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Diels-Alder Adducts of 4-Chloro-1,6-Dihydrophosphinine Derivatives: A New Precursor of 2-Phosphapropene

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ABSTRACT

The 4-chloro-1,6-dihydrophosphinine derivatives, prepared as a mixture of 3- and 5-methyl isomers from the thermolysis of dichlorocarbene adducts with 1-R-3-methylphospholene oxide (R = Me, MeO, EtO, n-PrO, i-PrO), participate in Diels-Alder reactions with dimethyl acetylenedicarboxylate and N-phenylmaleimide. The former reactant is of special value since the 2-phosphabicyclo[2.2.2]octa-5,7-diene framework is thermally labile and undergoes retrocycloaddition by a different path, eliminating the C–P bridging unit as a low-coordinate species. Thus, in the case of R = Me, the initial phosphine oxides (a mixture of isomers) have been reduced to the phosphines, and these undergo straightforward fragmentations on heating at 50°C to produce 2-phosphapropene. The reactions of this transient species with water and alcohols have been investigated. Unlike the case of stabilized phosphaalkenes, hydration occurs smoothly without catalysis to produce $Me_2P(O)H$; addition of alcohols gives phosphinites, Me_2POR. The structure of the Diels-Alder adducts was confirmed by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. Each of the isomeric 1,6-dihydrophosphinine oxides gives two diastereomeric adducts; partial separation of some of the resulting four-component mixtures was achieved with silica gel chromatography.

*To whom correspondence should be addressed.
Dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

RESULTS AND DISCUSSION

We have reported a new method, outlined in Scheme 1, for the synthesis of derivatives of the 1,6-dihydrophosphinine system (**2,3**) starting with a 3-phospholene oxide (**1**). We proceeded to use these compounds as dienes in the Diels-Alder reaction to obtain new derivatives of the 2-phosphabicyclo[2.2.2]oct-5-ene and -octa-5,7-diene ring systems [1]. With phosphorus in the phosphine state, derivatives of this ring system were shown to be valuable as precursors of two-coordinate phosphines (phosphaalkenes) through an apparent retro-cycloaddition reaction (Scheme 2). The highly reactive species Me–P=CH_2 and Ph–P=CH_2 were generated in solution for the first time by this approach [2].

3-Phospholene oxides can also be the starting materials for another route [3] to 1,6-dihydrophosphinine oxides, which has fewer steps than the method outlined in Scheme 1, and which therefore seemed to offer easier access to the bridged structure needed as a precursor to the phosphaalkenes. This route (Scheme 3) consists of only two steps: (1) the addition of dichlorocarbene (generated from $CHCl_3$ and NaOH) to the double bond of 3-phospholene oxide derivatives to form the 2-phosphabicyclo[3.1.0]hexane ring system (**7**) [3], which requires phase-transfer conditions employing triethylbenzylammonium chloride (TEBAC) to effect the reaction, and (2) thermal or base-promoted loss of HCl with opening of the cyclopropane ring to generate the 4-chloro-1,6-dihydrophosphinine ring system (**8**, in isomeric forms A and B if R′ is other than H) [4].

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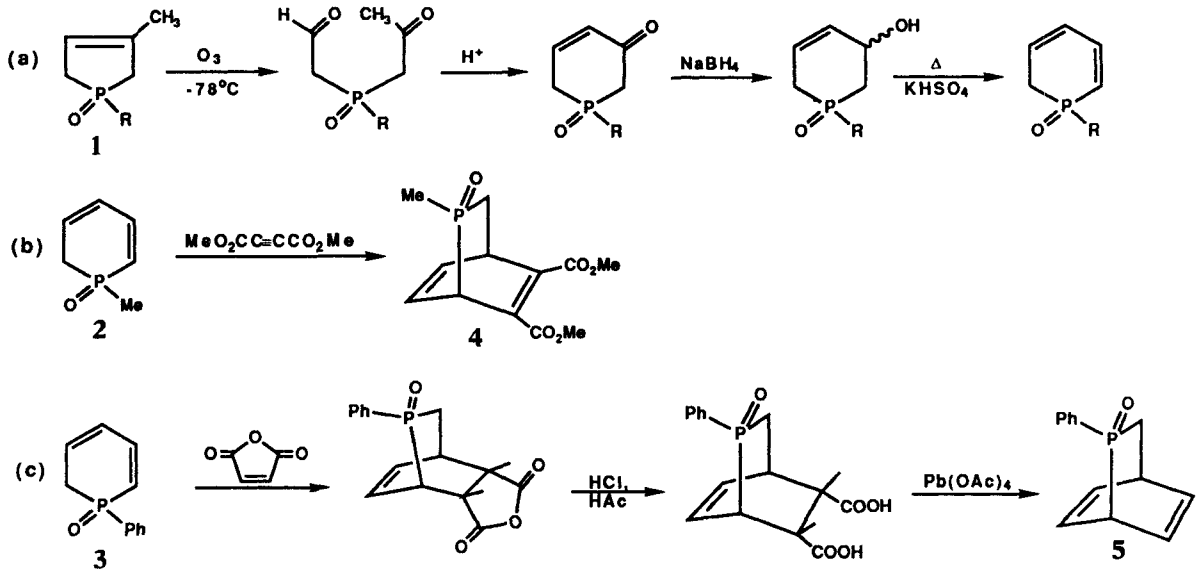
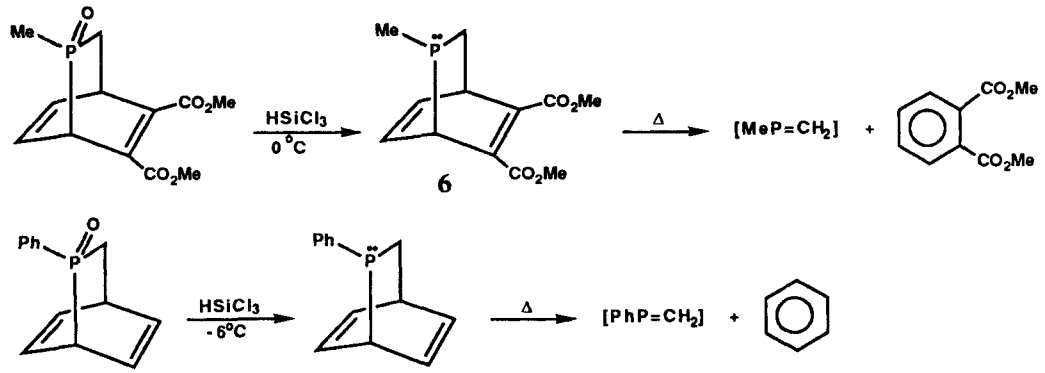


SCHEME 1



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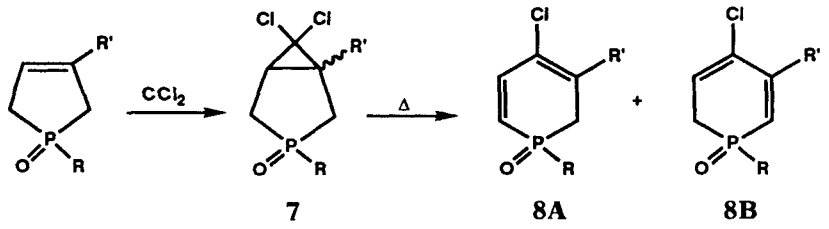


7 8A 8B

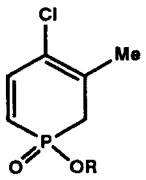
SCHEME 3

In this paper, we examine first the usefulness of the 1,6-dihydrophosphinines prepared by this route in the Diels-Alder reaction to give the 2-phosphabicyclo[2.2.2]octa-5,7-diene 2-oxide ring system. Both carbon and alkoxy substituents have been present on phosphorus, and as will be seen the method is quite versatile and practical for the construction of the desired ring system. The formation of two isomers in the thermal reaction of the dichlorocarbene adducts is a drawback, since additionally each gives two diastereoisomeric Diels-Alder adducts from the two possible configurations at phosphorus. The practical separation of the four-isomer mixtures has proved to be difficult but is in fact unnecessary if the product is to be used for the generation of low-coordinate phosphorus species, since all isomers give the same fragment on retrocycloaddition. We include in this paper our work on the construction of the 2-phosphabicyclo[2.2.2]octa-5,7-diene ring system with phospho-

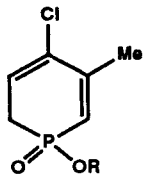
rus in the phosphine state and demonstrate the utility of the isomer mixture for the generation of the highly reactive 2-phosphapropene. In a later paper, we will report on successful fragmentations that have been performed with the *P*-oxides.

Synthesis of 1,6-Dihydrophosphinine Oxides

The procedure for the synthesis of 1,6-dihydrophosphinine oxides from 3-phospholene oxides according to Scheme 3, where phosphorus is in the phosphinate state, has been reported [5]. This earlier work provided the four phosphinates **9a–d** as position isomers **A** and **B**, and these were used in



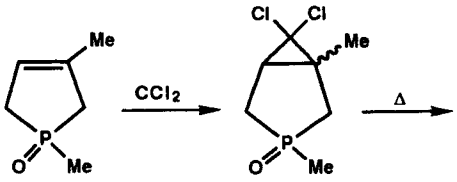
9A, a–d



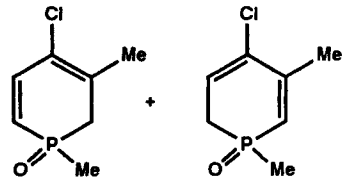
9B, a–d

	R
a	Me
b	Et
c	*n*-Pr
d	*i*-Pr

the present study. Phosphine oxide **11** [4b] was also prepared. With some modification of the isolation procedure, a 57.5% yield of dichlorocarbene adduct **10** was achieved. The conversion to the dihydrophosphinine oxide system was accomplished as published [4b] by brief (4 min) heating of small batches (2–3 g) at 135°C, and the product was purified by silica gel chromatography. This provided a 94% yield of a mixture of isomers **11A** (75%) and **11B** (25%).

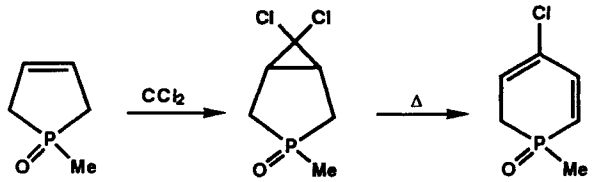


10



11A **11B**

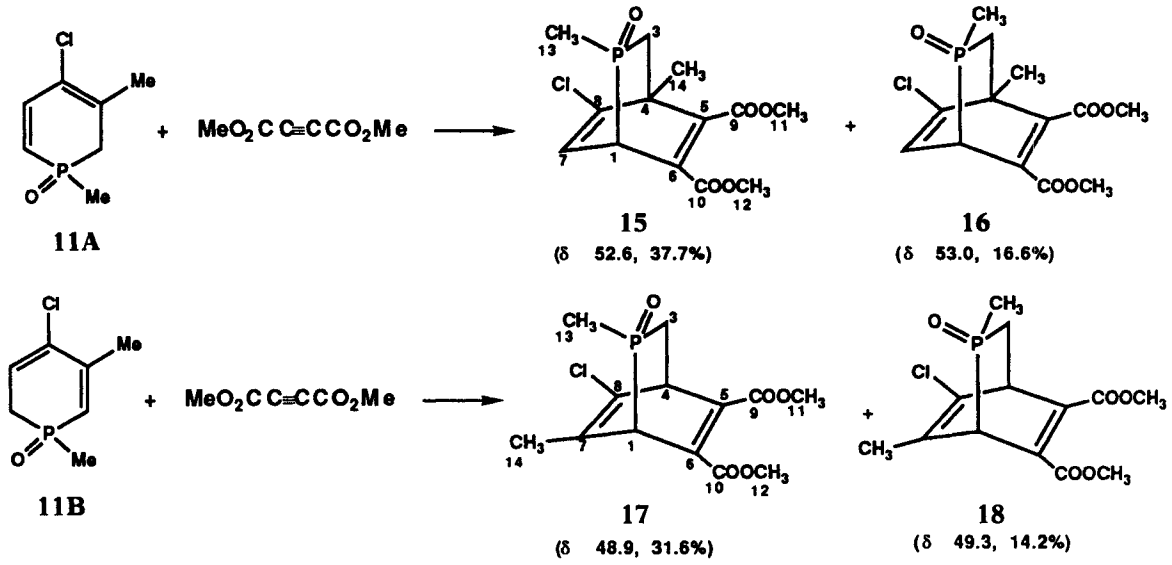
The formation of an isomer mixture can be avoided by the use of 1-methyl-3-phospholene oxide (**12**) as starting material, but this compound is less reactive to electrophiles and when it was used in the cyclopropanation reaction it gave only a 17.1% yield of **13** even after nine successive treatments with fresh NaOH-TEBAC. Compound **13** did undergo the ring-enlargement on heating to give the expected product **14**, but this compound was not very stable and was not further studied.



12 **13** **14**

Diels-Alder Reactions of the Dihydrophosphinine Oxides

For the generation of low-covalent species, the Diels-Alder adducts with acetylenic derivatives are the preferred precursors, since their fragmentation (leading to benzene derivatives) is known [2] to occur with much greater ease than does the fragmentation of adducts with olefinic derivatives. The exploratory studies on Diels-Alder additions were performed primarily on the mixed *P*-methyl 1,6-dihydrophosphinine oxides **11A–B**. Diphenylacetylene failed to react with **11A–B** after refluxing in benzene for 6 days. Dimethyl acetylenedicarboxylate, however, was much more reactive under these conditions, and after 34 h all of the starting 1,6-dihydrophosphinine oxide was consumed, according to analysis by ^{31}P NMR spectroscopy. Catalysis by aluminum chloride had been found to be effective in our earlier work [1] with this dienophile, but led to quite complex mixtures in the present case. The thermal process provided four adducts (Scheme 4) indicated to be of similar structure by the proximity of their ^{31}P NMR signals (in $CDCl_3$, δ 53.0, 52.6, 49.3, and 48.9). These signals were in the expected position based on the shift for the previously prepared [1] analogous adduct of Scheme 1 (**4**, δ ^{31}P 50.0). The product was recovered in 58.4% yield after chromatography on silica gel. Partial separation of the isomers was obtained during chromatography, but only at its end was a single, crystalline isomer (δ ^{31}P 53.0) eluted. Its ^{13}C and ^{1}H NMR spectra showed that it had been formed from 1,6-dihydrophosphinine oxide **11A** since it contained an olefinic carbon bearing hydrogen. Attempts were made to grow a crystal suitable for structure confirmation by X-ray diffraction analysis, but an unsatisfactory twinned crystalline form was produced. Tentatively, the configuration at phosphorus is assumed (vide infra) to be *that shown* by **16**. An early chromatographic fraction contained only the isomers with δ ^{31}P 52.6 and 48.9; ^{13}C and ^{1}H NMR spectroscopy showed that they were position isomers. The isomer with δ ^{31}P 52.6 contained an olefinic proton and was assigned structure **15**. The other isomer was tentatively assigned structure **17**. It was found that this isomer mixture could be



SCHEME 4

TABLE 1 $^{1}H^{a}$ and Partial^{b} ^{13}C NMR Data for Bicyclic Oxides 15-18^{c}

	15^{d}	16^{e}	17^{d}	18^{f}
C_1–*H*	4.39(dd, 12.5$_P$, 7.4$_{H-7}$)	4.53(dd, 12.5$_P$, 7.5$_{H-7}$)	4.15(d, 11.5$_P$)	4.05–4.29(m)
C_3–H	1.68–1.81(m)	1.65(m)	1.76–1.99(m)	1.82–1.89(m)
C_4–H	—	—	4.14(ddd, 21.7$_P$, 3.5$_{H-3a}$, 6.5$_{H-3b}$)	4.05–4.19(m)
C_7–H	6.60(dd, 4.2$_P$, 7.4$_{H-1}$)	6.27(dd, 5.7$_P$, 7.5$_{H-1}$)	—	—
C_{11}–*H*, C_{12}–*H*	3.81, 3.85	3.76, 3.82	3.81, 3.83	3.83, 3.86
C_{13}–*H*	1.61(d, 14.5$_P$)	1.65(d, 12.9$_P$)	1.69(d, 10.3$_P$)	1.60(d, 10.7$_P$)
C_{14}–*H*	1.58^{d}	1.53(d, 2.2$_P$)	2.07(d, 2.6$_P$)	1.94(s)
C-1	43.7(49.9)	43.4(49.9)	50.5(48.9)	51.7(49.1)
C-3	32.5(94.0)	32.4(94.2)	24.6(95.2)	25.6(95.7)
C-4	47.5(8.7)	47.2(8.7)	45.5(9.2)	46.9(9.3)
C-9,10	162.8(2.9), 164.4(3.9)	162.2(2.1), 166.2(3.0)	165.0(2.7), 166.2(3.7)	166.2(s), 165.9(s)
C-11,12	52.6, 53.0	52.6, 53.0	52.8, 53.0	54.0, 53.5
C-13	15.1(68.0)	15.9(70.6)	15.8(67.2)	16.5(69.7)
C-14	20.2(9.8)	20.2(9.5)	18.7(s)	18.4(s)

[a] Coupling constants (Hz) in parentheses, with coupled nucleus noted as a subscript.
[b] The weak olefinic carbons could not be discerned or assigned with confidence, except as noted. Coupling constants to ^{31}P in parentheses (Hz).
[c] $CDCl_3$ solutions.
[d] Obtained on a mixture of **15** and **17**. Also **15** δ C-7 124.3 (12.4 Hz), 138.8 (20.2), 149.5 (16.9). Values for **15** confirmed with a pure specimen.
[e] Obtained on a pure specimen; also δ C-7 124.5 (7.5), 130.9 (10.1), 140.1 (19.2), 148.8 (17.6).
[f] Obtained on a mixture of **16** and **18**.

partially separated by crystallization from benzene–hexane. The first crop of crystals consisted only of the isomer (**15**) with δ ^{31}P 52.6. This isomer was used for high-resolution mass spectral analysis, which confirmed its composition as the cycloaddition product. Attempts to grow single crystals of **15** for confirmation of the stereochemistry by X-ray analysis were again unsuccessful. Yet another intermediate chromatographic fraction contained only the isomers with δ ^{31}P 53.0 (**16**) and 49.3; the latter contained no olefinic proton and is tentatively assigned structure **18**. In Table 1 are provided NMR data for the four isomers **15–18**. Interpretation of the data was aided by the work done previously [1], where 2-D COSY and HETCOR NMR techniques were employed.

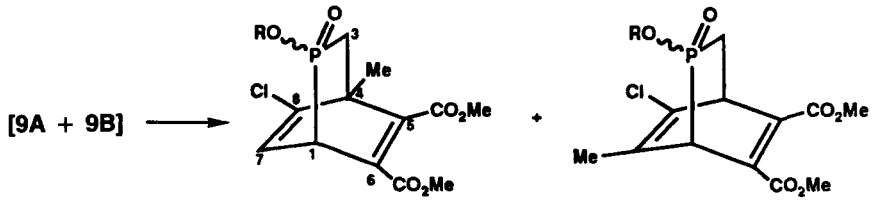
The tentative assignments of configuration at phosphorus in the four isomers were based on the assumption that the preferred mode of attack by the dienophile would be at the least crowded face of the 1,6-dihydrophosphinine; **15** and **17** are the major isomers formed and therefore are assigned

structures with *P*-methyl anti to the ester groups. This is the exclusive structure formed [1] in the cycloaddition with the C-unsubstituted 1,6-dihydrophosphinine oxide **2** (Scheme 1), and this provides support for these tentative assignments. A peculiarity in the ^{13}C NMR spectra first detected for phosphine oxides with this bridging structure [1] is reproduced in all of the new phosphine oxide isomers; the hybridization-sensitive one-bond coupling of ^{31}P to the bridging carbon-3 is abnormally large (94–95 Hz), while that at the bridgehead carbon-1 is much smaller (49 Hz). Chemical shift effects from the different positions of the methyl and chlorine substituents are evident in the data and were useful in making isomer assignments. For example, when present at C-4 methyl causes substantial downfield shifting (β-effect) at C-3. Similarly, when methyl is present at olefinic carbon-7, it causes deshielding at C-1.

The same synthetic procedure was then applied successfully to the group of phosphinates **9a–d**. In every case, ^{31}P NMR revealed that four-isomer mixtures were obtained (Table 2); yields in the cycloadditions were 20 to 50%. The ^{1}H NMR spectra of the four-component mixtures from the methyl, ethyl, and *n*-propyl esters are summarized in Table 3. The spectra were consistent with the structures, although resolution was poor except in the case of the olefinic region and for the bridgehead CH on P.

Only in the case of the *P*-isopropoxy ester mixture (**19d, 20d**) was a chromatographic separation attempted. This provided two fractions, each with only two isomers. ^{1}H and ^{13}C NMR spectral effects (Table 4) showed that for each fraction the isomers therein differed in the position of the methyl substituent since one component contained ^{1}H and ^{13}C signals for a =CH unit. The large differences in the one-bond ^{31}P coupling to C-1 and C-3 (73–74 Hz and 130–132 Hz, respectively) are again reproduced in these isomers.

TABLE 2 Reaction of P-Alkoxy 1,6-Dihydrophosphinine Oxides and Dimethyl Acetylenedicarboxylate



	R	*Solvent*	*Days*	*Yield*	*δ* $^{31}P^{a}$			
a	CH_3	T[b]	1	22	59.59(36.3)	58.96(21.9)	57.97(11.8)	55.94(29.9)
b	CH_3CH_2	B[c]	6.5	50.2	57.62(31.5)	57.20(23.3)	55.96(28.1)	54.17(17.2)
c	$CH_3CH_2CH_2$	B[c]	6.5	50.0	57.43(32.5)	56.62(31.0)	55.57(24.4)	53.91(12.1)
d	$(CH_3)_2CH$	T[b]	1.5	50.2	56.57(34.1)	55.95(20.0)	54.44(37.4)	52.92(8.5)

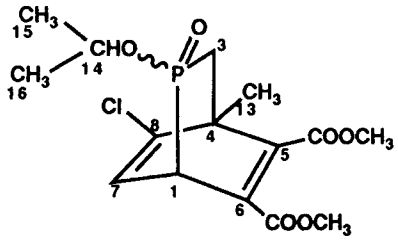
[a] In benzene with D_2O as external lock. Values in parentheses are relative peak areas.
[b] Toluene at reflux.
[c] Benzene at reflux.

TABLE 3 ^{1}H NMR[a] Features of Bicyclic Phosphinates **19a–c, 20a–c**

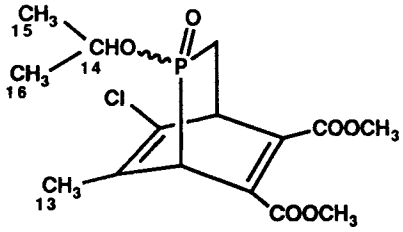
	a	b	c
19–20			
PCH_2, CCH_3	1.18–2.05	1.17–2.05[b]	0.85–2.05[c]
$COCH_3$, POCH	3.38–3.86	3.42–3.86	3.43–3.86
19			
C=CH	6.55(6.4, 7.5), 6.42(6.2, 7.4)	6.41(6.2, 7.4), 6.53(6.2, 7.6)	6.39(6.3, 7.3), 6.55(6.4, 7.4)
P–C_1–H	4.41(17.8, 7.4), 4.44(17.7, 7.5)	4.38(17.7, 7.4), 4.41(17.7, 7.6)	4.39(17.6, 7.3), 4.41(17.7, 7.4)
20			
C_4–H, C_1–H	3.80–4.11	3.91–4.13	3.89–4.11

[a] Taken on 4-isomer mixtures. Signals for C=CH and P–C_1–H of the diastereoisomers of **19** were well resolved; other signals were composites. For **19**, values in parentheses are coupling constants (Hz) to ^{31}P and for H_1–H_7, respectively.
[b] Includes CH_3CH_2O.
[c] Includes $CH_3CH_2CH_2O$.

TABLE 4 Partial ^1H and ^{13}C NMR Data for Bicyclic Phosphinates **19d, 20d**[a]



19d



20d

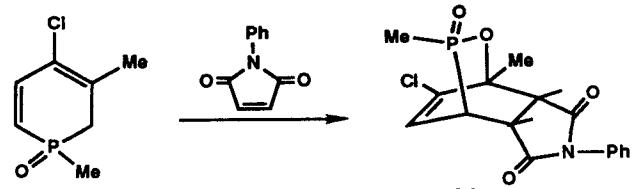
	19d		20d	
δ ^{31}P	55.18[b]	55.67[c]	52.19[d]	53.61[e]
C_1–*H*	4.29(dd, 17.8$_P$, 7.7$_{H-7}$)	4.35(dd, 10.2$_P$, 7.4$_{H-7}$)	4.4–4.7[f]	4.75(d, 8.1$_P$)[f]
C_3–*H*	2.27–2.91(m)	1.48–1.70(m)	1.45–1.56(m), 1.67–1.80(m)	1.48–1.70(m)
C_4–*H*	—	—	4.4–4.7[f]	4.66–4.82[f]
C_7–*H*	6.47(dd, 7.0$_P$, 7.7$_{H-1}$)	6.41(dd, 7.3$_P$, 7.4$_{H-1}$)	—	—
C_{13}–*H*	1.28(d, 2.6$_P$)	1.53(d, 2.9$_P$)	1.9(d, 2.9$_P$)	1.95(d, 2.8$_P$)
C_{14}–*H*	3.81–3.99(m)	3.76–4.09(m)	3.81–3.99(m)	3.76–4.05(m)
C_{15}–*H*	1.20[g]	1.33[g]	1.20[g]	1.33[g]
C-1	44.1(73.7)	44.0(72.7)	50.5(72.9)	51.0(73.9)
C-3	29.5(130.0)	29.2(131.0)	21.5(132.0)	—[h]
C-4	48.6(8.2)	48.3(8.0)	47.2(8.9)	46.9(9.1)
C-13	21.6(12.2)	21.6(12.1)	19.3(s)	19.0(s)
C-14	—[h]	72.3(6.0)	72.9(7.0)	72.6(6.6)
C-15, C-16	25.6	25.3	25.4, 25.0	25.3

[a] Obtained on 2-component mixtures from chromatography: (1) δ ^{31}P 55.18 (18%) and 52.19 (82%), (2) 55.67 (81%) and 53.61 (19%). Intensity differences aided signal assignments.
[b] Also C-7, δ 129.6 (21.9).
[c] Also C-7, δ 126.7 (10.7) and 132.5 (7.2), 139.8 (20.0), 151.0 (19.1).
[d] Also C-7, δ 125.9 (9.8) and 133.0 (10.1), 137.8 (9.1), 141.9 (19.6).
[e] Also olefinic C δ 133.2 (10.2).
[f] Overlap of C_1–H and C_4–H.
[g] Overlap of two isomeric signals.
[h] Not clearly observed.

It was also found that the *P*-methyl phosphine oxides **11A**, **11B** reacted readily with *N*-phenylmaleimide as the dienophile under the same conditions as used for the acetylenic ester. In this case, the adduct from **11A** (**21**) precipitated from the solution on formation. Curiously, this proved to be a single isomer, although four are possible from each of the endo and exo fusion of the rings. The compound was obtained in analytically pure form. As before, ^{13}C and ^1H NMR spectroscopy (Table 5) proved that it had a proton on the olefinic carbon, and the *P*-methyl was anti to the imide function (as expected, from attack at the least-crowded face) by the stereospecific coupling effects in the corresponding phosphine (vide infra). The endo fusion was revealed by the magnitude of the three-bond ^{31}P coupling to carbonyl carbon 10, which was of the size (16.6 Hz) expected for the large dihedral angle [7] in this structure. The structure therefore is the same as that established for the *N*-phenylmaleimide adduct from 1-phenyl-1,6-dihydrophosphinine oxide prepared in our earlier work [1]; in that case also only one of the several possible isomers was formed.

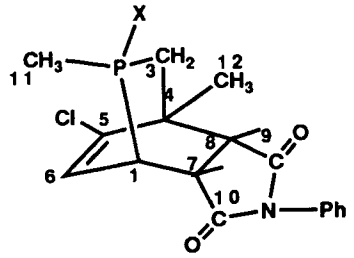
P-*Deoxygenation of the Diels-Alder Adducts with* P-*Methyl Substitution*

Trichlorosilane is the most widely used reagent for the removal of oxygen from phosphine oxides, and



11A **21**

TABLE 5 ^1H and ^{13}C NMR of **21**, **27**, and **28**



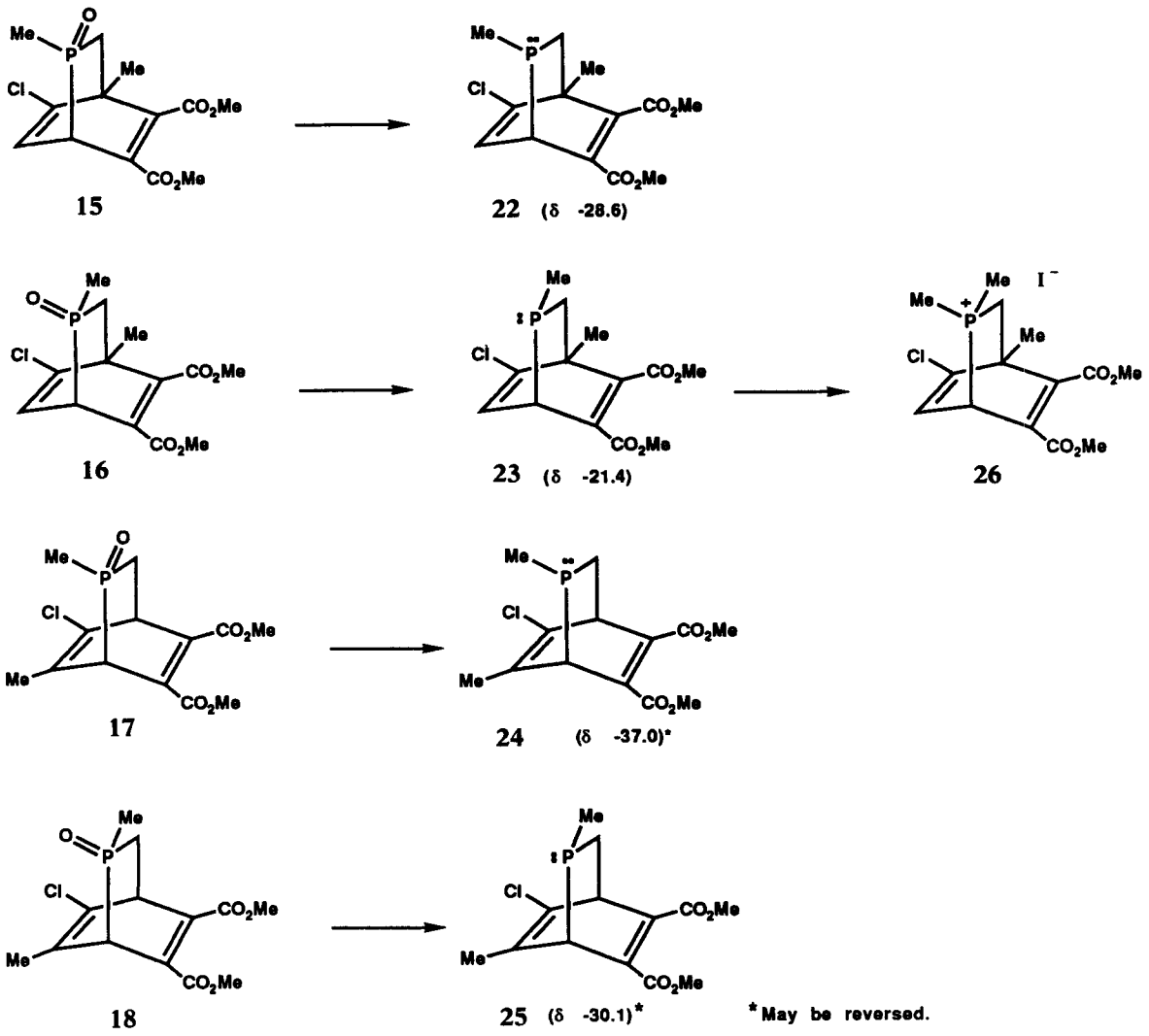
	21 (X = O)	**27** (X = lone pair)	**28** (X = Me^+I^-)
C_1–*H*	3.64(dd, 11.3$_P$, 8.0$_{H\text{-}6}$)	3.06–3.14(m)	4.23(dd, 9.1$_P$, 7.5$_{H\text{-}6}$)
C_3–*H*	1.79–1.86(m)	**a**: 1.14(13.9$_{H\text{-}3b}$, 6.2$_P$)	**a**: 2.44(17.6$_H$, 10.0$_P$)
		b: 2.04(13.9$_{H\text{-}3a}$, 29.2$_P$)	**b**: 2.78(17.6$_H$, 5.6$_P$)
C_6–*H*	6.18(dd, 8.9$_P$, 8.0$_{H\text{-}1}$)	6.26(d, 7.5$_H$)	6.56(dd, 7.5$_P$, 7.5$_{H\text{-}6}$)
C_7–*H*	3.93(dd, 8.1$_P$, 8.3$_{H\text{-}8}$)	3.38–3.47(m)	3.58–3.72(m)
C_8–H	3.24(d, 8.3$_{H\text{-}7}$)	2.68(dd, 8.6$_{H\text{-}7}$, 3.7$_P$)	3.58–3.72(m)
C_{11}–H	1.63(d, 13.3$_P$)	0.87(d, 3.7$_P$)	1.85(d, 15.1$_P$); 2.18(d, 14.9$_P$)
C_{12}–H	1.73(d, 2.38$_P$)	1.74(s)	1.65(2.7$_P$)
C-1	38.6(61.4)	34.9(14.8)	—[b]
C-3	36.9(73.4)	40.2(24.0)	30.4(49.5)
C-4	39.9(s)	43.9(3.7)	—[b]
C-5	140.0(11.3)	135.1(4.2)	140.9(12.3)
C-6	122.1(5.7)	127.1(4.0)	121.2(9.0)
C-7	44.3(6.3)	45.2(23.3)	42.8(7.1)
C-8	49.3(11.0)	51.1(s)	47.4(10.1)
C-9	173.9(s)	176.3(s)	174.0(0)
C-10	175.8(14.6)	178(17.1)	174.7(17.1)
C-11	15.2(71.8)	13.0(18.1)	6.3(45.4), 7.6(55.9)
C-12	23.6(10.5)	25.4(s)	22.0(11.9)

[a] Phenyl signals omitted. Solvents: $CDCl_3$ for **21**, **27**; DMSO for **28**. ^1H–^1H couplings for **21** and **27** confirmed by 2-D COSY. ^1H coupling constants (Hz) in parentheses, with coupled nucleus shown as a subscript. ^{31}P–^{13}C coupling constants (Hz) in parentheses.

[b] Not clearly observed.

was used successfully under especially mild conditions (0–10°C, to prevent ring fragmentation) with the Diels-Alder adducts (**4**, **5**; Scheme 1) formed from the 1,6-dihydrophosphinines in our earlier work [1]. We have applied this method to the reduction of various mixtures of the isomeric phosphine oxides from reaction of dimethyl acetylenedicarboxylate with 1,6-dihydrophosphinine oxide **11A**, **11B**. Conversions of the oxides **15–18** to the phosphines **22–25** (Scheme 5) were 70–95%. These phosphines are thermally unstable and very reactive to oxygen; however, one of them (**22**) was successfully converted to the methiodide (**26**), which gave the correct elemental analysis. The thermal instability also complicated the procurement of ^1H and ^{13}C NMR spectra; solutions developed additional signals due to the elimination of the bridging P–C unit with formation of a phthalate, to be discussed in the next section. However, the data collected (Table 6) provide adequate proof that the desired phosphines were obtained. Again the previous work [1] gave a sound basis for the spectral interpretations; effects on chemical shifts from the presence of the methyl substituent were useful also in making the assignments. There are also considerable differences in the ^{31}P NMR spectra of the isomers (Scheme 5). For each pair of positional isomers, the phosphine tentatively assigned to have the methyl group syn to the ester groups has a ^{31}P NMR shift downfield of the anti form by almost exactly the same amount (7.2 ppm for **22** and **23**; 6.9 ppm for **24** and **25**). This consistent relation adds validity to the assignments, although the cause of the shift difference is not obvious. It is furthermore noted that the phosphine (**6**) synthesized in the earlier work [1] has a ^{31}P NMR shift of δ −36.0, a value well upfield of those seen here for the two isomers of opposite configuration (**23**, −21.4; **25**, −30.2) but consistent with the large value seen for at least one of the two isomers thought to have the same configuration (**24**, −37.0).

The trichlorosilane reduction was also applied



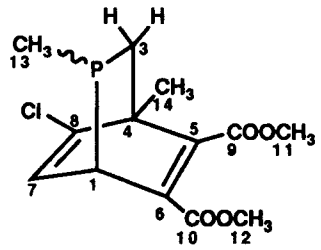
SCHEME 5

to the phosphine oxide **21**. However, this oxide was insoluble in the usual solvents used in this reduction (benzene, toluene, chloroform). Pyridine was found to be a reasonable solvent for **21**, although it forms a solid complex with the silane. This complex is frequently used in silane reductions (e.g., ref. 6) and the medium used in the present work was quite satisfactory for the reduction of oxide **21**. The ^{13}C NMR spectrum of the phosphine (**27**) and its methiodide **28** are given in Table 5. The phosphine showed strong coupling to C-7 (23.3 Hz); this allowed the assignment of structure **27** to the phosphine, since it is well known [7] that the magnitude of two-bond $^{31}P-^{13}C$ coupling in phosphines is controlled by the orientation of the lone pair on phosphorus relative to the coupled carbon. A $^{2}J_{PC}$ value of 23.3 Hz convincingly proves the lone pair to be close to C-7, and rules out the other configurational possibility.

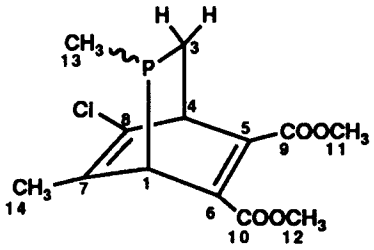
Generation of 2-Phosphapropene from the Bicyclic Phosphines

To demonstrate the utility of the new phosphines as precursors of the highly reactive two-coordinate phosphaalkene on thermal fragmentation, a solution of freshly-prepared phosphines **22** and **24** (2:1) that had been dried over magnesium sulfate was heated in the presence of isoprene as a trapping agent for the released highly reactive species $MeP{=}CH_2$. The fragmentation of one phosphine (**22**) was complete after 1 h at 50°C in chloroform solution and the expected [2] tetrahydrophosphinines **29** and **30** were formed. The fragmentation of phosphine **24** was significantly slower than that of **22** and required 9 h at 50°C for complete fragmentation. The final reaction mixture gave only the expected [2] ^{31}P NMR signals for the trapping products **29** and **30**; these were oxidized on addition of

TABLE 6 Partial ^1H and ^{13}C NMR Data for Phosphines **22–25**[a]



22, 23



24, 25

	22	23	24	25
C_1–H_b	4.45(13.0$_P$, 7.5$_{H\text{-}7}$)	4.46(dd, 11.9$_P$, 7.0$_{H\text{-}7}$)	4.07(d, 13.7$_P$)	4.16(d, 12.6$_P$)
C_3–H_a[b]	1.21(4.2$_P$, 12.5$_{H\text{-}3b}$)	1.14–1.23(m)	1.10(ddd, 14.9$_P$, 12.4$_{H\text{-}3b}$, 4.2$_{H\text{-}4}$)	1.25–1.38(m)
C_3–H_b[c]	2.04(dd, 28.2$_P$, 12.5$_{H\text{-}3a}$)	1.89–1.93(m)	2.36(ddd, 28.7$_P$, 12.4$_{H\text{-}3a}$, 3.1$_{H\text{-}4}$)	1.99–2.19(m)
C_4–H	—	—	4.29(ddd, 7.5$_P$, 3.1$_{H\text{-}3b}$, 4.2$_{H\text{-}3a}$)	4.29–4.36(m)
C_7–H	6.24(dd, 3.1$_P$, 7.5$_{H\text{-}1}$)	6.39(d, 7.0$_{H\text{-}1}$)	—	—
C_{13}–H	0.88(5.3$_P$)	0.91(d, 5.3$_P$)	0.82(d, 5.3)	0.85(d, 5.5$_P$)
C_{14}–H	1.65(s)	1.66(s)	1.84(d, 2.6$_P$)	1.89(s)
C-1	38.9(21.0)	37.2(20.0)	47.0(25.3)[d]	45.4(24.7)[d]
C-3	40.2(30.5)[d]	39.0(32.3)[d]	33.3(29.9)	29.9(32.3)
C-4	47.3(4.8)[e]	48.2(6.6)[e]	48.7(5.3)[e]	46.2(5.4)[e]
C-13	13.9(25.8)[e]	12.4(26.2)[e]	13.2(26.2)[e]	12.5(24.0)[e]
C-14	17.6(s)[e]	19.4(s)[e]	18.3[e]	17.0[e]

[a] Taken on crude mixtures at about 0°C of **22** (60%) with **24** (40%), and of **23** (40%) with **25** (60%). Olefinic ^{13}C could not be recognized with confidence. For ^1H spectra, coupling constants (Hz) are in parentheses, with the coupled nucleus indicated as a subscript. ^{13}C–^{31}P coupling constants (Hz) are given in parentheses.

[b] On same face as P–Me.

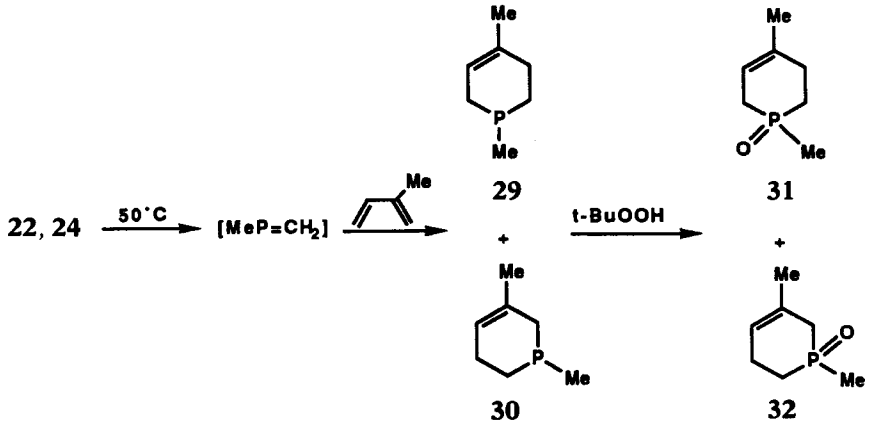
[c] On opposite face of P–Me.

[d] Based on β-deshielding effect of methyl.

[e] Based on relative intensities in a mixture; could be reversed.

t-butyl hydroperoxide to give phosphine oxides **31** and **32**.

Therefore, the utility of the new type of phosphine prepared in the present study as a precursor of 2-phosphapropene is firmly established, and it is clearly seen that the short overall reaction sequence (four steps, yield 31%) is superior to the more complicated one employed in our initial studies [1, 2] that required six steps and gave a 5% overall yield. This made 2-phosphapropene readily available to us for further studies of its reactivity, and allowed us to re-examine the reaction with hydroxylic species since only partly satisfactory results had been obtained in our earlier study using alcohols as reac-



tants. The isomeric phosphine mixture **22** and **24** was again used to supply the 2-phosphapropene, and when water was included in the reaction medium as trapping agent, the only phosphorus compound observed at the end of the 11.5 h of heating was identified as dimethylphosphine oxide (**33**). Again it was observed that phosphine **22** was decomposed after 1 h, but the isomer **24** required the full reaction period. The identity of **33** was easily established by its ^{31}P NMR signal (δ 20.2), which was in agreement with a literature value [8]. Supporting data also came from ^{1}H and ^{13}C NMR measurements. It was then found that the use of ethanol as the trapping agent was equally successful and clearly provided the expected phosphinite **34**, recognized from the characteristic low-field ^{31}P NMR signal at δ 118.2, and from its oxidation product **35**, which had a shift of δ 52.7 ($CDCl_3$) in accord with the literature (δ 50.3 neat [9]). However, in spite of careful drying of the ethanol and apparatus, a trace of water always remained, and this led to the simultaneous formation of some dimethylphosphine oxide (**33**). Similarly, isopropyl alcohol gave phosphinite **36**, δ 112.6 (along with some **33**), which was oxidized to phosphinate **37** (δ 53.3). All of these reactions with hydroxylic species therefore proceeded cleanly with exclusive attack of the oxygen atom on phosphorus, and occurred in preference to self-condensation of the P=C species. In the context of the literature, this high reactivity to an alcohol seems unexpected, since acid or base catalysis is customarily required [10] to effect such reactions with stabilized phosphaalkenes such as $MesP{=}CPh_2$ [11]. This reveals one of the advantages of using unstabilized phosphaalkenes for reactivity studies; the groups that are used to give stability to the species appear at the same time to reduce other forms of reactivity, and may obscure the true character of the P=C bond.

Similar results were obtained when others of the isomeric phosphines were used as precursors of 2-phosphapropene. Thus, a sample of pure phosphine **23** decomposed after 1 h and the trapping product **34** (along with the water product, **33**) was formed when ethanol was present. Also, a mixture of phosphines **23** and **25** decomposed completely after 12 h and with water as the trapping agent gave only dimethylphosphine oxide. Again the isomeric phosphine with the bridgehead methyl substituent **23** was decomposed after only 1 h, with the full 12 h period being required for the isomer with no bridgehead substituent (**25**). This interesting effect perhaps may arise from steric crowding at the site of the departing bridging carbon, although other effects may also be operative.

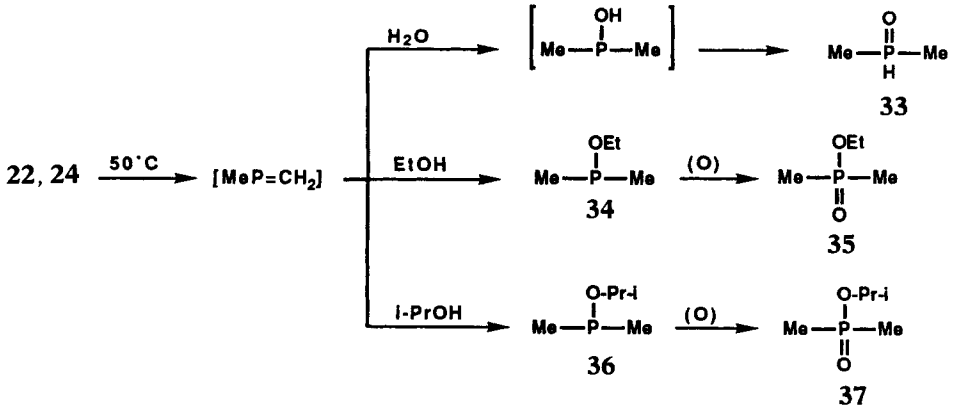
EXPERIMENTAL

General

FT ^{31}P NMR spectra were recorded with an IBM NR-80 spectrometer using 85% H_3PO_4 as external standard with $CDCl_3$ as solvent and internal lock. Downfield shifts have positive signs. FT ^{1}H and ^{13}C NMR spectra were recorded with Varian XL-200 and 300 NMR spectrometers, respectively, with Me_4Si as internal standard. Microanalyses were performed by the University of Massachusetts Microanalysis Laboratory. The high resolution mass spectrum of compound **15** was obtained at the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, Nebraska. Other MS data were obtained with a Hewlett-Packard GC-MS system.

6,6-Dichloro-1,3-dimethyl-3-phosphabicyclo[3.1.0]hexane-3-oxide (**10**)

The published procedure [3] was used with some modifications. A vigorously stirred and ice-cooled solution of 46.0 g (0.354 mol) of 1,3-dimethyl-3-phospholene-1-oxide in 1.125 L of alcohol-free chloroform containing 18.1 g (0.08 mol) of triethylbenzylammonium chloride (TEBAC) was treated over a period of 6 h with a solution of 623 g of sodium hydroxide in 623 mL of water. The layers were separated and the water layer extracted with about 500 mL of chloroform. The combined chloroform solutions were used in the same manner with the



same amount of fresh sodium hydroxide solution, and the procedure was completed with a third such treatment. No starting material remained in the final chloroform solution, which was then evaporated to leave a solid residue. Addition of 250 mL of benzene caused the TEBAC to precipitate, and it was removed by filtration. The filtrate was concentrated to about 200 mL; addition of 50 mL of hexane completed the precipitation of the TEBAC. On evaporation of the solvent, the product **10** (43.1 g, 57.5%) was obtained, mp 90–92°C, ^{31}P NMR ($CDCl_3$) δ 84.7 (lit. [4b] mp 90–92°C, ^{31}P δ 84.7, yield 32%).

6,6-Dichloro-3-methyl-3-phosphabicyclo[3.1.0]hexane-3-oxide (**13**)

1-Methyl-3-phospholene-1-oxide (21.3 g, 0.183 mol) was treated as above using 9.8 g of TEBAC, 700 mL of chloroform, and 320 g of sodium hydroxide in 320 mL of water. The addition required 3 h; stirring was continued for 3 h in the ice bath and then for 10 h at room temperature. The organic layer, and a chloroform extract of the aqueous later, were treated again with the same amount of sodium hydroxide solution and 4.6 g of TEBAC. This entire procedure was performed a total of 9 times, maintaining the original volume of chloroform. The residue from evaporating the solvent was treated with 25 mL of benzene and then 10 mL of hexane to precipitate TEBAC. The solid was washed on the funnel with four 50-mL portions of benzene. The combined organic solutions were concentrated to about 10 mL, and the crystals of **13** were recovered (6.23 g, 17.1%) as a mixture of diastereoisomers (shown only by ^{13}C NMR); ^{31}P NMR ($CDCl_3$) δ 87.6; ^{1}H NMR ($CDCl_3$) δ 1.71 (d, $^2J_{PH}$ = 12.8 Hz, P–CH_3), 1.92–2.03 (m, 2H, C–CH) and 2.34–2.56 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) for minor isomer (10%) δ 15.8 (J_{PC} = 61.5 Hz, P–CH_3), 29.7 (J_{PC} = 65.9, P–CH_2), 32.7 ($^2J_{PC}$ = 6.0, C–CH), 66.9 ($^3J_{PC}$ = 6.8, Cl_2C); ^{13}C NMR for major isomer (90%) δ 15.3 (J_{PC} = 61.2, P–CH_3), 29.2 (J_{PC} = 66.3), 32.2 (s, C–CH), 66.4 ($^3J_{PC}$ = 7.7, Cl_2C). A small sample was recrystallized from chloroform–hexane to give a sample for analysis, mp 156.6–158.5°C.

Anal. Calcd. for $C_6H_9Cl_2OP$: C, 36.19; H, 4.56. Found: C, 36.31; H, 4.56.

1,5-Dimethyl-(**11A**) *and 1,3-Dimethyl-*(**11B**) *4-Chloro-1,6-dihydrophosphinine-1-oxides*

A dry 2.3-g (0.0105 mol) sample of **10** spread on the bottom of a 250-mL Erlenmeyer flask was immersed in a bath set at 135°C for 4 min (the same procedure can be applied to larger samples, with caution due to the vigorous HCl evolution). The brown oil was chromatographed on a silica gel column with chloroform–methanol (97.5–2.5) to give 1.74 g, 94.1%, of an oily mixture of **11A** [^{31}P NMR δ 20.4 (lit. [4b] 20.7), 75%] and **11B** [^{31}P δ 19.9 (lit. [4b] 20.0), 25%].

4-Chloro-1-methyl-1,6-dihydrophosphinine-1-oxide (**14**)

A 0.1-g (0.5 mmol) sample of **13** heated at 161°C for 3.5 min was partially (20%) converted to **14**, which was isolated by silica gel chromatography (chloroform–methanol, 99.5:0.5). Spectral data could be obtained but the compound decomposed during these measurements, and was not further examined: ^{31}P NMR ($CDCl_3$) δ 18.1; ^{1}H NMR δ 1.61 (d, $^2J_{PH}$ = 12 Hz, P–CH_3), 2.56 (d of d, $^2J_{PH}$ = 12, $^3J_{HH}$ = 6, P–CH_2), 6.07–6.2 (m, 2H, C_2H and C_5H), 6.54 (d of d, $^3J_{PH}$ = 28, $^3J_{HH}$ = 11, C_3H); ^{13}C NMR ($CDCl_3$) 16.5 (J_{PC} = 75.6, P–CH_3), 29.3 (J_{PC} = 71.0, C-2), 122.1 ($^2J_{PC}$ = 10.5, C-3), 123.6 ($^1J_{PC}$ = 90.7, C-6), 128.8 ($^3J_{PC}$ = 23.6, C-4), 141.6 (s, C-5).

Reaction of Dimethyl Acetylenedicarboxylate with 1,6-Dihydrophosphinines **11A, 11B**

A solution of 8.9 g (0.050 mol) of the **11A** (75%)–**11B** (25%) mixture and 17.4 g (0.12 mol) of dimethyl acetylenedicarboxylate in 30 mL of benzene was refluxed for 34 h. The ^{31}P NMR spectrum of the very dark benzene solution (with D_2O as external lock) showed that all **11A, 11B** had reacted and that four new products with shifts in the range δ 47.9 to 52.5 had been formed. Solvent was removed and the ^{31}P NMR spectrum taken in $CDCl_3$: δ 52.95 (16.6%), 52.58 (37.7%), 49.30 (14.2%), and 48.91 (31.6%). After chromatography on silica gel using first chloroform and then chloroform–methanol (99:1), the total product recovered was 9.3 g (58.4%). The first fraction (4.90 g) had ^{31}P NMR signals at δ 52.58 and 48.91, and on the basis of their NMR properties and those of the phosphines formed on reduction (vide infra) were assigned structures **15** and **17**, respectively. An intermediate fraction (3.79 g) had ^{31}P NMR 52.95 and 49.30, and as before structures were deduced to be **16** and **18**, respectively. At the end of the elution, a single compound (**16**, 0.70 g) with ^{31}P NMR δ 52.95 was obtained. The first fraction (**15** and **17**) was recrystallized from benzene–hexane, and provided a single compound (**15**) with ^{31}P NMR δ 52.58, mp 111.0–112.5°C. The FAB MS spectrum showed at low resolution the two expected signals with the chlorine isotopes for $[M + H]^+$ of 319 and 321. The high resolution FAB MS of the former gave m/z 319.0502 (calcd. for $C_{13}H_{16}{}^{35}ClO_5P$ 319.0498). The ^{1}H and ^{13}C NMR spectra were obtained on the 2-component mixtures or single isomers, and are recorded in Table 1. Attempts to improve on the separation procedure have not yet been successful.

Reaction of Phosphinates **9A–9B** *with Dimethyl Acetylenedicarboxylate*

The same general procedure was used for each of the mixtures of isomeric 1-RO-1,6-dihydrophosphinine-1-oxides **9A,9B** with R = Me (**a**), Et (**b**), *n*-Pr (**c**), or *i*-Pr (**d**). A solution of about 1 g (about 5 mmol) of the **9A,9B** mixture (usually about 3:1) and 1.6 mL (about 12.5 mmol) of dimethyl acetylenedicarboxylate in 10 mL of solvent (see Table 2) was refluxed until analysis by ^{31}P NMR indicated that all starting material had been consumed. Crude yields and ^{31}P NMR data for all products (**19**, **20**) are given in Table 2. For all products, the solvent was removed by rotary evaporation and the residue purified by silica gel chromatography with elution by benzene–acetone 40:60, or for **19Ad–19Bd** as below. Elemental or MS (data for CI method shown) analysis follows; for **a**, **b**, and **c** ^1H NMR are given in Table 3.

19a, **20a**: MS M^+ 334 (1%), $M^+ - CH_3$ 319 (18%), 275 (92%), 211 (100%); CI-MS $M^+ + 1$, 335 (14%).

19b, **20b**: Calcd. for $C_{14}H_{18}ClO_6P$: C, 48.22; H, 5.17. Found: C, 48.57; H, 5.09. MS $M^+ + 1$ 349 (26%).

19c, **20c**: Calcd. for $C_{15}H_{20}ClO_6P$: C, 49.66; H, 5.32. Found: C, 49.87; H, 5.31. MS $M^+ + 1$ 363 (4%).

19d, **20d**: Calcd. for $C_{15}H_{20}ClO_6P$: C, 49.66; H, 5.32. Found: C, 49.36; H, 5.21. MS $M^+ + 1$ 363 (66%).

Chromatographic separation of the products (**19d, 20d**) from **9Ad–9Bd** was performed on silica gel using chloroform and then chloroform with 1% methanol as eluents. The first fraction (0.20 g) consisted of two isomers with ^{31}P NMR δ 55.18 and 52.19 (1:4.5). Following some intermediate fractions, a two-isomer mixtuure (0.71 g) was obtained at the end of the elution, ^{31}P NMR δ 55.67 and 53.61 (ratio 4.4:1). The ^1H and ^{13}C NMR spectra for each fraction are given in Table 4.

Reaction of 1,6-Dihydrophosphinine-1-oxides **11A,11B** *with* N-*Phenylmaleimide*

A solution of 0.44 g (2.5 mmol) of the 3:1 mixture of 1,6-dihydrophosphinine-1-oxides **11A,11B** and 0.52 g (3.0 mmol) of *N*-phenylmaleimide in 30 mL of benzene was heated at 60–65°C for 92 h. A small amount of yellow solid formed on the flask walls. Examination of the solution by ^{31}P NMR showed that essentially all starting material had reacted and a product with ^{31}P NMR δ 44.2 (benzene with D_2O lock) had been formed. The solution deposited 0.476 g (54.9%) of pale yellow solid on cooling. It was recrystallized from chloroform–hexane to give white crystals of **21**, mp 301–302°C (dec); ^{31}P NMR ($CDCl_3$) δ 45.9; ^1H and ^{13}C NMR spectra, Table 5.

Anal. Calcd. for $C_{17}H_{17}ClNO_3P$: C, 58.38; H, 4.90; N, 4.00. Found: C, 58.13; H, 4.82; N, 3.98.

Reduction of Isomeric Phosphine Oxides **15–18** *to Phosphines*

The reductions of individual oxides **15** and **16**, of mixtures of oxides **15** and **17**, and of mixtures of oxides **16** and **18**, were performed by the same general procedure. The oxide (about 0.5 mmol) was dissolved in a mixture of 8 mL of benzene and 1 mL of toluene. The solution was chilled to 0°C and treated with an excess (about 10 mmol) of trichlorosilane. The solution was stirred for 6 h, then warmed to room temperature and evaporated in vacuo to remove solvent and excess trichlorosilane. The residual oils were dissolved in methylene chloride and shaken with 1 mL of 30% NaOH at 0°C. The organic layer was dried for 1 day over $MgSO_4$ and 1 day over $CaSO_4$. Solvent was removed, and the residues used immediately for NMR spectral measurements (Table 6) or as reactants. Yields of the phosphines were 70–95%.

Synthesis of the Methiodide (**26**) *from Phosphine* **23**

Phosphine **23** (0.15 g, 0.5 mmol) was converted to the methiodide **26** by treatment with 0.5 mL of methyl iodide in 5 mL of benzene at 0°C for 2 h, and then 25°C for 15 h. The salt **26** (0.14 g) crystallized and was used directly for analysis.

Anal. Calcd. for $C_{14}H_{22}ClIO_4P$: C, 37.56; H, 4.95. Found: C, 37.22; H, 4.71.

Synthesis of Phosphine **27** *and its Methiodide* **28**

Oxide **21** (0.13 g, 0.38 mmol) was dissolved in 20 mL of dry pyridine. Trichlorosilane (2.5 mL) was added at 0°C, resulting in formation of the solid complex with pyridine. The suspension was heated at 80–90°C for 3 h. Volatiles were removed in vacuo, and the residue was dissolved in 100 mL of methylene chloride. The solution was cooled to 0°C and treated slowly with 30 mL of 30% NaOH. After 10 min, the layers were separated and the aqueous layer was extracted twice with 50-mL portions of methylene chloride. The combined organic layers were evaporated to leave 0.12 g (95.3%) of solid phosphine **27**, used immediately for NMR measurements (Table 5) and conversion to the methiodide **28**. This was accomplished by reaction with methyl iodide in methylene chloride. The product crystallized from the solution (73.8%) and was recrystallized from acetonitrile. NMR data are given in Table 5.

Anal. Calcd. for $C_{18}H_{20}ClINO_2P$: C, 45.45; H, 4.24. Found: C, 45.22; H, 4.48.

Generation of 2-Phosphapropene by Thermolysis of a Mixture of Phosphines **22** *and* **24**

A solution of 50 mg of the (dried) mixture of phosphines **22** and **24** prepared above and 0.8 mL of isoprene in dry $CDCl_3$ (2 mL) was heated under argon for 1 h at 50°C. Analysis by ^{31}P NMR showed that all of phosphine **22** (δ −28.6) had reacted, and new signals appeared at −62.7 and −67.1 (ratio 2:1). These correspond to previously reported [2] adducts **29** and **30**, respectively. Phosphine **24** required an additional 9 h at 50°C for complete decomposition. Addition of 10 drops of *t*-butyl hydroperoxide caused oxidation of these phosphines to the corresponding oxides **31** (δ ^{31}P 41.4) and **32** (δ ^{31}P 39.8) in the ratio 2:1; these oxides were not further characterized.

Generation of 2-Phosphapropene from Phosphines **22, 24** *in the Presence of Water*

A solution of 50 mg of a freshly prepared mixture of phosphines **22, 24** and 2 drops of water in 2.5 mL of $CDCl_3$ was heated at 50°C. As before, the ^{31}P NMR signal for **22** disappeared after 1 h and that for **24** after 11.5 h. The only ^{31}P signal in the final product had δ 20.2 (lit. [8], δ ^{31}P 20.5 for $Me_2P(O)H$, **33**); ^1H NMR δ 1.61 (d of d, $^2J_{PH}$ = 14.2 Hz, $^3J_{HH}$ = 3.8 Hz, Me_2), 7.19 (d of septets, $^1J_{PH}$ = 463 Hz, $^3J_{HH}$ = 3.8 Hz, P*H*); ^{13}C NMR δ 16.3 (J_{PC} = 68.3 Hz, CH_3). The $CDCl_3$ solution also gave ^1H and ^{13}C NMR signals for the phthalates resulting from the loss of 2-phosphapropene; especially characteristic for the phthalate from **22** were aromatic protons at δ 7.35 and 7.70 (both d, ^3J = 9 Hz); for the phthalate from **24**, δ 7.58 and 7.71 (both s).

Generation of 2-Phosphapropene from Phosphines **22, 24** *in the Presence of Ethanol*

A freshly-prepared **22, 24** mixture was dried in vacuo over $MgSO_4$ for 24 h, and then over $CaSO_4$ for 24 h, both at 0° to avoid decomposition. A solution in dry $CDCl_3$ (2.5 mL) containing 0.5 mL of dry ethanol was heated at 50°C, with **22** disappearing after 1 h, **24** after 10 h. The only new signals appeared at δ ^{31}P 118.2 (phosphinite **34**, 48%) and 24.0 (**33**, 52%). The compound with δ 118.2 was completely converted to a new product (phosphinate **35**) with δ 52.6 (lit. [9] 50.3 (neat) on oxidation at 0°C with *t*-butyl hydroperoxide for 2 h, or in the atmosphere at room temperature for 7 days.

Generation of 2-Phosphapropene from Phosphines **22, 24** *in the Presence of* i*-Propyl Alcohol*

The same procedure used for reaction with ethanol was followed and gave only phosphinite **36** (δ ^{31}P 112.6, 40%) and Me_2PHO (**33**, δ 22.7, 60%). Peroxide oxidation of **36** gave phosphinate **37**, δ ^{31}P 53.3.

Generation of 2-Phosphapropene from Other Phosphines

Pure phosphine **22** was decomposed after 1 h at 50°C; with ethanol present, phosphinate **34** (with oxide **33**) was formed. Similarly, a mixture of phosphines **23** and **25** was decomposed at 50°C in the presence of water, with **23** reacting after 1 h, **25** after 12 h, to give oxide **33**.

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