The Synthesis of Olefins from β-Hydroxyphosphonamides. Stereochemistry and Extension to the Formation of Conjugated Dienes

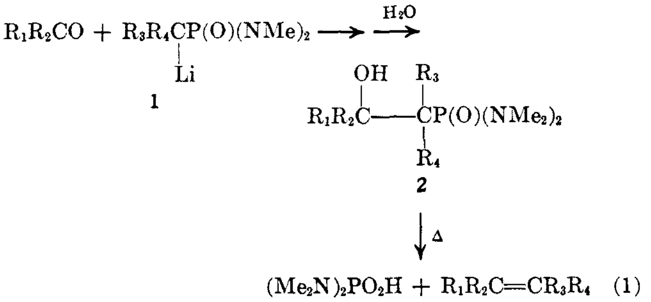
E. J. COREY AND DAVID E. CANE

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received December 17, 1968

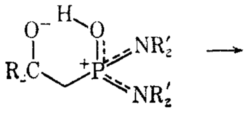
The thermal decomposition of β-hydroxyphosphonamides to olefins has been shown to involve preferential *cis* elimination. The phosphonamide route to olefins has also been extended to conjugated dienes using a modified phosphonamide **13** in which the bulk of the diamide is minimized so as to allow α attack on the corresponding anion by unhindered ketones and aldehydes. The resulting adducts are converted into dienes by thermal decomposition at 80–120°.

β-Hydroxyphosphonamides, available by reaction of α-lithiophosphonamide derivatives with aldehydes or ketones or by reduction of β-ketophosphonamides, undergo decomposition to olefins stereospecifically upon heating in refluxing benzene or toluene[1] (eq 1). We have now demonstrated that the decomposition reaction is a *cis* elimination and that the phosphonamide reaction may be extended to the synthesis of dienes. If the decomposition of β-hydroxyphosphonamides to form olefins were to proceed *via* betaines of type **3**, which should be susceptible to cycloelimination of the sort already established for the Wittig reaction itself and also for the related betaines from β-hydroxysulfinamides,[2] a *cis*-elimination pathway would be expected (eq 2).

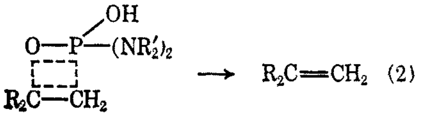


$$R_1R_2CO + R_3R_4\underset{\underset{\textstyle Li}{|}}{C}P(O)(NMe_2)_2 \longrightarrow \xrightarrow{H_2O} R_1R_2\overset{\overset{\textstyle OH}{|}}{C}-\overset{\overset{\textstyle R_3}{|}}{\underset{\underset{\textstyle R_4}{|}}{C}}P(O)(NMe_2)_2 \xrightarrow{\Delta} (Me_2N)_2PO_2H + R_1R_2C{=}CR_3R_4 \quad (1)$$

1 2



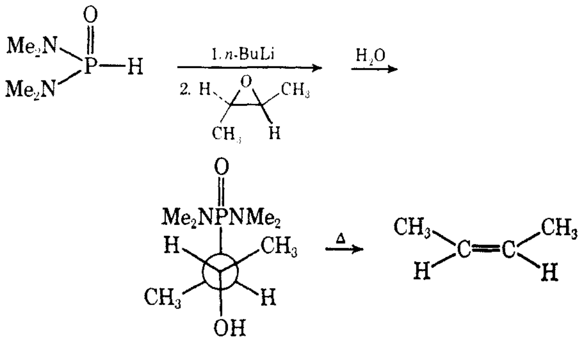
3



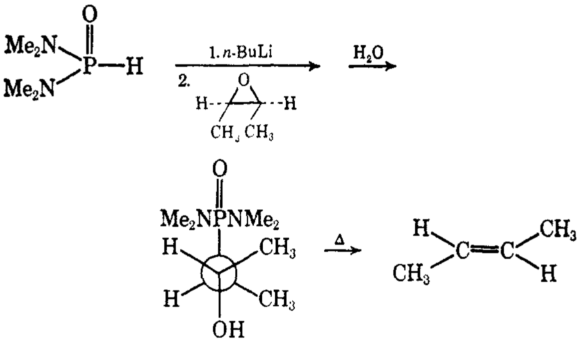
4 (2)

As a first step in these studies, we undertook the synthesis of two diastereomeric β-hydroxyphosphonamides of known geometrical configuration which by thermal decomposition would generate isomeric olefins of known stereochemistry. The report by Normant[3] that the diamidophosphite anion (**5**) reacts with a number of alkyl halides to give the corresponding alkylphosphonodiamides, the products of P alkylation, suggested that such an anion might react with a suitable epoxide to produce a β-hydroxyphosphonamide, stereochemically pure and of unambiguous configuration. *cis*- and *trans*-2,3-oxidobutanes were chosen as the substrates. Both are readily available in high purity from the corresponding olefins and are sufficiently unhindered to allow attack by bulky nucleophiles. As illustrated below, when lithium diamidophosphite, generated in tetrahydrofuran by addition of *n*-butyllithium to a solution of bis(dimethylamino)phosphorous acid, was allowed to react with the *trans*- and *cis*-2,3-oxidobutanes, the diastereomeric displacement products **6** and **7**, respectively, were formed (eq 3 and 4). These diastereomers are readily distinguishable by nmr spectroscopy.[4]

5



6 (3)



7 (4)

The stereochemistry of olefin formation from **6** and **7** was easily demonstrated. Thermal decomposition of **7** gave a product which was shown by vapor phase

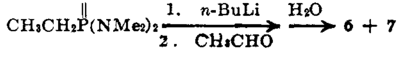
---

[1] (a) E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5652, 5653 (1966); (b) E. J. Corey and G. T. Kwiatkowski, *ibid.*, **90**, 6816 (1968); (c) E. J. Corey *Pure Appl. Chem.*, **14**, 19 (1967).

[2] E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **90**, 5553 (1968).

[3] H. Normant, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1050 (1967).

[4] Generation of a mixture of **6** and **7** by an alternative, nonstereospecific method gave rise to an nmr spectrum which was completely equivalent to a superposition of the spectra of **6** and **7**.



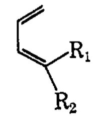
$$CH_3CH_2\overset{\overset{\textstyle O}{\|}}{P}(NMe_2)_2 \xrightarrow[2.\ CH_3CHO]{1.\ n\text{-BuLi}} \xrightarrow{H_2O} 6 + 7$$

chromatography (vpc) to be greater than 99% *trans*-2-butene, while similar thermolysis of **6** gave 96% *cis*- plus 4% *trans*-2-butene. These reactions were carried out at 80° in toluene in the presence of calcium carbonate–silica gel, necessary to neutralize the acidic phosphoric amide as it is formed and prevent isomerization of the olefinic products. These data clearly indicate a strong preference for *cis* elimination.

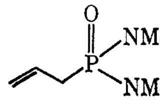
As a further test of the *cis*-elimination pathway, *trans*-2-hydroxy bis(dimethylamino)phosphonylcyclohexane (**8**) was synthesized from cyclohexene oxide. Elimination by a *cis* mechanism would now be extremely unfavorable, since it would lead to at least transient formation of the unknown and highly strained *trans*-cyclohexene. On the other hand, a *trans* elimination, if it were to take place at all, would lead directly to *cis*-cyclohexene. In accord with prediction, thermolysis of **8** at 100° for 72 hr, conditions more than sufficient to bring about olefin formation in acyclic β-hydroxyphosphonamides, yielded less than 0.01% cyclohexene. Under drastic conditions (170° for 20 hr) the thermolysis of **8** led to cyclohexene in 25% yield. This result could mean that *trans* elimination can occur at sufficiently high temperatures or that high temperatures cause isomerization of **8** to the *cis* isomer, *e.g.*, by cleavage of the α,β bond (reverse Wittig) and recyclization.

Diene Synthesis.—In order to probe further the generality and limitations of the phosphonamide olefin synthesis, we turned our attention to the possibility of synthesizing 1,1-disubstituted butadienes of type **9** by means of allylphosphonamides.

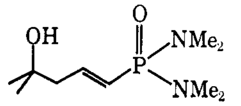
N,N,N′,N′-Tetramethylallylphosphonodiamide (**10**), when treated with *n*-butyllithium followed by acetone, gave exclusively the product of carbon attachment γ to the phosphorus atom, **11**. This product was stable to thermolysis under the standard conditions for olefin synthesis.



9

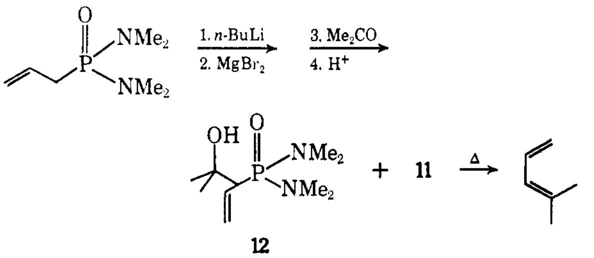


10



11

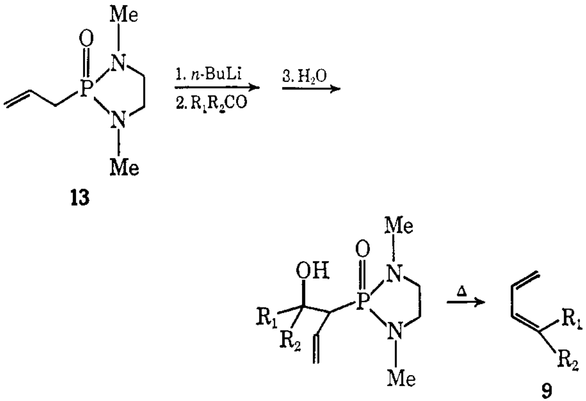
An attempt was made to control the position of electrophilic attack by the addition of Lewis acids so as to force the incoming carbonyl group to become attached selectively to the carbon α to the phosphorus. Formation of the organozinc or organocadmium reagents, by the addition of zinc chloride or cadmium iodide, respectively, to the lithio derivative of **10**, led only to the product of γ attack, **11**, upon reaction with acetone. Reaction of the Grignard reagent, formed from magnesium bromide and the anion of **10**, with acetone gave, under optimum conditions, a product consisting of a 3:1 mixture of α/γ adduct (eq 5), based on nmr analysis of the N-methyl resonances. The two components, **12** and **11**, could be separated by preparative tlc or, with more difficulty and in lower yield, by recrystallization. Thermal decomposition of **12** gave a 50% yield of 4-methyl-1,3-pentadiene.



12 (5)

When the sodio derivative, generated by reaction of **10** with phenylsodium, was treated with acetone, only **11** was obtained.

Modification of the phosphonamide so as to reduce the bulk of the amide was more successful. Reaction of symmetrical dimethylethylenediamine with allylphosphonyl dichloride gave a good yield of N,N′-dimethyl-2-allyl-1,3,2-diazaphospholidine 2-oxide (**13**). When **13** was treated with *n*-butyllithium followed by acetone, α adduct **14a** was formed in high yield, essentially uncontaminated by γ-addition product. Thermolysis under vacuum of crude **14a** in mineral oil in the presence of calcium carbonate, added to preserve the neutrality of the reaction mixture, produced the butadiene in 75% yield (eq 6).



13

9 (6)

14a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = CH_3CH_2$
c, $R_1 = (CH_3)_3C$; $R_2 = H$
d, $R_1 = C_6H_5$; $R_2 = H$
e, $R_1R_2 = (CH_2)_5$

Methyl ethyl ketone added to the α carbon of the anion of **13** to give **14b** as a mixture of diastereomers. Thermal decomposition of **14b** resulted in the formation of a mixture of the isomeric butadienes **9a** ($R_1 = CH_3CH_2$; $R_2 = CH_3$) and **9b** ($R_1 = CH_3$; $R_2 = CH_3CH_2$) in a ratio of 3:5. The minor component was identified as **9a** by comparison with an authentic sample prepared by reaction of the homoallylic tosylate **15** with potassium *t*-butoxide. All attempts to separate the diastereomers of **14b** by recrystallization or tlc and thus allow generation of isomerically pure **9a** or **9b** were unsuccessful.

Reaction of pivalaldehyde with the anion of **13** gave a mixture of **14c** and **16a** in about equal amounts. Pinacolone and benzophenone each attacked exclusively the γ carbon of **13**. The adducts **16b** and **16c** were stable to heating under the normal conditions for olefin synthesis.

The yields of adducts **14** and of the butadienes resulting from the thermolysis of these adducts are summarized in Table I.

In summary, the controlling factor in the cases examined governing the ratio of α to γ addition seems to be steric. If the greatest degree of negative charge resides on the carbon α to the phosphorus atom, then, all other things being equal, addition should be

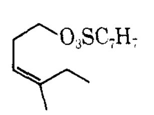
TABLE I

CONVERSION $R_1R_2C{=}O \longrightarrow R_1R_2C{=}CHCH{=}CH_2$ *via* ALLYLDIAZAPHOSPHOLIDINE ADDUCTS

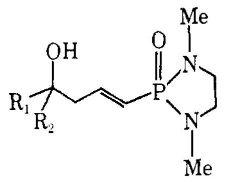
Carbonyl compound	Yield of adduct, %	Yield of diene, %[a,b]
Acetone	75	75
Methyl ethyl ketone	80	90
Pivalaldehyde	30[c]	50[c,d]
Benzaldehyde	85	60[e]
Cyclohexanone	90	90

[a] Thermolysis of adduct in mineral oil in the presence of calcium carbonate. [b] Yield of isolated product. [c] Corrected for presence of **16a**. [d] Yield as determined by vpc. [e] Elimination carried out in benzene at reflux and in the presence of triethylamine to prevent polymerization of the product.

at the α carbon. If the position α to the phosphorus atom is hindered, however, as in the bis(dimethylamide) **10**, or when the carbonyl compound contains bulky groups, then condensation takes place at an alternative site to give the γ-substituted adduct. Only when both the α position and the carbonyl are unhindered will there be selective addition to the α site.[5]



15



16a, $R_1 = (CH_3)_3C$; $R_2 = H$
b, $R_1 = (CH_3)_3C$; $R_2 = CH_3$
c, $R_1 = R_2 = C_6H_5$

For suitable cases the phosphonamide reaction may thus be modified allowing an extension to the synthesis of dienes, although stereochemical control has not been achieved. Work is now in progress with phosphonamide reagents bearing electron-withdrawing functional groups.

Experimental Section

Infrared spectra were taken using a Perkin-Elmer Model 137 Infracord, and nmr data were obtained using Varian Associates Models A-60, T-60, or HA-100 spectrometers. Nmr shifts are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra were recorded on an AEI-MS-9 double focusing spectrometer. Vpc analyses were performed on F & M Models 300 or 810, and preparative vpc, on an Aerograph Autoprep. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and A. Bernhardt, Mülheim, Germany.

Reagents.—The following reagents were used: *n*-butyllithium (Foote Mineral Co.), 1.6 *M* hexane or pentane solution, untitrated; tetrahydrofuran, distilled from lithium aluminum hydride, stored under argon; benzene and toluene dried over sodium wire.

Bis(dimethylamino)phosphorous Acid.[6,7]—Phosphorous acid (7.55 g, 0.092 mol) was added slowly to 30.06 g (0.184 mol) of hexamethylphosphorustriamide. The reaction mixture was stirred for 1 hr at 60°, then overnight at room temperature. The crude reaction mixture was vacuum distilled, the pot temperature being maintained below 80° to prevent thermal decomposition, yielding 11.47 g of bis(dimethylamino)phosphorous acid: bp 67° (0.4 mm); $n^{25}\text{D}$ 1.4506 (lit.[7] $n^{25}\text{D}$ 1.4518); nmr ($CDCl_3$), δ 2.65 (d, J = 11 Hz, NCH_3, 12 H), 4.82 (d, J = 579 Hz, PH, 1 H); ir λ_{max}^{neat} 4.30, 10.4 μ.

***trans*-2-Bis(dimethylamino)phosphonylcyclohexanol (8).**—To a solution of 0.591 g (4.35 mmol) of bis(dimethylamino)phosphorous acid in 10 ml of tetrahyrofuran was added 2.90 ml (4.64 mmol) of 1.6 *M* *n*-butyllithium with stirring at −78° under argon. The reaction mixture was allowed to warm to room temperature during an hour, following which 0.465 g (4.78 mmol) of cyclohexene oxide was added. After 44 hr a Gilman test[8] indicated the disappearance of all lithium diamidophosphite. Water (5 ml) was then added, the tetrahydrofuran was evaporated, and the residue was extracted with three 100-ml portions of methylene chloride. After the mixture was dried over magnesium sulfate evaporation of the solvent and purification by preparative tlc (silica gel; chloroform–methanol, 19:1) gave 0.210 g of **8** as a slightly yellow oil: nmr ($CDCl_3$), δ 1.0–2.4 (m, 9 H), 2.65 (d, J = 14 Hz), and 2.73 (d, J = 11.5 Hz), (NCH_3, 12 H), 3.50–3.95 (m, CHOH, 1 H), 6.0 (s, OH, 1 H); ir λ_{max}^{neat} 3.03 μ.

A sample of **8** was prepared for analysis by bulb-to-bulb distillation [oven temperature, 100° (0.005 mm)].

Anal. Calcd for $C_{10}H_{23}N_2O_2P$: C, 51.27; H, 9.90; N, 11.96. Found: C, 51.34; H, 9.54; N, 11.76.

Attempted Thermal Decomposition of 8.—A mixture of **8** (0.274 g, 1.15 mmol) and 0.75 g of 1:4 (w/w) calcium carbonate–silica gel was heated for 72 hr at 100° in a sealed tube under argon. The tube was cooled and opened, and the volatile products were collected in a trap at −196°, then dissolved in pentane along with 0.25 mmol of *n*-octane as an internal vpc standard. Analysis by vpc, which was capable of detecting a 0.01% yield of cyclohexene, showed no cyclohexene.

Pyrolysis of 8.—A mixture of **8** (0.540 g, 2.3 mmol) and 1.5 g of 1:4 (w/w) calcium carbonate–silica gel was heated for 20 hr at 170° in a sealed tube under argon. The tube was cooled and opened, and the volatile products were collected in a trap at −196°, then dissolved in pentane along with 0.5 mmol of *n*-octane. Analysis by vpc (15 ft × 0.125 in. 10% TCEP on Chromosorb, 60°) showed the presence of cyclohexene in 25% yield.

Reaction of Lithium Diamidophosphite with *cis*-2,3-Oxidobutane.—To a solution of 5.143 g (37.8 mmol) of bis(dimethylamino)phosphorous acid in 75 ml of tetrahydrofuran was added 24.5 ml (39.2 mmol) of 1.6 *M* *n*-butyllithium with stirring at −78° under argon. The reaction mixture was allowed to warm to room temperature during an hour, following which 3.0 g (42 mmol) of *cis*-2,3-oxidobutane, prepared by the method of Pasto and Cumbo,[9] was added. After 72 hr of stirring, saturated ammonium chloride solution was added, the tetrahydrofuran was evaporated, and the residue was extracted with several portions of methylene chloride. The solvent was dried over magnesium sulfate and evaporated to yield 1.88 g of crude solid **7** which could be used without further purification. Alternatively, 1.8 g of **7** was purified by recrystallization from *n*-butyl acetate to yield 0.7 g of white solid: mp 76–80°; nmr ($CDCl_3$), δ 1.06 (d × d, J_{HH} = 8 Hz, J_{PH} = 18 Hz, CCH_3, 3 H), 1.24 (d, J = 6 Hz, $HOCCH_3$, 3 H), 2.0–2.5 (m, PCH, 1 H), 2.65 (d), and 2.75 (d, J = 11 Hz, J = 10 Hz, NCH_3, 12 H), 3.75–4.25 (m, CHOH, 1 H), 5.0 (s, OH, 1 H); ir λ_{max}^{neat} 3.0, 10.3 μ.

An analytical sample of **7** was prepared by sublimation at 45° (0.005 mm).

Anal. Calcd for $C_8H_{21}N_2O_2P$: C, 46.14; H, 10.16; N, 13.45. Found: C, 46.00; H, 10.19; N, 13.13.

Reaction of Lithium Diamidophosphite with *trans*-2,3-Oxidobutane.—Lithium diamidophosphite (0.07 mmol), generated in the usual manner, was stirred for 5 days in 125 ml of tetrahydrofuran with 5.75 g (0.08 mmol) of *trans*-2,3-oxidobutane.[9] Saturated ammonium chloride solution was added to the reaction mixture, and the product was isolated as before to yield 1.97 g of oil which was purified by preparative tlc (silica gel; chloroform–methanol, 19:1) to give 1.18 g of **6**: nmr ($CDCl_3$), δ 1.11 (d × d, J_{HH} = 8 Hz, J_{PH} = 18 Hz, CCH_3) and 1.20 (d, J = 7 Hz, $HOCCH_3$) (total 6 H), 2.0–2.5 (m, PCH, 1 H), 2.68 (d, J = 11 Hz, NCH_3, 12 H), 3.6–4.6 (m, CHOH, 1 H), 5.0 (s, OH, 1 H); ir λ_{max}^{neat} 3.0, 10.3 μ.

The trimethylsilyl ether of **6**, prepared by the reaction of **6** with bis(trimethylsilyl)acetamide, had *m/e* 280.1740 (calcd for $C_{11}H_{29}N_2O_2PSi$: 280.1736).

N,N,N′,N′-Tetramethyl-2-hydroxy-1-methylpropylphosphono-

---

[5] Ramirez has recently demonstrated a difference in steric hindrance involving bis(dimethylamino) and *s*-dimethylethylenediamino groups attached to phosphorus. See. F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967).

[6] A. Zwierzak, *Bull. Acad. Pol. Sci.*, **13**, 609 (1965)

[7] E. N. Walsh, DAS 1.125.424 (1960); *Chem. Zentr.*, 14666 (1962).

[8] H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925).

[9] D. J. Pasto and C. C. Cumbo, *J. Org. Chem.*, **30**, 1271 (1965).

diamide (6 and 7).—To a solution of 1.074 g (6.55 mmol) of N,N,N′,N′-tetramethylethylphosphonodiamide[1] in 15 ml of tetrahydrofuran was added 4.3 ml (6.88 mmol) of 1.6 *M* *n*-butyllithium at −78° under argon. The solution was stirred for 1 hr at −78° and 2 hr at −20°, whereupon 0.5 ml (9 mmol) of acetaldehyde was added and stirring was continued for 3 hr at −78°. Addition of 5 ml of half-saturated ammonium chloride solution, extraction with methylene chloride, drying over magnesium sulfate, and evaporation of solvent yielded 1.5 g of oil, shown by nmr analysis to be a mixture of *ca.* 2:1 **6** and **7**.

Thermal Decomposition of 7.—A mixture of 0.137 g of **7** and 0.45 g of 1:4 (w/w) calcium carbonate–silica gel was stirred in a closed system at 80° in 1.5 ml of toluene. The volatile butene was trapped at −78°. After 20 hr a small amount of solvent was added to the liquid in the trap, along with a measured volume of *n*-pentane. The mixture was then analyzed by vpc on a 45 ft × 0.125 in. 15% dimethylsulfolane on Chromosorb P column. The mixture contained greater than 99% *trans*- and only a trace of *cis*-2-butene. The yield, based on the internal standard, *n*-pentane, was about 20%.

Thermal Decomposition of 6.—In exactly the same manner as described above, **6** was heated for 18 hr. Vpc analysis of the product showed 96% *cis*- and 4% *trans*-2-butene, in 20% yield based on the internal standard.

In a control experiment the olefinic product was analyzed after 8- and 32-hr reaction time. No variation in product composition was observed.

Allylphosphonic Dichloride.[10]—Aluminum chloride (60 g, 0.5 mol) was added to 137 g (1.0 mol) of phosphorus trichloride and the mixture was stirred vigorously at 45° under inert atmosphere while 19 g (0.25 mol) of 3-chloropropene was added over 30 min. The reaction mixture was then stirred an additional 20 min until all of the aluminum chloride had dissolved, whereupon excess phosphorus trichloride was removed on the rotary evaporator and the residue was dissolved in 300 ml of methylene chloride and cooled to −20°. Water (81 ml) was added slowly *via* syringe with vigorous stirring. The solid precipitate was filtered and washed with methylene chloride and the filtrate was dried over magnesium sulfate and concentrated *in vacuo*. Distillation under reduced pressure gave 22.28 g (56%) of clear liquid, bp 79–79.5° (15 mm).

N,N,N′,N′-Tetramethylallylphosphonodiamide (10).—Dimethylamine (56 ml, 36 g, 0.84 mol) in 500 ml of ether was cooled and stirred at 0° under argon while 22.3 g (0.14 mol) of allylphosphonic dichloride was added over 10 min. Stirring was continued for 1 hr at 0° and 3 hr at room temperature. The solution was then filtered, calcium oxide was added to the filtrate, the mixture was refiltered, and the solvent was removed. The residue was distilled from calcium hydride to give 20.03 g of a clear liquid, bp 61° (0.03 mm), which solidified upon standing: nmr ($CDCl_3$), δ 2.6 (m, PCH_2) and 2.63 (d, J = 9.5 Hz, NCH_3) (total 14 H), 4.9–6.3 (m, $CH{=}CH_2$, 3 H); ir $\lambda_{max}^{CCl_4}$ 6.12, 10.1, 10.3, 10.95 μ.

N,N′-Dimethyl-2-allyl-1,3,2-diazaphospholidine 2-Oxide (13).—To a solution of 2.527 g (28.7 mmol) of *s*-dimethylethylenediamine in 200 ml of ether and 50 ml of triethylamine was added 4.574 g (28.8 mmol) of allylphosphonic dichloride in ether with stirring at 0° under argon. The solution was stirred for 1.5 hr at 0° and overnight at room temperature. Methylene chloride (50 ml) was then added, the solution was filtered, and the solvent was evaporated. Distillation from calcium hydride through a 6-in. Vigreux column gave 2.575 g (51%) of a clear liquid, bp 98.5–100.5° (0.40–0.45 mm), which solidified on standing: nmr ($CDCl_3$), δ 2.67 (d, J = 9 Hz NCH_3) and 2.6 (m, PCH_2) (total 8 H), 3.1 (m, NCH_2, 4 H), 4.8–6.0 (m, $CH{=}CH_2$, 3 H); ir $\lambda_{max}^{CCl_4}$ 6.11 μ; mass spectrum, *m/e* 174, 133, 90, 42.

Anal. Calcd for $C_7H_{15}N_2OP$: C, 48.27; H, 8.68; N, 16.08. Found: C, 48.31; H, 8.87; N, 16.39.

Generation of the Anion of 10. Reaction with Acetone.—To a stirred solution of 0.829 g (4.71 mmol) of **10** in 15 ml of tetrahydrofuran was added 2.95 ml (4.71 mmol) of 1.6 *M* *n*-butyllithium at −70° under argon. The solution was stirred for 0.5 hr and 0.292 g (5.04 mmol) of acetone was added. After stirring for 20 min at −70°, the solution was allowed to warm to room temperature, following which 5 ml of half-saturated sodium bicarbonate solution was added, and the reaction mixture was extracted with ether. Drying of the ether layers and evaporation of solvent left 0.723 g of **11** as a yellow oil: nmr ($CDCl_3$), δ 1.23 (s, CCH_3, 6 H), 2.6 (m, $=CCH_2$) and 2.62 (d, J = 10 Hz, NCH_3) (total 14 H), 4.7 (s, OH, 1 H), 5.73 (d × d, J_{HH} = 17 Hz, J_{PH} = 22 Hz, PCH, 1 H), 6.2–7.2 (m, $=CH$, 1 H); ir $\lambda_{max}^{CHCl_3}$ 6.13, 10.2, 11.0 μ

Addition of the Anion of 10 to Cadmium Iodide. Reaction with Acetone.—To a stirred solution of 0.387 g (2.22 mmol) of **10** in 8 ml of tetrahydrofuran was added 1.45 ml (2.32 mmol) of 1.6 *M* *n*-butyllithium at −78° under argon. After the solution was stirred for 0.5 hr, 22.2 ml (4.44 mmol) of 0.2 *M* cadmium iodide in tetrahydrofuran was added, and the mixture was stirred for 0.5 hr at −78° and 45 min at −20°. Acetone (0.13 g, 2.22 mmol) was then added, and the reaction mixture was stirred for 1 hr at −78° and 3.5 hr at 0°. Half-saturated ammonium chloride solution (15 ml) was then added, the tetrahydrofuran was removed under reduced pressure, and the residue was extracted with methylene chloride. After the extracts were dried, the solvent was evaporated, leaving 0.588 g of red-yellow oil. A sample (0.2 g) of this oil was purified by preparative tlc (silica gel; chloroform–methanol, 9:1) to give 0.1 g of a clear oil whose nmr and ir spectra were identical with those of independently prepared **11**.

Reaction of the Magnesium Salt of 10 with Acetone.—To a stirred solution of 0.359 g (2.06 mmol) of **10** in 8 ml of tetrahydrofuran was added 1.35 ml (2.16 mmol) of 1.6 *M* *n*-butyllithium at −78° under argon. After 0.5 hr, 1.7 ml (4.33 mmol) of 2.6 *M* magnesium bromide etherate was added, and the resulting mixture was stirred for 15 min at −78° and 45 min at −20°. Acetone (0.120 g, 2.06 mmol) was then added, and the solution was stirred for 1 hr at −78° and 3.5 hr at −20°. Following addition of half-saturated ammonium chloride solution (15 ml), the tetrahydrofuran was evaporated, and the residue was extracted with methylene chloride. Drying and evaporation of the extracts led to recovery of 0.494 g of crude product. The nmr spectrum of this material showed it to be roughly a 3:1 mixture of **12** and **11**.

Recrystallization at −20° from pentane containing a trace of ether gave a white solid, mp 54–55°. The mother liquor was concentrated and cooled to yield additional material, mp 53.5–54.5°. The total recovery from both crops was 0.16 g.

Preparative tlc (silica gel; chloroform–methanol, 9:1) of 0.3 g of similarly prepared crude product gave 38 mg of oil, R_f 0.4, identified as **11** by ir and nmr, and 108 mg of white solid, R_f 0.6, mp 52–56°, identified as **12**: nmr (**12**) ($CDCl_3$), δ 1.25 (d, CCH_3, 6 H), 2.69 (d, J = 8 Hz) and 2.68 (d, J = 10 Hz, NCH_3, 12 H), 3.06 (d × d, J_{HH} = 13 Hz, J_{PH} = 10 Hz, PCH, 1 H), 4.9–6.2 (m, $CH{=}CH_2$ and OH, 4 H); ir $\lambda_{max}^{CHCl_3}$ 6.12, 10.0, 10.2, 10.82 μ.

Generation of the Sodio Derivative of 10. Reaction with Acetone.—A suspension of phenylsodium in toluene (2.486 g, 2.68 mmol) was added to a tared flask and mixed with 3 ml of dry *n*-pentane followed by 0.467 g (2.68 mmol) of **10** in 2 ml of *n*-pentane. The reaction mixture was stirred for 2 hr at 0°, after which 15 ml of tetrahydrofuran was introduced. The mixture was stirred for 15 min, and 0.4 ml (5.4 mmol) of acetone was added at 0°. After 10 min, ammonium chloride was added and the product was isolated in the usual fashion to yield 0.724 g of **11**.

Generation of the Lithio Derivative of 13. Reaction with Acetone.—To a stirred solution of 0.423 g (2.43 mmol) of **13** in 10 ml of tetrahydrofuran was added 1.6 ml (2.56 mmol) of 1.6 *M* *n*-butyllithium at −78° under argon. After 30 min, 0.35 ml (4.8 mmol) of acetone was added, and the solution was stirred an additional 15 min at −78° and 5 min at −20°. Water (0.2 ml) was added, followed by 100 ml of methylene chloride. The reaction mixture was filtered through a sintered-glass filter or glass wool plug, and the solution was dried over sodium sulfate and refiltered. Evaporation of the solvent yielded 0.565 g of a sticky yellow syrup, **14a** (this material contained a residual amount of methylene chloride which could not be removed without thermal decomposition of the adduct: nmr (**14a**) ($CDCl_3$), δ 1.22 (d, CCH_3, 6 H), 2.71 (d, J = 9.5 Hz), 2.66 (d, J = 9 Hz) (NCH_3), and 2.8–3.4 (m, NCH_2 and PCH) (total area 11 H), 4.8–6.0 (m, $CH{=}CH_2$ and OH, 4 H); ir $\lambda_{max}^{CHCl_3}$ 3.0, 6.15, 10.1, 10.9 μ.

Reaction of the Lithio Derivative of 13 with Methyl Ethyl Ketone.—To a stirred solution of 0.628 g (3.61 mmol) of **13** in 10 ml of tetrahydrofuran was added 2.4 ml (3.84 mmol) of 1.6 *M* *n*-butyllithium at −78° under argon. After 0.5 hr, 0.285 g (4.18 mmol) of methyl ethyl ketone was added. Water (0.2 ml) was added after an additional 10 min, and the solution was allowed to warm to room temperature, whereupon the reaction mixture was diluted with 100 ml of methylene chloride and filtered through a glass wool plug. The solution was dried over sodium

---

[10] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

sulfate and refiltered, and the solvent was evaporated under vacuum at room temperature to yield 0.816 g of a sticky yellow syrup containing some residual methylene chloride: nmr ($CDCl_3$) δ 0.7–2.0 (m, 8 H), 2.68 (d) and 2.74 (d, *J* = 9 Hz, NCH_3) superimposed on 2.5–2.9 (m, PCH) (total 7 H), 3.0–3.3 (m, NCH_2, 4 H), 4.8–6.0 (m, $CH{=}CH_2$ and OH, 4 H); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.95, 6.12, 10.10, 10.9 μ.

Reaction of the Lithio Derivative of 13 with Benzophenone.—To 2.24 mmol of the anion of **13**, generated in the manner described above, was added 0.425 g (2.34 mmol) of benzophenone. The solution was stirred for 15 min at −78° and 15 min at −20°. Water (0.2 ml) was added, followed by 100 ml of methylene chloride, and the product was isolated as above to yield 0.732 g of a crude solid, mp 134–137° (remains cloudy until *ca.* 150°). Two recrystallizations of 0.54 g of this solid from chloroform–hexane gave 0.29 g of **16c**: mp 157–157.5°; nmr ($CDCl_3$), δ 2.29 (d, *J* = 10 Hz, NCH_3, 6 H), 3.0 (m, NCH_2 and $=CCH_2$, 6 H), 4.12 (s, OH, 1 H), 5.39 (d × d, J_{HH} = 17 Hz, J_{PH} = 22 Hz, PCH, 1 H), 6.1–7.0 (m, =CH, 1 H), 7.3 (m, aromatic, 10 H); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.75, 10.25 μ.

Anal. Calcd for $C_{20}H_{25}N_2O_2P$: C, 67.40; H, 7.07; N, 7.86. Found: C, 67.57; H, 7.20; N, 7.78.

Reaction of the Lithio Derivative of 13 with Pinacolone.—To 2.03 mmol of the anion of **13**, generated in the manner described above, was added 0.220 g (2.20 mmol) of pinacolone. The solution was stirred for 10 min at −78°. Water (0.2 ml) was added and the solution was allowed to warm to room temperature. Addition of 100 ml of methylene chloride and isolation of the product as above gave 0.472 g of an oil which slowly crystallized. A portion of this solid (0.3 g) was twice recrystallized from ethyl acetate to yield 0.1 g of **16b**: mp 126–128°; nmr ($CDCl_3$), δ 0.97 (s, CCH_3, 9 H), 1.13 (s, CH_3, 3 H), 2.59 (d, *J* = 10 Hz, NCH_3) on 2.3–2.8 (m, $=CCH_2$ and OH) (total 9 H), 2.9–3.4 (m, NCH_2, 4 H), 5.52 (d × d, J_{HH} = 17 Hz, J_{PH} = 22 Hz, PCH, 1 H), 6.3–7.3 (m, =CH, 1 H); ir $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.95, 6.15, 10.15 μ.

Anal. Calcd for $C_{13}H_{27}N_2O_2P$: C, 56.90; H, 9.92; N, 10.21. Found: C, 56.61; H, 9.94; N, 10.16.

Generation of 4-Methyl-1,3-pentadiene from 12.—A dry flask containing 0.111 g (0.84 mmol) of **12** was heated to 110° and the volatile products swept with argon (flow rate, 100 ml/min) into a trap held at −78°. Within 0.5 hr gas began to evolve from the melt. The thermolysis was allowed to continue overnight (16 hr). At the conclusion of the reaction the trap contained 20 mg (50%) of a clear liquid contaminated with *ca.* 1 mg of water. The infrared spectrum and vpc retention time (10-ft 10% TCEP on Chromosorb P, 50°) of the product were identical with those of an authentic sample of 4-methyl-1,3-pentadiene.

Formation of 1,1-Disubstituted 1,3-Butadienes by Thermolysis of Allyldiazaphospholidine Adducts. General Procedure Illustrated by Generation of 4-Methyl-1,3-pentadiene from 14a.—A suspension of 0.123 g (0.53 mmol) of **14a** (containing some methylene chloride) in 1 ml of Nujol along with 100 mg of anhydrous calcium carbonate was degassed and then heated to 110–120° for 4 hr under vacuum, the volatile products being condensed in a trap held at −196°. At the conclusion of the reaction the trapped material was distilled into a tared flask to yield 43 mg of liquid. Vpc analysis (10-ft 10% TCEP on Chromosorb, 50°) showed the product to be a mixture of 4-methyl-1,3-pentadiene and methylene chloride, the former in 75% yield. Comparison of the infrared spectrum of the product with that of an authentic sample confirmed the identification of the diene.

Generation of *cis*-and *trans*-4-Methyl-1,3-hexadiene from 14b.—A suspension of 0.389 g (1.58 mmol) of **14b** (containing some methylene chloride) in 0.5 ml of Nujol along with 0.4 g of anhydrous calcium carbonate was degassed and then heated to 133° for 2 hr under vacuum, the volatile products being collected in a trap held at −196°. At the conclusion of the reaction the trapped material was distilled into a tared flask to yield 0.175 g of liquid. Vpc analysis (10-ft 10% TCEP on Chromosorb P, 60°) showed the presence of two components in addition to methylene chloride: **9a** (retention time 7.9 min, relative area 3) and **9b** (retention time 8.9 min, relative area 5). Correcting for methylene chloride in the starting material and product, the over-all yield of diene was 90%. **9a** and **9b** were separated by preparative vpc (16 ft × 0.375 in. 15% β,β′-oxydipropionitrile on 60–80 kg, 70°). The spectra of **9a** follow: nmr (CCl_4), δ 0.97 (t, *J* = 7.5 Hz, CH_3, 3 H), 1.72 (s, $=CCH_3$, 3H), 2.12 (q, *J* = 7.5 Hz, CH_2, 2 H), 4.7–6.7 (m, vinyl, 4 H); ir $\lambda_{\max}^{\mathrm{CCl_4}}$ 6.1, 6.25, 10.15 μ; mass spectrum, *m/e* 96, 81, 55, 53, 44, 41, 39. The spectra of **9b** follow: nmr (CCl_4), δ 0.95 (t, *J* = 7 Hz, CH_3, 3 H), 1.65 (s, $=CCH_3$, 3 H), 1.98 (q, *J* = 7 Hz, CH_2, 2 H), 4.6–5.1 (m, vinyl, 2 H), 5.5–5.8 (m, vinyl, 1 H), 6.1–6.8 (m, vinyl, 1 H); ir $\lambda_{\max}^{\mathrm{CCl_4}}$ 6.03, 6.24, 10.13, 11.1 μ; mass spectrum, *m/e* 96, 81, 55, 53, 44, 41, 39.

***cis*-4-Methyl-1,3-hexadiene from *cis*-4-Methyl-3-hexenyl Tosylate.**—To 0.150 g (1.1 mmol) of 80% potassium *t*-butoxide in dry hexamethylphosphoramide was added 0.229 g (0.88 mmol) of *cis*-4-methyl-3-hexenyl tosylate (**15**)[11] with stirring at 0°. The solution instantly turned deep green. After 1 hr at 0° the system was evacuated and the volatile products were collected in a trap held at −196°, then distilled into a tared flask to give 31 mg of liquid which was shown by nmr and vpc analysis on two columns to be identical with compound **9a** obtained from the thermal decomposition of **14b**.

Generation of 5,5-Dimethyl-1,3-hexadiene from 14c.[12]—A sample of the crude **14c–16a** mixture was heated for 2 hr at 105° in mineral oil in the presence of $CaCO_3$ and the volatile products were isolated in the usual fashion. The yield of diene, after correction for **16a** in the initial adduct mixture, was 50%: nmr (CCl_4), δ 1.04 (s, CH_3, 9 H), 4.7–5.3 (m, vinyl, 3 H), 5.6–5.9 (m, vinyl, 2 H); ir $\lambda_{\max}^{\mathrm{CCl_4}}$ 6.05, 6.24, 10.49 μ.

Generation of Allylidene cyclohexane from 14e.[13]—Thermolysis of **14e** in the usual manner led to isolation of allylidenecyclohexane in 80% yield: nmr (CCl_4), δ 1.6 (m, 6 H), 1.9–2.35 (m, allyl, 4 H), 4.7–5.2 (m, vinyl, 2 H), 5.55–5.85 (m, vinyl, 1 H), 6.2–6.7 (m, vinyl, 1 H); ir $\lambda_{\max}^{\mathrm{CCl_4}}$ 6.03, 6.24 μ.

Generation of 1-Phenyl-1,3-butadiene from 14d.[14]—Benzene (4 ml) containing 0.321 g (1.15 mmol) of **14d** and 1 ml of triethylamine was stirred and refluxed for 3 hr. At the completion of the reaction, pentane was added, and the solvent was evaporated. The residue was washed with additional pentane and filtered to remove the ammonium phosphodiamidate salts, and the solvent was re-evaporated. Bulb-to-bulb distillation, employing anhydrous potassium carbonate to suppress polymerization, gave 1-phenyl-1,3-butadiene as a clear liquid (89 mg, 60%): nmr (CCl_4), δ 4.9–5.5 (m, vinyl 2 H), 6.1–6.7 (m, vinyl, 3 H), 7.0–7.35 (m, aromatic, 5 H); ir $\lambda_{\max}^{\mathrm{neat}}$ 6.11, 6.24, 10.56 μ.

Attempted Thermolysis of 16c.—A benzene or toluene solution of **16c** was refluxed in the presence of silica gel. Filtration and washing of the silica gel with methylene chloride led to recovery of unchanged starting material.

Registry No.—**6**, 20628-39-1; **7**, 20628-40-4; **8**, 20628-82-4; **9a**, 20628-83-5; **9b**, 20628-84-6; **10**, 17070-81-4; **11**, 20628-88-0; **12**, 20628-89-1; **13**, 20628-90-4; **14a**, 20628-91-5; **16b**, 20628-92-8; **16c**, 20628-93-7; bis(dimethylamino)phosphorous acid, 5843-26-5; 5,5-dimethyl-1,3-hexadiene, 1515-79-3; allylidenecyclohexane, 5664-10-8; 1-phenyl-1,3-butadiene, 1515-78-2.

Acknowledgment.—We are grateful to the National Science Foundation and the National Institutes of Health for financial assistance.

---

[11] E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, **90**, 5618 (1968).

[12] *Cf.* F. Bohlmann, *Chem. Ber.*, **86**, 657 (1953).

[13] *Cf.* H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1462 (1940).

[14] *Cf.* O. Grummitt and E. I. Becker, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 771; O. Grummitt and F. J. Christoph, *J. Amer. Chem. Soc.*, **71**, 4157 (1949).