(S)-(−)-11, 1515-99-7; (R)-(+)-11, 17170-48-8; (±)-11, 2328-23-6; 18, 6362-87-4; 19a, 7735-85-5; 19b, 7735-81-1; cis-20, 40781-04-2; trans-20, 40781-03-1; 21, 4789-36-0; 22, 4789-37-1; 23, 20698-84-4; 24, 13153-89-4; sodium methoxide, 124-41-4; benzylmethylphenyl-n-propylphosphonium dibenzoyl hydrogen tartrate isomer 1, 57215-13-1; benzylmethylphenyl-n-propylphosphonium dibenzoyl hydrogen tartrate isomer 2, 57215-15-3; hydrogen peroxide, 7722-84-1.

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1-Vinylcycloalkenes in the McCormack Cycloaddition with Phosphonous Dihalides. Stereochemistry of Some Resulting Bicyclic Phospholene Oxides[1]

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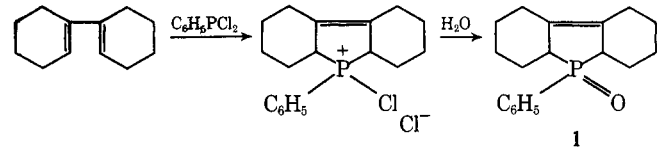
1-Vinylcyclohexene condenses at 25° with methylphosphonous dichloride. Hydrolysis of the cycloadduct gives the 3-phospholene oxide with a tetramethylene group at the 2,3 positions. The product consists of a mixture of stereoisomers (72% trans, 28% cis); their structures were assigned with the aid of ^{13}C, ^{31}P, and ^{1}H NMR spectral relations. 1-Vinylcyclohexenes containing bromine or chlorine on the α-vinyl carbon also participate smoothly in the cycloaddition. A new type of diene, containing a 2-trimethylsiloxy group, was used in the cycloaddition; 1-acetylcyclohexene gave such a siloxy diene with $LiN(i\text{-}Pr)_2$ and $(CH_3)_3SiCl$, and on hydrolysis of the cycloadduct formed with CH_3PCl_2 there was obtained a 3-keto phospholane derivative. The 4-vinyl derivative of 1,2-dihydronaphthalene also participated readily in the cycloaddition, giving a tricyclic phospholene oxide derivative. Two examples of further utilization of the bicyclic phospholene oxides are provided, namely, P-deoxygenation to the bicyclic phosphines and hydrogenation of the double bond to perhydrophosphindole derivatives.

The cycloaddition of conjugated dienes and trivalent phosphorus halides, first described by McCormack,[2] has proved to be an excellent route to derivatives of the phospholene ring system. To the present, however, this reaction has been used primarily to form monocyclic structures, although it has far greater potential through extension to the synthesis of multicyclic structures. McCormack did report[2] the use of 1,1′-biscyclohexenyl in the reaction with phenylphosphonous dichloride to form a tricyclic adduct which on hydrolysis gave phospholene oxide **1**, and the same compound was later obtained by other workers.[3] Phosphorus trichloride also adds to this diene.[4] Bridged phospholene

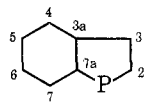


1

oxides (**2**) can be obtained by cycloaddition with cycloheptadienes.[5]

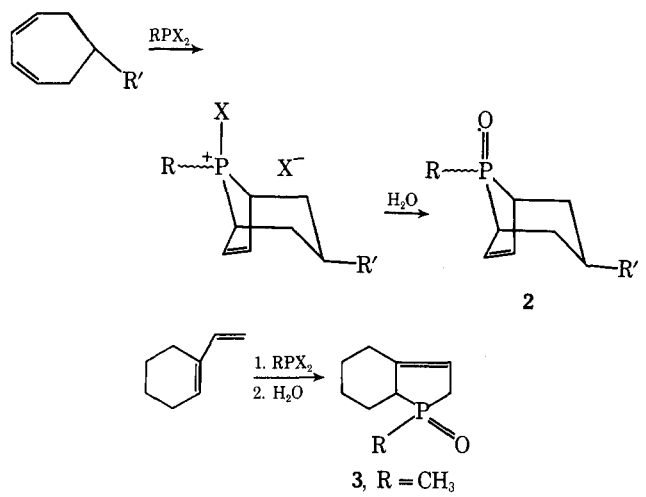
1-Vinyl cyclic alkenes are readily obtainable dienes, and should serve as valuable precursors of bicyclic phospholene derivatives. Thus, with 1-vinylcyclohexene, members of the hexahydrophosphindole family would be formed. While

Table I
^{13}C NMR Spectral Data[a]



Compd[b]	C-2	C-3	C-3a	C-4,5,6,7[c]	C-7a	PCH_3
3a	31.4 (60)	112.9 (11)	144.6 (13)	21.1–29.9	39.9 (68)	13.6 (63)
3b	30.1 (65)	113.8 (12)	143.5 (14)	21.1–29.9	40.8 (70)	9.6 (63)
6	24.8 (65)	28.5 (10)	144.1 (30)	20.4–22.6	130.3 (85)	15.9 (70)
trans-8	39.6 (60)	108.9 (10)	140.5 (10)	22.6–28.3	42.7 (70)	16.8 (63)
cis-8	38.5 (60)	109.3 (14)	139.4 (10)	22.6–28.3	43.6 (70)	12.6 (65)
13a	33.8 (10)	119.2 (3)	146.7 (3)	26.9–37.2	51.5 (10)	14.6 (18)
13b	33.2 (13)	120.7 (3)	144.0 (3)	26.9–37.2	44.0 (15)	9.2 (23)
15a	*d*	*d*	*d*	*d*	39.8 (70)	13.7 (60)
15b	*d*	*d*	*d*	*d*	38.1 (70)	17.3 (60)

[a] Chemical shifts are in parts per million downfield from Me_4Si. Values in parentheses are J_{P-C} in hertz. Solutions in $CDCl_3$ were used. [b] Samples of **3**, **8**, **13**, and **15** were run as isomer mixtures. [c] Insufficiently resolved for firm assignments. [d] Occurred at δ 18.5–28.2.



2

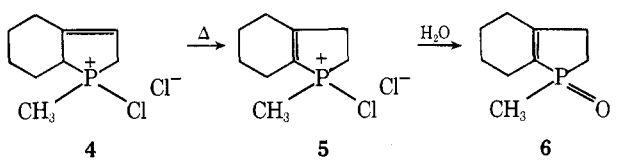
3, R = CH_3

McCormack's patent[2] included this diene among those said to undergo the cycloaddition, no examples were given, and no products were characterized; the process remains to be exploited for the synthesis of reduced phosphindoles. There are only a few examples known of such compounds;[6] they have been prepared by quite different methods and have different substitution and/or unsaturation patterns than those afforded by the McCormack route.

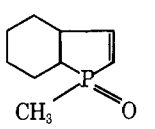
In this paper we will show that the McCormack reaction is eminently suitable for the synthesis of multicyclic phospholene derivatives. Both bicyclic and tricyclic derivatives have been obtained from appropriate 1-vinyl cyclic olefins, and the method appears quite capable of extension to other systems as well. Spectral techniques for unraveling the stereochemical consequence of fusing a cycloalkane ring onto a phospholene ring have also been developed in this study.

Synthesis of Bicyclic Phospholene Oxides. Under the mild conditions normally used for acyclic dienes in the McCormack reaction (room temperature in an alkane solvent), 1-vinylcyclohexene and methylphosphonous dichloride combined slowly to give a white, crystalline solid. After 25 days, the solid was hydrolyzed and the bicyclic phospholene oxide **3** was obtained in 37% yield. That the double bond was in the 3 position was readily apparent from the proton NMR spectrum; there was only a single olefinic proton (δ 5.43), showing the expected[7] large coupling to ^{31}P (29 Hz).

In an attempt to improve the yield in the cycloaddition, the reaction was conducted in refluxing hexane. Hydrolysis of the adduct that had precipitated after 42 hr gave a phospholene oxide in 64% yield, but the product proved to be isomeric with **3**. Since it gave no olefinic proton NMR signals, but had ir absorption for a double bond (1630 cm^{-1}), it was assigned structure **6**. Apparently, the initially formed cycloadduct **4** undergoes rearrangement on heating, forming **5**. The relationship between oxides **3** and **6** was confirmed by performing base-catalyzed rearrangement[7] of the double bond in the former into conjugation with the phosphoryl group. Of the two possible conjugated products, **6** and **7**, only **6** was formed (65%).



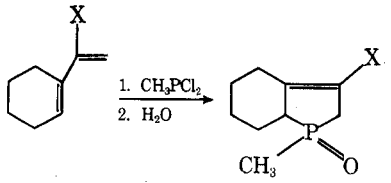
4 **5** **6**



7

The ^{13}C NMR spectra (Table I) of oxides **3** and **6** confirmed the position of the double bond. The signals for carbons in the sp^2 region for **6** were very weak; these carbons are not coupled to hydrogen and their signals lack intensification of the nuclear Overhauser effect. That sp^2 carbon α to phosphorus was easily distinguished by its large coupling[8] to ^{31}P of 85 Hz. For **3**, stereoisomers were present, as is discussed in the next section. The two sp^2 carbons in each isomer had relatively small coupling to ^{31}P (11–14 Hz), proving their β location to phosphorus.

1-(α-Halovinyl)cyclohexenes, readily obtained by the reaction of aqueous hydrogen halides with 1-ethynylcyclohexene[9] or of thionyl chloride and pyridine on 1-ethynylcyclohexanol,[10] also condensed readily with methylphosphonous dichloride.

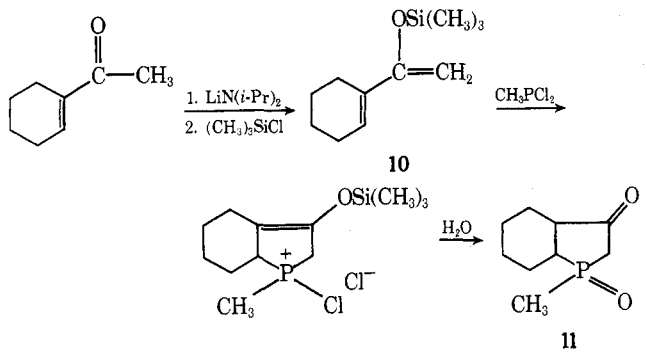


8, X = Br
9, X = Cl

Oxide **8** was established by ^{13}C NMR spectroscopy (Table I); the sp^2 carbons were easily distinguished, and from the small coupling to ^{31}P (10–14 Hz) it was obvious that both were located β to phosphorus. Also, in the proton

NMR spectrum, there was no signal for CH bearing bromine, as would be required for the rearranged structure corresponding to **6**. The latter point was useful in assigning structure **9** to the chloro derivative.

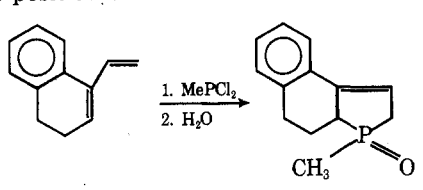
To demonstrate further the synthetic possibilities in the bicyclic system, we sought also the 3-keto derivative, which as for the monocyclic compound should be a useful intermediate to other structures. A new route to such ketones resulted from the present study. It employs a 1-acetylalkene as a starting material, which is converted to a siloxydiene by the lithium diisopropylamide–trimethylchlorosilane sequence.[12] Thus **10** was obtained as a distillable liquid in 60% yield. This siloxydiene participates in the McCormack reaction, and the acidic medium developing on adduct hydrolysis causes simultaneous generation of the keto group. Recently, others[13] have also shown that siloxydienes are readily accessible from α,β-unsaturated ketones by silylation techniques, and it is quite possible that such compounds will be of general utility in 3-phospholanone synthesis. The overall route is very attractive since the desired phospholanone can be obtained in only two steps from the readily available α,β-unsaturated carbonyl compounds. Further investigation of this new method is in progress.



10 **11**

The bicyclic 3-phospholanone did not show spectral indications of any unusually high enol content. For the monocyclic compound, both ir and NMR spectra show clearly that large concentrations of enol can exist in equilibrium with the keto form.[11,14]

A 1-vinylcyclohexene bearing a benzo group was found to react especially readily with methylphosphonous dichloride, and demonstrates the great potential of the McCormack reaction for forming multicyclic phosphorus compounds. Hydrolysis after 10 days gave oxide **12** in 36% yield. The position of the double bond was established by spectral features as used for the bicyclic compounds. Oxide **12** retains considerable water solubility in spite of its high carbon content.



12

Stereochemistry of Bicyclic Phospholene Oxides. 3-Phospholene oxides such as **3**, **8**, **9**, and **12** have two chiral centers and are capable of cis,trans isomerism.[15] These are illustrated for **3**. That the oxide product formed on hydrolysis of the diene–CH_3PCl_2 cycloadducts was a mixture of stereoisomers was evident from NMR spectral features; this was especially noticeable from signals associated with the CH_3–P unit, since steric differences are most pronounced at this site. Thus, the ^{13}C NMR spectrum of **3** (Table I) showed two CH_3 carbons (δ 13.6 and 9.6), with the downfield signal predominating (70:30). Also there were two methyl proton signals and two ^{31}P signals. The steric crowding from cis orientation of PCH_3 with a 2 substitutent causes an upfield shift of this CH_3 signal,[8] and thus the minor isomer of **3** with the upfield signal is assigned cis structure **3b**. The order of ^{31}P NMR signals resulting from this assignment (in D_2O, trans δ −70.5; cis, −77.1) is also that expected from monocyclic compounds; thus for 1,2-dimethyl-3-phospholene oxide, the trans signal is at −60.0 and cis is at −67.2.

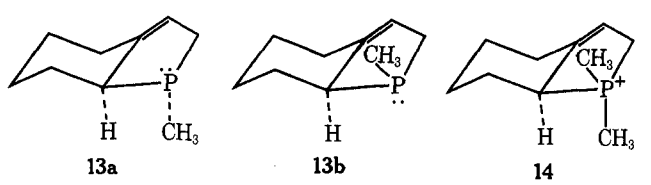
3a (trans) **3b** (cis)

Tricyclic oxide **12** was obtained primarily (71%) in cis form, as judged from the ^{31}P NMR signals (major isomer δ − 77.1, minor −71.2). Stereoisomers were also obtained for halo compounds **8** and **9**, but in these cases, the isomer ratio was nearly 1:1. The isomer ratios from cycloadduct hydrolysis are not necessarily of mechanistic significance, since it is known that they may be influenced by conditions of the hydrolysis,[15] in ways that are yet to be defined.

The keto oxide **11** has three chiral centers, and the sample prepared is a mixture of the four possible cis, trans forms, as judged from the ^{31}P NMR spectrum with four close-lying signals (−44.8 to −49.2 ppm).

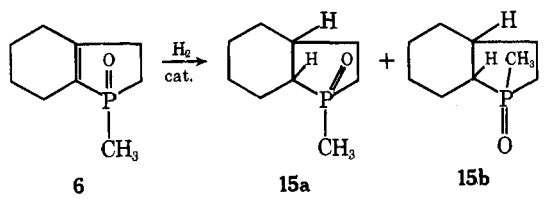
We have had some success in separating the mixture of isomers **3a** and **3b** by distillation through a short column of glass helices. The lower boiling trans isomer was obtained in 90% purity, leaving a cis-enriched pot residue. Pure samples seem obtainable, if desired, by this technique.

Stereochemistry of Other Bicyclic Phosphorus Derivatives. Phosphines. Oxide **3** was readily deoxygenated with trichlorosilane to form a mixture of stereoisomeric phosphines **13a** and **13b**, which gave the same quaternary salt **14** with methyl iodide. The reduction is known[16] to proceed with retention of configuration, and thus the ratio of phosphines **13a** and **13b** remained the same as for the oxides **3a** and **3b**. That the major isomer indeed had the trans structure (**13a**) was confirmed by the ^{13}C NMR spectrum (Table I); this isomer had its CH_3 signal downfield (δ 15.4 ppm) from that of the minor isomer (δ 9.2), where the cis configuration caused steric crowding. The ^{31}P shifts (trans, δ +28.7; cis, +26.2) again were in the order expected from the monocyclic model, 1,2-dimethyl-3-phospholene[12] (trans, δ +28.2; cis, +16.7), as were the proton NMR shifts for the *P*-methyl groups (**13a**, δ 0.88, and **13b**, 0.73; the monocyclics had trans 0.83, cis 0.73).



13a **13b** **14**

Perhydrophosphindole Oxides. Cis addition of hydrogen to the double bond of the phospholene oxide **6** produced the perhydrophosphindole derivatives **15a** and **15b** in nearly equal amounts. That compound with the more



6 **15a** **15b**

upfield ^{13}C methyl signal (Table I) was assumed to have structure **15a** on the basis of the greater steric crowding in this isomer. Catalytic hydrogenation is known to proceed by the cis addition of hydrogen, with attack on the less hindered face of the molecule where a choice is possible. In the case of **6**, hydrogen can approach a face where phosphoryl oxygen is present or a face where methyl is present. From the 1:1 mixture of products, it appears that the rates of approach to the two faces must be equivalent. This is, we believe, the first test of the relative directing influence of *P*-methyl vs. *P*-oxygen toward hydrogen in a 2-phospholene oxide system.[18]

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of phosphines were conducted under nitrogen in a glove bag. ^1H NMR spectra were taken with a JEOL MH-100 spectrometer; chemical shifts are relative to internal tetramethylsilane. ^{31}P NMR spectra were obtained on a Bruker HFX-10 system at 36.43 MHz with proton noise decoupling; chemical shifts are referenced to 85% H_3PO_4, with positive shifts upfield, negative downfield. Proton noise decoupled Fourier transform ^{13}C NMR spectra (Table I) were also obtained on the Bruker spectrometer, at 22.62 MHz, utilizing C_6F_6 in a 3-mm coaxial capillary as an external heteronuclear lock. Chemical shifts are given in parts per million downfield from Me_4Si as zero. Methylphosphonous dichloride was obtained from the Ethyl Corp. Elemental analyses were performed by commercial laboratories.

1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1(*H*)-phosphindole 1-Oxide (3). To a wide-mouth, screw-cap brown bottle was added 37.8 g (0.35 mol) of 1-vinylcyclohexene, 32.2 ml (0.36 mol) of methylphosphonous dichloride, 1 g of copper stearate, and 100 ml of pentane. The bottle was sealed and allowed to stand for 2 months. The resulting cycloadduct was filtered off and washed with pentane (2 × 50 ml). The solid was added cautiously to 25 ml of water and the resulting mixture made slightly basic with solid $NaHCO_3$. The aqueous solution was then extracted continuously for 24 hr with chloroform. The chloroform extract was dried ($MgSO_4$) and concentrated on the rotary evaporator. Distillation of the residue gave 22.2 g of **3** (37%) as a colorless oil, bp 115–120° (0.2 mm), which crystallized on standing to a hygroscopic white solid: ^1H NMR ($CDCl_3$) δ 1.46 and 1.58 (each d, $^2J_{PH}$ = 13 Hz, for PCH_3 of **3b** and **3a**, respectively), 1.71–2.73 (m, ring $-CH_2-$), 5.42 (d, $^3J_{PH}$ = 29 Hz, >C=CH–); ir (neat) 1640 (C=C), 1205 cm^{-1} (P=O); ^{31}P NMR (D_2O, 50%) δ −70.5 (trans, 72%) and −77.1 (cis, 28%).

Anal. Calcd for $C_9H_{15}OP$: C, 63.52; H, 8.89; P, 18.19. Found: C, 63.18; H, 9.16; P, 17.80.

Twenty grams of a 70:30 mixture of **3a** and **3b** was distilled through a 0.25 × 12 in. column packed with glass helices. A total of nine equal-sized fractions was received over the range 90–106° (0.04 mm). It was found by GC and ^{31}P NMR that the trans isomer **3a** had been concentrated (90%) in the first several fractions. The last fraction and the pot residue contained the cis isomer **3b** in a purity of greater than 90%.

1-Methyl-$\Delta^{3a(7a)}$-2,3,4,5,6,7-hexahydro-1(*H*)-phosphindole 1-Oxide (6). To a heated (70°) mixture of 2.0 ml (22.3 mmol) of methylphosphonous dichloride, 500 mg of copper stearate, and 10 ml of *n*-hexane was added 2.0 g (18.5 mmol) of 1-vinylcyclohexene over a 90-min period. The resulting mixture was then refluxed for 42 hr. The flask was cooled (0°) and water (25 ml) was added. The solution was neutralized with solid $NaHCO_3$ and extracted continuously for 12 hr with chloroform. The chloroform extract was dried ($MgSO_4$) and concentrated on the rotary evaporator. Kugelrohr distillation of the residue at 110° (0.1 mm) gave 2.0 g of **6** (64%) as a colorless oil which crystallized on standing to a hygroscopic white solid: ^1H NMR ($CDCl_3$) δ 1.48 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.40–2.70 (m, $-CH_2-$); ir (neat) 1630 (C=C), 1175 cm^{-1} (P=O); ^{31}P NMR δ −63.2 ($CDCl_3$, 50%) or −76.5 (D_2O, 50%).

The same compound was obtained by rearrangement of **3**. A mixture of 1 g (5.88 mmol) of **3** and 10 ml of 3 *N* NaOH was refluxed under N_2 for 72 hr. The resulting solution was cooled, neutralized, and extracted with chloroform (4 × 75 ml). The organic extracts were combined, dried ($MgSO_4$), and concentrated under vacuum. Distillation of the residual oil gave 620 mg of **6** (62%), bp 120–125° (0.2 mm), as a colorless oil which slowly solidified on standing; spectral properties were the same as those reported in the preceding paragraph.

Anal. Calcd for $C_9H_{15}OP$: C, 63.52; H, 8.89; P, 18.19. Found: C, 63.29; H, 9.10; P, 17.85.

3-Bromo-$\Delta^{3(3a)}$-1-methyl-2,4,5,6,7,7a-hexahydro-1(*H*)-phosphindole 1-Oxide (8). A mixture of 45 g (0.24 mol) of 1-(α-bromovinyl)-1-cyclohexene,[9] 22.5 ml (0.25 mol) of methylphosphonous dichloride, 2 g of copper stearate, and 200 ml of pentane was allowed to stand for 2 months. The resulting white solid was filtered off and washed with pentane. The solid was then added slowly to 100 ml of a saturated $NaHCO_3$ solution. The aqueous mixture was extracted continuously with chloroform for 12 hr. The chloroform was then dried ($MgSO_4$) and concentrated. Distillation gave 15.0 g of **8** (25%), bp 144–149° (0.02 mm), which solidified on standing: mp 77–82°; ^1H NMR ($CDCl_3$) δ 1.60 and 1.69 (each d, $^2J_{PH}$ = 12 Hz, PCH_3, for cis and trans isomers, respectively), 1.2–3.2 (m, $-CH_2-$); ir ($CDCl_3$ solution between salt plates) 1190 cm^{-1} (P=O); ^{31}P NMR (50% in D_2O) δ −67.2 (cis, 51%) and −61.6 (trans, 49%).

Anal. Calcd for $C_9H_{14}BrOP$: C, 43.40; H, 5.66; Br, 32.08; P, 12.44. Found: C, 43.36; H, 5.72; Br, 31.88; P, 12.43.

3-Chloro-$\Delta^{3(3a)}$-1-methyl-2,4,5,6,7,7a-hexahydro-1(*H*)-phosphindole 1-Oxide (9). A mixture of 14.2 g (0.1 mol) of 1-(α-chlorovinyl)cyclohexene,[10] 9.0 ml (0.1 mol) of methylphosphonous dichloride, 1 g of copper stearate, and 75 ml of pentane was allowed to stand for 3 weeks. The resulting white solid was filtered off and washed with pentane. The solid was then added slowly to 100 ml of a saturated $NaHCO_3$ solution. The aqueous mixture was extracted continuously with chloroform for 12 hr. The chloroform was then dried ($MgSO_4$) and concentrated. Distillation of the crude oil gave 6.1 g of **9** (30%), bp 133–138° (0.02 mm), as an oil which crystallized on standing to give a hygroscopic solid: mp 65–70°; ^1H NMR (D_2O) δ 1.65 and 1.73 (each d, $^2J_{PH}$ = 12.5 Hz, cis and trans PCH_3, respectively), 1.10–3.05 (m, $-CH_2-$); ir (Nujol) 1190 cm^{-1} (P=O); ^{31}P NMR (50% in D_2O) δ −66.4 (cis, 49.3%) and −60.7 (trans, 50.7%).

Anal. Calcd for $C_9H_{14}ClOP$: C, 52.81; H, 6.85; P, 15.16. Found: C, 53.05; H, 6.98; P, 15.08.

1-(α-Trimethylsiloxyvinyl)cyclohexene (10). To a cooled (−78°) solution of 2.12 g (0.21 mol) of diisopropylamine in 50 ml of tetrahydrofuran (THF) was added 87.5 ml of 2.4 *M* *n*-butyllithium (0.21 mol) in hexane. The lithium diisopropylamide precipitated from solution to form a white slurry. Stirring was continued for 15 min and then 25.1 g (0.20 mol) of 1-acetylcyclohexene in 10 ml of THF was added over a 10-min period. The slurry turned pale green; stirring was continued for 5 min at −78°. Chlorotrimethylsilane (27.2 g, 0.25 mol) was then added in one portion. The resulting mixture was stirred at −78° for 5 min and then at room temperature for 1 hr. The mixture was partitioned between pentane (250 ml) and saturated aqueous $NaHCO_3$ (200 ml). The layers were separated and the aqueous layer extracted with pentane (2 × 100 ml). The pentane extracts were combined, dried ($MgSO_4$), and concentrated to give a clear white oil. Distillation gave 24.1 g of **10** (60.2%): bp 111–115° (18 mm); ^1H NMR ($CDCl_3$) δ 0.20 [s, 9 H, $Si(CH_3)_3$], 1.60 (m, 4 H, $-CH_2-$), 2.11 (m, 4 H, allylic CH_2), 4.23 (d, *J* = 15 Hz, $-C=CH_2$), 6.20 (m, 1, H, $-CH_2CH=$); ir (neat) 1660 (internal C=C), 1610 cm^{-1} (terminal C=C).

1-Methyl-3-oxo-4,5,6,7-tetrahydrophosphindoline 1-Oxide (11). A solution of 4.2 g (0.02 mol) of diene **10**, 2.2 ml (0.025 mol) of methylphosphonous dichloride, 100 mg of copper stearate, and 50 ml of pentane was allowed to stand for 5 days. The resulting yellow solid was filtered off and washed with pentane (2 × 10 ml). The solid was added slowly to 10 ml of water and the resulting mixture stirred for 30 min. The solution was made slightly basic with 3 *N* sodium hydroxide and then extracted continuously with chloroform. The chloroform extract was dried ($MgSO_4$) and concentrated. The resulting gummy solid (1.8 g, 49%) was sublimed at 140° (0.5 mm) to give 1.02 g of **11** (37%): mp 77–82°; ^1H NMR ($CDCl_3$) δ 1.18–35 (complex multiplet, $-CH_2-$), 1.71 (d, $^2J_{PH}$ = 15 Hz, PCH_3), 1.74 (d, $^2J_{PH}$ = 14.5 Hz, PCH_3), 1.76 (d, $^2J_{PH}$ = 14 Hz, PCH_3), 1.78 (d, $^2J_{PH}$ = 14 Hz, PCH_3); ir ($CDCl_3$) 1715 cm^{-1} (C=O), 1180 cm^{-1} (P=O); ^{31}P NMR ($CDCl_3$) δ −44.8 (42%), −45.3 (32%), −46.2 (19%), and −49.2 (7%).

Anal. Calcd for $C_9H_{15}O_2P$: C, 58.07; H, 8.12; P, 16.64. Found: C, 57.97; H, 8.33; P, 16.38.

1-Methyl-$\Delta^{3(3a)}$-2,8,9,9a-tetrahydro-1(*H*)-benzo[*e*]phosphindole 1-Oxide (12). A solution of 6.61 g (42 mmol) of 1,2-dihydro-4-vinylnaphthalene prepared in 65% yield by the method of Robins and Walker,[20] 3.7 ml (42 mmol) of methylphosphonous dichloride, 1 g of copper stearate, and 50 ml of pentane was allowed to stand for 1 month. The resulting cycloadduct was filtered off and washed with pentane (2 × 50 ml). The solid was dissolved in

25 ml of water and the solution was made slightly basic with solid $NaHCO_3$. The aqueous mixture was then extracted with chloroform (4 × 50 ml). The organic extracts were combined, dried ($MgSO_4$), and concentrated to give 5.1 g (56%) of crude solid. Sublimation at 100° (0.05 mm) gave 3.30 g (36%) of **12**: mp 111–115°; ^1H NMR ($CDCl_3$) δ 1.44 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.72 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.90–3.62 (complex m, $-CH_2-$), 6.28 (d, $^3J_{PH}$ = 28 Hz, $-C=CH-$), 7.04–7.76 (4 H, aromatic); ^{31}P NMR (D_2O, 2 *M*) δ −77.7 (71%) and −71.2 (29%); ir (Nujol) 1200 cm^{-1} (P=O).

Anal. Calcd for $C_{13}H_{15}OP$: C, 71.55; H, 6.88; P, 14.20. Found: C, 71.49; H, 6.94; P, 14.41.

***trans*- (13a) and *cis*- (13b) 1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1(*H*)-phosphindole.** To a solution of 5.1 g (30 mmol) of **3a** (60%) and **3b** (40%) in 200 ml of dry benzene at 0° was added a solution of 13.1 ml (130 mmol) of trichlorosilane in 25 ml of benzene over a 1-hr period. The ice bath was removed and the mixture was refluxed for 12 hr. It was cooled and carefully hydrolyzed by addition of 50 ml of a 20% NaOH solution. The layers were separated and the aqueous layer was extracted with benzene (4 × 25 ml). The organic extracts were combined and dried ($MgSO_4$) and the benzene was distilled off at atmospheric pressure. The remaining yellow oil was distilled to give 3.1 g of the isomers of **13** (68%) as a colorless liquid: bp 104–106° (16 mm); ^1H NMR ($CDCl_3$) δ 0.73 and 0.88 (each d, $^2J_{PH}$ = 3.5 Hz, PCH_3 for **13b** and **13a**, respectively), 1.10–2.85 (m, $-CH_2-$), 5.15–5.65 (m, $>C=CH-$); ^{31}P NMR (neat) δ +26.2 (**13a**, 56%) and +28.6 (**13b**, 44%).

The methiodide **14** was prepared by treating a small amount of the phosphine with excess methyl iodide. Recrystallization from methanol–ether gave white needles, mp 265° dec.

Anal. Calcd for $C_{10}H_{18}IP$: C, 40.54; H, 6.08; P, 10.47. Found: C, 40.71; H, 5.95; P, 10.28.

1-Methylperhydrophosphindole 1-Oxide (15a and 15b). A mixture of 1 g (5.8 mmol) of **6**, 100 ml of absolute ethanol, and 500 mg of 5% rhodium on alumina was placed in a Parr pressure bottle and shaken under H_2 (50 psi) for 13 hr. The catalyst was removed by filtration and the ethanol by rotary evaporation. The residual oil solidified and was sublimed at 70° (0.01 mm) to give 725 mg of **15** (73%): mp 88–94°; ^1H NMR (D_2O δ 1.57 and 1.62 (each d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.15–2.60 (m, $-CH_2-$); ir (Nujol) 1160 cm^{-1} (P=O); ^{31}P NMR (50% in D_2O) δ −82.8 (49.5%) and −78.8 (50.5%).

Anal. Calcd for $C_9H_{17}OP$: C, 62.79; H, 9.88; P, 18.02. Found: C, 62.95; H, 10.05; P, 17.88.

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Registry No.—**3a**, 57065-62-0; **3b**, 57065-63-1; **6**, 57065-64-2; *trans*-**8**, 57065-65-3; *cis*-**8**, 57065-66-4; *trans*-**9**, 57065-67-5; *cis*-**9**, 57065-68-6; **10**, 54781-35-0; **11** isomer A, 57065-69-7; **11** isomer B, 51728-59-3; **11** isomer C, 57128-60-6; **11** isomer D, 57128-61-7; **12**, 57065-70-0; **13a**, 57065-71-1; **13b**, 57065-72-2; **14**, 57065-73-3; **15a**, 57065-74-4; **15b**, 57128-62-8; 1-vinylcyclohexene, 2622-21-1; methylphosphonous dichloride, 676-83-5; 1-(α-bromovinyl)-1-cyclohexene, 57065-75-5; 1-(α-chlorovinyl)cyclohexene, 57065-76-6; 1-acetylcyclohexene, 932-66-1; chlorotrimethylsilane, 1,2-dihydro-4-vinylnaphthalene, 57065-77-7.

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Scope of the 1,6 Addition of Sulfur Dioxide to *cis*-3-Hexatrienes

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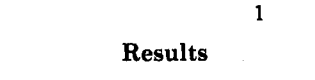
Reaction between *cis*-3-hexatriene and sulfur dioxide yields an adduct, 2,7-dihydrothiepin 1,1-dioxide. Similarly prepared were the seven-membered-ring sulfones with the following substituents: 3-isopropyl-6-methyl, 3,5-dimethyl, 2,4,6-trimethyl, and 3-acetoxymethyl. Sulfolenes only were obtained from *cis*-1,2-dicyclohex-1-enylethylene and 1,3,5-cyclooctatriene, as well as from 4,6-dimethyl-2,3,5-heptatriene. The structure of the adducts is described, and the influence of substituents on the course of the addition reaction is discussed.

The sulfolene reaction (the addition of sulfur dioxide to a conjugated diene) provides a valuable synthesis of five-membered-ring sulfones. Since the reaction is fully reversible, the sulfones have been exploited as intermediates for the modification and purification of dienes.[2] We have reported that the reaction between hexatriene and sulfur dioxide yields a seven-membered-ring sulfone, 2,7-dihydrothiepin 1,1-dioxide (**1**).[3] This transformation is also reversible. In this article we examine the generality of the cycloaddition with variously substituted trienes. The details of the mechanism of the reaction are considered elsewhere.[4]



1

Results

2,7-Dihydrothiepin 1,1-Dioxide (1). The reaction of *cis*-hexatriene with excess sulfur dioxide gives an excellent