC} = 42.5, PCH_3), 20.7 (s, CH_3), 21.1 (s, CH_3), 21.3 (s, CH_3), 25.4 [d, J_{PC} = 34.0, $C(CH_3)_2$], 27.5 (d, J_{PC} = 24.3, 2-CH_3-*anti*), 94.9 (d, J_{PC} = 45.0, P*C*=C=C), 97.3 (s, PC=C=*C*), 190.5 (d, J_{PC} = 5.0, C=*C*=C). − ^{13}P NMR (162 MHz): δ = −152.8. − IR (KBr, film): $\tilde{\nu}$ = 1970 cm^{-1} m.

1-tert-Butyl-2,3-diisopropylidene-1-methylphosphiranium Iodide (**8b**): **5b** (3.93 g, 20.0 mmol) and iodomethane (2.84 g, 20.0 mmol) were stirred at room temp. in $CHCl_3$ (20 ml) for 3 h. The slightly yellow solution was evaporated to dryness and the residue was treated with pentane (50 ml) to give **8b** (6.20 g, 92%) after filtration. Recrystallization from acetone at −25°C gave pure **8b** (5.74 g, 85%), m.p. 156−157°C (dec.). − ^{1}H NMR (400 MHz): δ = 1.42 [d, J_{PH} = 21.5, $C(CH_3)_3$], 2.19 (s, $=CCH_3$), 2.23 (s, $=CCH_3$), 2.40 (d, J_{PH} = 14.9, PCH_3). − ^{13}C NMR (100 MHz): δ = 4.6 (d, J_{PC} = 29.2, PCH_3), 24.9 (d, J_{PC} = 14.7, $=CCH_3$), 26.7 [s, $C(CH_3)_3$], 28.5 (d, J_{PC} = 11.0, $=CCH_3$), 32.9 [$C(CH_3)_3$], 104.3 (d, J_{PC} = 13.1, P*C*=C), 145.6 (s, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −78.1.

$C_{13}H_{24}IP$ (338.2)
Calcd. C 46.17 H 7.15 I 37.52 P 9.16
Found C 46.48 H 6.89 I 37.34 P 9.00

1-Isopropyl-2,3-diisopropylidene-1-methylphosphiranium Iodide (**8c**): **5c** (3.64 g, 20.0 mmol) and iodomethane (2.84 g, 20.0 mmol) were stirred at room temp. in $CHCl_3$ (20 ml) for 3 h. The solution was worked up as described for **8b** to give **8c** (5.72 g, 88%). Recrystallization from acetone/hexane (2:1) at −25°C gave pure **8c** (5.21 g, 80%), m.p. 115−117°C (dec.). − ^{1}H NMR (400 MHz): δ = 1.27 [dd, J_{PH} = 24.1, J_{HH} = 7.2, $CH(CH_3)_2$], 2.25 (s, $=CCH_3$), 2.29 (s, $=CCH_3$), 2.47 (d, J_{PH} = 15.7, PCH_3), 4.00 [dsept, J_{PH} = 10.9, J_{HH} = 7.1, $CH(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = 7.5 (d, J_{PC} = 34.2, PCH_3), 17.4 [s, $CH(CH_3)_2$], 25.1 (d, J_{PC} = 16.1, $=CCH_3$), 25.7 [d, J_{PC} = 32.5, $CH(CH_3)_2$], 28.4 (d, J_{PC} = 10.1, $=CCH_3$), 103.8 (d, J_{PC} = 15.1, P*C*=C), 145.6 (s, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −82.7.

$C_{12}H_{22}IP$ (338.2)
Calcd. C 44.46 H 6.84 I 39.15 P 9.55
Found C 44.52 H 6.91 I 39.13 P 9.33

1-Ethyl-2,3-diisopropylidene-1-methylphosphiranium Iodide (**8d**): **5d** (3.36 g, 20.0 mmol) and iodomethane (2.84 g, 20.0 mmol) were stirred at room temp. in $CHCl_3$ (20 ml) for 3 h. The solution was worked up as described for **8b** to give crude **8d** (4.84 g, 78%), m.p. 75−80°C (dec.). Recrystallization from acetone/hexane has not been successful. − ^{1}H NMR (400 MHz): δ = 1.14 (dt, J_{PH} = 26.0, J_{HH} = 7.4, CH_2CH_3), 2.33 (s, $=CCH_3$), 2.40 (s, $=CCH_3$), 2.61 (d, J_{PH} = 16.6, PCH_3), 3.24 (dq, J_{PH} = 14.3, J_{HH} = 7.4, CH_2CH_3). − ^{13}C NMR (100 MHz): δ = 6.3 (d, J_{PC} = 6.1, CH_2CH_3), 8.3 (d, J_{PC} = 39.3, PCH_3), 16.4 (d, J_{PC} = 38.4, CH_2CH_3), 24.3 (d, J_{PC} = 17.0, $=CCH_3$), 27.3 (d, J_{PC} = 11.3, $=CCH_3$), 102.7 (d, J_{PC} = 16.8, P*C*=C), 144.9 (s, PC=*C*). − ^{31}P NMR (32.4 MHz): δ = −89.2.

3-(Dimethylphenylphosphonio)-4-iodo-2,5-dimethyl-2,4-hexadiene Iodide (**9a**): **5a** (2.16 g, 10.0 mmol) and iodomethane (4.54 g, 32.0 mmol) were stirred at room temp. in ether (20 ml) for 2 d. The crystalline solid formed was collected by filtration to give crude **9a** (3.13 g, 63%); recrystallization from ethanol gave pure **9a** (2.84 g, 57%), m.p. 149−150°C. − ^{1}H NMR (400 MHz, CD_3OD): δ = 1.91 (d, J_{PH} = 2.4, $=CCH_3$), 1.98 (d, J_{PH} = 1.9, $=CCH_3$), 2.00 (d, J_{PH} = 3.0, $=CCH_3$), 2.11 (d, J_{PH} = 4.2, $=CCH_3$), 2.36 (d, J_{PH} = 13.6, PCH_3), 2.47 (d, J_{PH} = 13.3, PCH_3), 7.75−7.83 (m, C_6H_5), 8.05−8.11 (m, C_6H_5). − ^{13}C NMR (100 MHz, CD_3OD): δ = 12.0 (d, J_{PC} = 55.8, PCH_3), 12.4 (d, J_{PC} = 58.4, PCH_3), 21.9 (s, $=CCH_3$), 24.9 (d, J_{PC} = 11.7, $=CCH_3$), 25.2 (d, J_{PC} = 8.8, $=CCH_3$), 30.3 (s, $=CCH_3$), 89.0 (d, J_{PC} = 10.1, I*C*=C), 120.9 (d, J_{PC} = 85.8, PC=C*), 123.2 (d, J_{PC} = 83.3, C-*i**), 131.3 (d, J_{PC} = 13.6, C-*m*), 132.6 (d, J_{PC} = 10.9, C-*o*), 135.5 (s, C-*p*), 148.3 [d, J_{PC} = 8.4, $=C(CH_3)_2$], 164.8 [d, J_{PC} = 10.9, $=C(CH_3)_2$]; * assignments interchangeable. − ^{31}P NMR (32.4 MHz, [D$_6$]DMSO): δ = 16.3.

$C_{16}H_{23}I_2P$ (500.1)
Calcd. C 38.42 H 4.64 I 50.75 P 6.19
Found C 38.22 H 4.94 I 50.53 P 6.23

3,4-Bis(chloroisopropylphosphino)-2,5-dimethyl-2,4-hexadiene (**10c**): Dichloroisopropylphosphane (2.90 g, 20.0 mmol) was added at room temp. to a solution of **5c** (3.64 g, 20.0 mmol) in CH_2Cl_2 (20 ml) with stirring (15 min). Removal of the solvent gave pure **10c** (6.54 g, 100%), b.p. 115−120°C/0.001 Torr. − ^{1}H NMR (80 MHz): δ = 1.02 (d, J_{HH} = 6.9, $CHCH_3$), 1.23 ("d"d, J_{PH} + $J_{P'H}$ = 3.9, J_{HH} = 6.9, $CHCH_3$), 1.74 ("d", J_{PH} + $J_{P'H}$ = 1.4, $=CCH_3$), 2.14 (s, $=CCH_3$), 2.20 ["quint", J_{PH} + $J_{P'H}$ = 6.9, J_{HH} = 6.9, $CH(CH_3)_2$]. − ^{13}C NMR (100 MHz): δ = 18.6 ("d", J_{PC} + $J_{P'C}$ = 18.1, $CHCH_3$), 19.2 ("d", J_{PC} + $J_{P'C}$ = 26.2, $CHCH_3$), 23.0 ("d", J_{PC} + $J_{P'C}$ = 32.2, $=CCH_3$), 25.2 (s, $=CCH_3$), 30.8 ["d", J_{PC} + $J_{P'C}$ = 28.2, $CH(CH_3)_2$], 133.1 ("d", J_{PC} + $J_{P'C}$ = 48.3, PC=C), 148.5 ("d", J_{PC} + $J_{P'C}$ = 31.2, PC=C). − ^{31}P NMR (32.4 MHz): δ = 108.2. − IR (KBr, film): $\tilde{\nu}$ = 1380 cm^{-1} s, 1365 s, 650 s. − MS: *m/z* (%) = 326 (6) [M$^+$], 291 (7) [M$^+$ − Cl], 285 (63), 283 (100), 205 (19), 139 (29), 108 (68), 107 (42), 93 (36).

$C_{14}H_{26}Cl_2P_2$ (327.2)
Calcd. C 51.39 H 8.01 Cl 21.67 P 18.93
Found C 51.40 H 8.09 Cl 21.51 P 19.02

3,4-Bis(chloroethylphosphino)-2,5-dimethyl-2,4-hexadiene (**10d**): Dichloroethylphosphane (2.62 g, 20.0 mmol) was added at room temp. to a solution of **5d** (3.36 g, 20.0 mmol) in CH_2Cl_2 (20 ml) with stirring (15 min). Removal of the solvent gave pure **10d** (5.98 g, 100%), b.p. 85−87°C/0.001 Torr. − ^{1}H NMR (80 MHz): δ = 1.26 ("d"t, J_{PH} + $J_{P'H}$ = 17.7, J_{HH} = 7.1, CH_2CH_3), 1.45−1.95 (m, CH_2CH_3), 1.77 ("d", J_{PH} + $J_{P'H}$ = 3.6, $=CCH_3$), 2.18 ("d", J_{PH} + $J_{P'H}$ = 1.4, $=CCH_3$). − ^{13}C NMR (20 MHz): δ = 9.2 ("d", J_{PC} + $J_{P'C}$ = 20.4, CH_2CH_3), 22.3 ("d", J_{PC} + $J_{P'C}$ = 29.3, $=CCH_3$), 24.9 (s, $=CCH_3$), 26.4 ("d", J_{PC} + $J_{P'C}$ = 28.3, CH_2CH_3), 133.6 ("d", J_{PC} + $J_{P'C}$ = 47.9, PC=C), 149.0 ("d", J_{PC} + $J_{P'C}$ = 34.2, PC=C). − ^{31}P NMR (32.4 MHz): δ = 104.7. − IR (KBr, film): $\tilde{\nu}$ = 1380 cm^{-1} s, 1365 s, 650 s. − MS: *m/z* (%) = 263 (4) [M$^+$ − Cl], 228 (6), 139 (13), 109 (14), 108 (100), 107 (36), 93 (33), 91 (30), 77 (18).

$C_{12}H_{22}Cl_2P_2$ (299.2)
Calcd. C 48.18 H 7.41 Cl 23.70 P 20.71
Found C 47.97 H 7.48 Cl 23.77 P 20.68

3,4-Bis(chloromethylphosphino)-2,5-dimethyl-2,4-hexadiene (**10e**): Dichloromethylphosphane (2.34 g, 20.0 mmol) was added at room temp. to a solution of **5e** (3.08 g, 20.0 mmol) in CH_2Cl_2 (20 ml) with stirring (15 min). Removal of the solvent gave pure **10e** (5.42 g, 100%), b.p. 104−108°C/0.001 Torr. − ^{1}H NMR (80 MHz): δ = 1.51 ("d", J_{PH} + $J_{P'H}$ = 11.7, PCH_3), 1.79 ("d", J_{PH} + $J_{P'H}$ = 3.6, $=CCH_3$), 2.23 ("d", J_{PH} + $J_{P'H}$ = 1.7, $=CCH_3$). − ^{13}C NMR (100 MHz): δ = 18.3 ("d", J_{PC} + $J_{P'C}$ = 29.2, PCH_3), 21.5 ("d", J_{PC} + $J_{P'C}$ = 30.2, $=CCH_3$), 24.3 (s, $=CCH_3$), 132.1 ("d", J_{PC} + $J_{P'C}$ = 46.3, PC=C), 149.2 ("d", J_{PC} + $J_{P'C}$ = 37.2, PC=C). − ^{31}P NMR (32.4 MHz): δ = 89.2. − IR (KBr, film): $\tilde{\nu}$ = 1370 cm^{-1} s, 895 s, 865 s. − MS: *m/z* (%) = 271 (12), 109 (10), 108 (100), 107 (30), 93 (16), 77 (8), 65 (7), 53 (8), 41 (11).

$C_{10}H_{18}Cl_2P_2$ (271.1)
Calcd. C 44.31 H 6.69 Cl 26.15 P 22.85
Found C 44.08 H 6.71 Cl 24.09 P 22.92

trans-2,3,5,6-Tetraisopropylidene-1,4-dimethyl-1,4-diphosphacyclohexane (**12e**): At 0°C a 1.0 M solution of **1** (20.0 ml, 20.0 mmol) in diethyl ether (diluted with 100 ml of diethyl ether) was added dropwise within 2 h to dichloromethylphosphane (2.34 g, 20 mmol) in diethyl ether (200 ml). After filtration and removal of the solvent, the residue was condensed in vacuo. **12e** (0.37 g, 12%) crystallized from the condensed oil after addition of acetone (5 ml), m.p. 204−205°C. − ^{1}H NMR (80 MHz): δ = 0.65 ("d", J_{PH} + $J_{P'H}$ = 6.2, PCH_3), 1.51 (s, $=CCH_3$), 2.20 ("d", J_{PH} + $J_{P'H}$ = 0.7, $=CCH_3$). − ^{13}C NMR (100 MHz): δ = 7.5 ("d", J_{PC} + $J_{P'C}$ = 8.5, PCH_3),

22.0 ("d", $J_{PC} + J_{P'C} = 35.2$, $=CCH_3$), 22.8 ("d", $J_{PC} + J_{P'C} = 6.2$, $=CCH_3$), 132.8 (m, PC=C), 140.1 ("d", $J_{PC} + J_{P'C} = 33.4$ PC=C). – ^{31}P NMR (32.4 MHz): $\delta = -55.6$. – MS: m/z (%) = 309 (17) [$M^+ + 1$], 308 (42) [M^+], 294 (18), 293 (100) [$M^+ - Me$], 201 (11), 185 (10), 107 (11), 93 (11), 91 (13).

$C_{18}H_{30}P_2$ (308.4)
Calcd. C 70.11 H 9.80 P 20.09
Found C 69.51 H 10.27 P 19.84

[1] Part XII: A. Maercker, U. Girreser, *Angew. Chem.* **102** (1990) 718; *Angew. Chem. Int. Ed. Engl.* **29** (1990) 667.
[2] A. Maercker, F. Brauers, W. Brieden, M. Jung, H. D. Lutz, *Angew. Chem.* **100** (1988) 413; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 404.
[3] A. Maercker, W. Brieden, T. Schmidt, H. D. Lutz, *Angew. Chem.* **101** (1989) 477; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 477.
[4] A. Maercker, F. Brauers, W. Brieden, B. Engelen, *J. Organomet. Chem.* **377** (1989) C45.
[5] A. Maercker, R. Dujardin, *Angew. Chem.* **97** (1985) 612; *Angew. Chem. Int. Ed. Engl.* **24** (1985) 571.
[6] A. Maercker, R. Dujardin, F. Brauers, *Organomet. Synth.* **4** (1988) 362.
[7] [7a] W. Ando, Y. Hanyu, Y. Kumamoto, T. Takata, *Tetrahedron* **42** (1986) 1989. – [7b] W. Ando, Y. Hanyu, T. Takata, *Tetrahedron Lett.* **22** (1981) 4815.
[8] W. Ando, N. Tokitoh, H. Hayakawa, *Tetrahedron Lett.* **29** (1988) 5161.
[9] In the meantime we have prepared **4a** (5% yield, not optimized) by addition of a 1.0 M solution of **1** in diethyl ether to a suspension of diimidazolyl sulfide and ether at room temperature.
[10] B. Weber, R. Luckenbach, H.-G. Padeken, M. Regitz, in *Methoden der organischen Chemie* (Houben-Weyl-Müller), 4th ed., vol. E1, p. 8–12, Thieme, Stuttgart 1982.
[11] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, p. 129, Thieme, Stuttgart 1984.
[12] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, p. 99, Thieme, Stuttgart 1982.
[13] J. K. Crandall, D. R. Pauson, *J. Am. Chem. Soc.* **88** (1966) 4302.
[14] K. Dimroth in *Comprehensive Heterocyclic Chemistry* (O. Meth-Cohn, Ed.), 1th ed., vol. 1, p. 525, Pergamon Press, Oxford 1984.
[15] [15a] H. Quast, M. Heuschmann, *Angew. Chem.* **90** (1978) 921; *Angew. Chem. Int. Ed. Engl.* **17** (1978) 867. – [15b] H. Quast, M. Heuschmann, *Liebigs Ann. Chem.* **1981**, 977.
[16] B. Buchner, L. B. Lockhart, *Org. Synth. Coll. Vol. IV* (N. Rabjohn, Ed.), p. 784, Wiley, New York 1963.
[17] M. Fild, O. Stelzer, R. Schmutzler, *Inorganic Syntheses* (A. Wold, J. K. Ruff, Ed.), vol. 14, p. 4, McGraw-Hill, New York 1973.
[18] [18a] J. B. Reesor, B. J. Perry, E. Sherlock, *Can. J. Chem.* **38** (1960) 1416. – [18b] J. B. Reesor, B. J. Perry, J. L. Ferron, *Can. J. Chem.* **41** (1963) 2299.

[326/90]