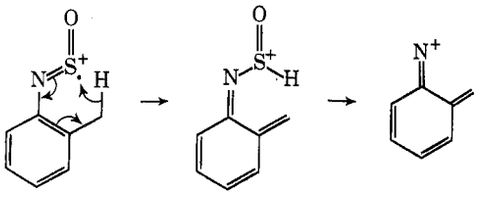
In view of the observed McLafferty rearrangement, the loss of the elements HS=O from 2-methylsulfinylaniline may be reinterpreted in terms of trans isomer (eq 1).



(1)

Although the molecular ions were in extremely small abundance, the nmr spectra and elemental analyses provide convincing evidence that the sulfinylamines are pure. The nmr spectrum of *N*-2,2-dimethyl-1-propylsulfinylamine showed a singlet resonance at δ 3.8 ppm for the methylene protons on carbon adjacent to nitrogen. This signal did not split or broaden at $-100°$, so that if rapid interconversion between trans and cis isomers is occurring at room temperature it should be slowed sufficiently at $-100°$ to observe two signals unless the cis isomer is a maximum on the rotational potential surface or is much less stable than the trans isomer. Also, *N*-2-methyl-2-propylsulfinylamine has a singlet proton resonance at δ 1.50 ppm which does not change at $-100°$.

Experimental Section

All mass spectra were measured with a Hitachi Perkin-Elmer RMU-6 mass spectrometer operating at 70 eV and with the inlet system at 200°. All nmr spectra were measured with a Jeolco C-60H spectrometer with TMS as the internal reference (δ = 0.00 ppm). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Procedure. Synthesis of Sulfinyl Amines.— Sulfinyl amines were prepared by the method described by Michaelis and Stornbeck[5] by adding thionyl chloride (0.095 mol in 75 ml of ether) to the appropriate alkyl amine (0.29 mol in 100 ml of ether) maintained at 0° for 1 hr. The ether was filtered and then removed by distillation at atmospheric pressure. The remaining residue is placed on a high vacuum line (10^{-5} mm) and fractionated through three traps maintained at $-45°$ (chlorobenzene slush), $-77°$ (Dry Ice–acetone), and $-196°$ (liquid N_2). Pure sulfinyl amine was obtained from the $-45°$ trap by distilling into bulbs fitted with a stopcock for all mass spectral samples, into nmr tubes which were sealed off under vacuum, and into 3-mm tubing sealed under vacuum for all analytically pure samples. A satisfactory analysis could not be obtained for *N*-3-methyl-1-butylsulfinylamine because this compound suffers a mysterious decomposition at room temperature within 0.5 hr, turning yellow and finally solid after a couple of days.

N-1-**Butylsulfinylamine**[6] had mass spectrum (70 eV) *m/e* (rel intensity) 77 (89), 76 (14), 75 (11), 71 (14), 70 (54), 55 (11), 50 (13), 43 (100), 42 (16), 41 (86), 39 (23), 30 (13), 29 (35), 27 (65).

N-2-**Butylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 104 (5), 91 (58), 90 (100), 89 (17), 71 (28), 70 (11), 63 (14), 60 (20), 57 (15), 56 (35), 55 (11), 44 (53), 43 (49), 42 (71), 41 (44), 39 (17), 29 (61), 27 (54); nmr δ (multiplicity) 0.90 (3 H, t, J = 7.0 Hz), 1.33 (3 H, d, J = 7.0 Hz), 1.50 (2 H, q, J = 7.0 Hz), and 4.73 (1 H, sextet, J = 7.0 Hz).

Anal. Calcd for C_4H_9NSO: C, 40.31; H, 7.61; N, 11.76; S, 26.90. Found: C, 40.43; H, 7.68; N, 11.47; S, 26.77.

N-2-**Methyl-2-propylsulfinylamine**[7] had mass spectrum (70 eV) *m/e* (rel intensity) 104 (100), 74 (12), 57 (49), 56 (19), 42 (17), 41 (60), 39 (15), 29 (22), 27 (13); nmr δ (multiplicity) 1.50 (9 H, s).

N-2-**Pentylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 91 (78), 90 (34), 89 (14), 70 (34), 56 (11), 55 (19), 43 (100), 42 (53), 41 (55), 39 (24), 29 (20), 27 (47); nmr δ (multiplicity) 0.90 (3 H, t, J = 7.0 Hz), 1.00 (2 H, q, J = 7.0 Hz), 1.22 (3 H, d, J = 7.0 Hz), 1.47 (2 H, q, J = 7.0 Hz), 4.83 (1 H, sextet, J = 7.0 Hz).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.51; S, 24.07. Found: C, 45.30; H, 8.43; N, 10.33; S, 23.90.

N-3-**Methyl-1-butylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 85 (17), 84 (24), 77 (74), 76 (19), 69 (16), 57 (63), 55 (36), 43 (80), 42 (26), 41 (100), 39 (33), 30 (16), 39 (70), 27 (40); nmr δ (multiplicity) 0.93 (6 H, d, J = 6.0 Hz), 1.57 (3 H, m), and 3.97 (2 H, t, J = 7.0 Hz). A satisfactory analysis was not obtained.

N-1,1-**Dimethyl-1-propylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 104 (100), 74 (17), 71 (13), 56 (12), 55 (20), 43 (29), 42 (34), 41 (34), 40 (17), 39 (15), 31 (10), 29 (14), 27 (46); nmr δ (multiplicity) 0.93 (3 H, t, J = 7.0 Hz), 1.47 (3 H, s), and 1.73 (2 H, q, J = 7.0 Hz).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.15; S, 24.07. Found: C, 44.95; H, 8.40; N, 10.37; S, 23.85.

N-2,2-**Dimethyl-1-propylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 118 (3), 77 (4), 76 (3), 57 (100), 55 (13), 41 (47), 39 (14), 29 (35), 27 (12); nmr δ (multiplicity) 1.00 (9 H, s), 3,80 (2 H, s).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.51; S, 24.07. Found: C, 45.25; H, 8.42; N, 10.39; S, 24.01.

Registry No.—*N*-1-Butylsulfinylamine, 13165-70-3; *N*-2-butylsulfinylamine, 13165-71-4; *N*-2-methyl-2-propylsulfinylamine, 38662-39-4; *N*-2-pentylsulfinylamine, 38662-35-0; *N*-3-methyl-1-butylsulfinylamine, 38662-36-1; *N*-1,1-dimethyl-1-propylsulfinylamine, 38662-37-2; *N*-2,2-dimethyl-1-propylsulfinylamine, 38662-38-3.

Acknowledgments.—We wish to thank the Miami University Faculty Research Committe for support and for a Summer Faculty Research Fellowship to J. R. G.

(5) A. Michaelis and O. Stornbeck, *Justus Liebigs Ann. Chem.*, **274**, 190 (1893).

(6) D. Klamann, C. Sass, and M. Zelenka, *Ber.*, **92**, 1910 (1959).

(7) W. T. Smith, P. A. Thio, and M. Grasley, *J. Org. Chem.*, **27**, 692 (1962).

Studies in the 1,4-Diphosphoniacyclohexadiene System. New Organophosphorus Heterocycles[1]

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Received September 8, 1972

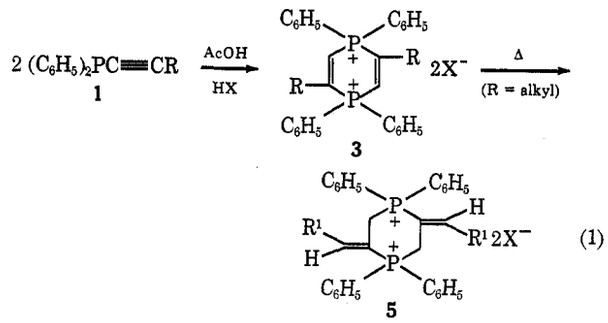
Some years ago it was found that alkynyl-1-phosphines **1** and **2** on treatment with HBr (or HCl) in glacial acetic acid produce the endocyclic dienes **3** and **4**, respectively (eq 1 and 2).[2-4] The endocyclic dienes **3** (R = primary or secondary alkyl) were found to readily isomerize on heating to the exocyclic dienes **5**;[3] however, unlike the P-phenylated dienes **3**, the P-alkylated dienes **4** failed to thermally isomerize to the corresponding P-alkylated exocyclic dienes **6** (eq 1 and 2).[4]

(1) Abstracted in part from the Ph.D. Dissertation of M. S. Chattha, Tulane University, New Orleans, La., 1971.

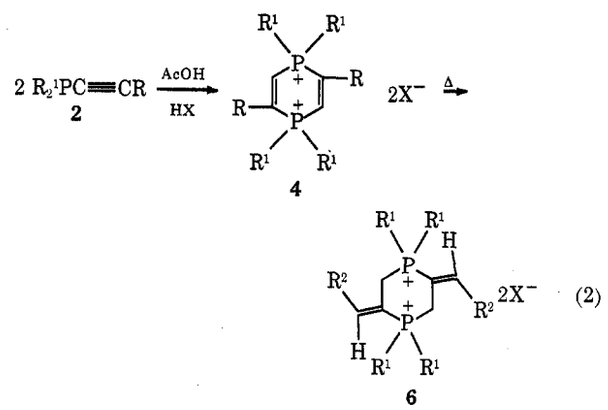
(2) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *J. Amer. Chem. Soc.*, **89**, 3067 (1967).

(3) A. M. Aguiar, G. W. Prejean, J. R. S. Irelan, and C. J. Morrow, *J. Org. Chem.*, **34**, 4024 (1969).

(4) A. M. Aguiar, J. R. S. Irelan, G. W. Prejean, J. P. John, and C. J. Morrow, *ibid.*, **34**, 2681 (1969).



R = alkyl, phenyl; X = Cl, Br; R^1 = alkyl, H

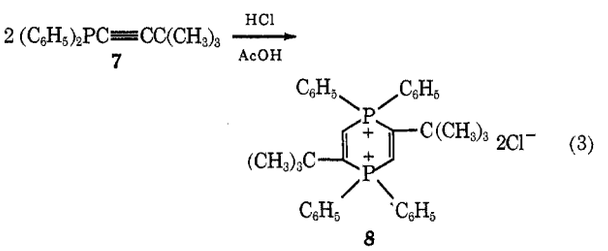


R = alkyl, phenyl; R^1 = alkyl; X = Br, Cl

However, the ^{31}P nmr spectra of the endocyclic dienes **4** displayed negative chemical shifts (relative to 85% phosphoric acid) similar to those of the exocyclic dienes **5**.

In order to study the effects exerted by various groups on phosphorus on the chemical shifts in the ^{31}P nmr spectra, and also on the amount of bond isomerization in the ring system, it was decided to synthesize a 1,4-diphosphoniacyclohexadiene system having an alkyl and a phenyl group on each phosphorus atom. Secondly, it was thought desirable to synthesize an endocyclic diene **3** with *tert*-butyl groups in the 2 and 5 positions; this compound would not isomerize to the exocyclic form and hence should permit us to investigate the effects exerted on the ^{31}P chemical shifts of the dienes **3** by the alkyl groups in the 2 and 5 positions.

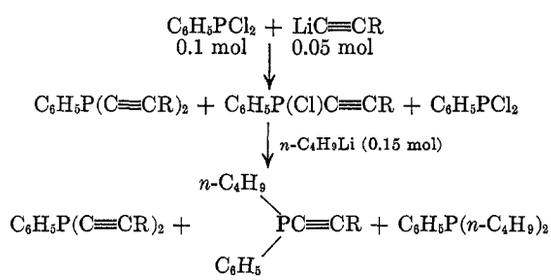
In order to synthesize a diene having *tert*-butyl groups at the 2 and 5 positions, the precursor, diphenyl-3,3-dimethylbutynylphosphine (**7**), was prepared by the reaction of diphenylphosphinous chloride with 3,3-dimethylbutynyllithium. Compound **7**, on treatment with HCl in glacial acetic acid, produced 1,1,4,4-tetraphenyl-1,4-diphosphonia-2,5-di-*tert*-butylcyclohexadiene 2,5-dichloride (**8**) in 70% yield (eq 3).



The ir spectrum (KBr) of **8** showed significant absorption bands at 6.12 (C=C) and 6.95 μ (PC_6H_5) and the nmr spectrum in trifluoroacetic acid (TFA) exhibited, in addition to the peaks corresponding to the phenyl and alkyl protons, a "pseudotriplet" (J = 28 Hz) at δ 8.46. This feature of the nmr spectrum seems to be very characteristic for these endocyclic dienes.[2-4] The structure of **8** was confirmed by the elemental analysis of its dipicrate.

To extend the investigation to the 1,4-diphosphoniacyclohexadiene system having an alkyl and a phenyl group on each phosphorus atom, alkyl phenyl alkynyl-1-phosphines **9** were needed as precursors. The alkynyl-1-phosphines **9** constitute a new class of unsaturated phosphorus compounds which have not yet been described. The phosphines **9** were prepared starting from phenylphosphonous dichloride and lithium alkynylides as shown in Scheme I.

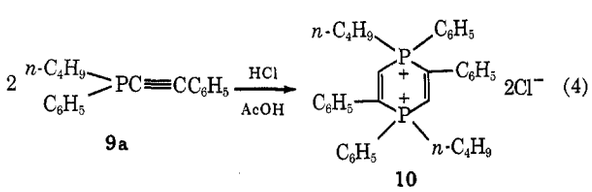
SCHEME I



a, R = C_6H_5; b, R = n-C_3H_7; c, R = n-C_4H_9

The usual work-up[3] and fractional distillation under reduced pressure afforded **9a-c** in 52-61% yield.

Treatment of **9a** with HCl in hot glacial acetic acid produced 1,4-di-*n*-butyl-1,2,4,5-tetraphenyl-1,4-diphosphoniacyclohexadiene 2,5-dichloride (**10**) in 41% yield (eq 4).

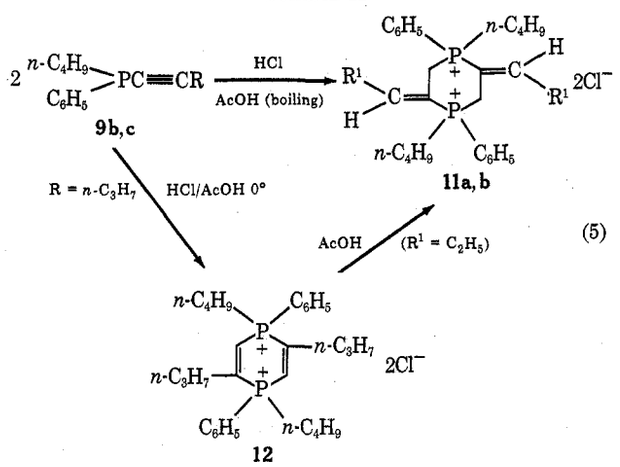


The ir and nmr spectra and the elemental analysis of the dipicrate of **10** supported its structure.

The phosphines **9b** and **9c**, when treated with HCl in hot glacial acetic acid, produced 1,4-di-*n*-butyl-1,4-diphenyl-1,4-diphosphonia-2,5-dialkylidenecyclohexane dichlorides (**11a** and **11b**, respectively, Scheme II). However, when **9b** was treated with HCl in glacial acetic acid at 0°, the endocyclic diene **12** was produced (Scheme II).

The ir spectra (KBr) of the dienes **11a,b** displayed strong absorption bands at 6.19 (C=C) and 6.95 μ (PC_6H_5) and the nmr spectra (TFA) of **11a,b** exhibited, in addition to other proton signals, a triplet (J = 13 Hz) at δ 4.25 and a doublet of two triplets (J_{PH} = 20, J_{HH} = 7 Hz) at 7.08. The triplet was assigned to the ring methylene protons, which are coupled to both the phosphorus atoms.[3] The signal centered at δ 7.08 is attributed to the olefinic protons, coupled to the vicinal chain methylene protons (J = 7 Hz).[3] The

SCHEME II



R = n-C_3H_7, n-C_4H_9; R^1 = C_2H_5, n-C_3H_7

stereochemistry of the butyl and phenyl groups on phosphorus in **10**, **11a**, and **11b** is not yet clear.

In order to demonstrate the thermal isomerization of the 1,4-diphosphoniacyclohexadienes, **12** was refluxed in acetic acid for 1 hr. The nmr spectra showed that **12** had completely isomerized to the corresponding exocyclic diene **11a** (R^1 = C_2H_5). At elevated temperatures the endocyclic dienes, having primary groups at the 2 and 5 positions, isomerize to the corresponding exocyclic dienes. It is also possible that at elevated temperatures, the P-phenylated alkynyl-1-phosphines rearrange to allene intermediates, which then cyclize to give the exocyclic isomers directly.

The only significant structural difference between the diphenylated exocyclic dienes **11a,b** and the tetraphenylated exocyclic dienes **5** is that the former compounds (**11a,b**) have one n-butyl and one phenyl group instead of two phenyl groups on each phosphorus atom. With this subtle difference, it seems reasonable to assume that the conformations of all these exocyclic dienes, in solution, are essentially the same. Based upon this assumption a comparison of ^{31}P chemical shifts of the diphenylated exocyclic dienes **11a,b** with those of tetraphenylated exocyclic dienes **5** (Table I) shows that

TABLE I

^{31}P CHEMICAL SHIFTS

Compd	Shift, ppm[a]
3 (R = C_6H_5)	+3.5[2]
10	−3.4
8	+3.7
5 (R^1 = n-C_5H_{11})	−17.0
11a	−23.2
11b	−23.3

[a] All the spectra were taken in methanol solution and the chemical shifts are relative to 85% phosphoric acid.

the phenyl groups on the phosphorus atoms exert a shielding effect on these atoms. Similarly, it may be assumed that the endocyclic diene **10** has the "boat" conformation like that of the endocyclic diene **3** (R = C_6H_5).[5] Again, the ^{31}P chemical shifts of these two endocyclic dienes, **3** (R = C_6H_5) and **10**, suggest that the phenyl groups on phosphorus atoms significantly shield these atoms. Further support for this is obtained from the fact that replacing a phenyl group by a n-butyl group on each phosphorus atom, in both the endocyclic and the exocyclic dienes, causes an essentially constant difference in the ^{31}P chemical shifts (Table I). The nature of this shielding is not yet well understood, but a possible explanation is a 2p–3d orbital overlap giving $p\pi$–$d\pi$ interaction; our current investigations are directed toward the understanding of these interactions.

(5) Dr. Louis Trefonas, Louisiana State University at New Orleans, private communication.

Experimental Section

General.—Reactions involving phosphines and organometallics were carried out under dry nitrogen. Diethyl ether was dried over sodium. Phenylphosphonous dichloride and diphenylphosphinous chloride were redistilled before use. Acetic acid was dried by addition of 50 ml of acetic anhydride to 1 gallon of reagent grade glacial acetic acid. Infrared spectra were taken with a Beckman IR-5A infrared spectrophotometer. Proton nuclear magnetic resonance spectra were taken with a Varian A-60 spectrometer. Melting points were determined in a Mel-Temp melting point apparatus and are uncorrected. All proton chemical shifts reported are in parts per million (δ) relative to an internal standard of tetramethylsilane.

Diphenyl 3,3-Dimethylbutynyl-1-phosphine (7).—This phosphine was prepared by the reaction of 3,3-dimethylbutynyllithium (0.05 mol) with diphenylphosphinous chloride (0.05 mol) in 250 ml of ether.[3] The usual work-up afforded the phosphine in 81% yield: bp 151–152° (0.2 mm); ir 4.6 μ (C≡C); nmr ($CDCl_3$) δ 7.85–7.18 (m, 10 H, phenyls), 1.32 (s, 9 H, *tert*-butyl group).

Anal. Calcd for $C_{18}H_{19}P$: C, 81.18; H, 7.19; P, 11.63. Found: C, 81.25; H, 7.07; P, 11.55.

Preparation of Phosphines 9a–c. General Procedure.—The alkyne (0.05 mol) was dissolved in 100 ml of ether under nitrogen and cooled with Dry Ice. A hexane solution of n-butyllithium (0.05 mol) was added slowly with continuous stirring. After 0.5 hr of stirring, this suspension of alkynyllithium was transferred to a dropping funnel with the help of a delivery tube under nitrogen pressure and then added dropwise to a Dry Ice cooled solution of 0.1 mol of phenylphosphonous dichloride in 100 ml of ether in a 500-ml three-necked flask. The reaction mixture was stirred for 45 min and then 0.15 mol of n-butyllithium solution in hexane was added slowly with Dry Ice cooling and continuous stirring. The reaction mixture was stirred for an additional 15 min and then 100 ml of saturated ammonium chloride solution was slowly added and the reaction mixture was stirred well. With the help of a bent tube under nitrogen pressure, the contents of the reaction vessel were transferred to a separatory funnel and the layers were separated. The organic layer was dried (Na_2SO_4), filtered, and fractionally distilled under reduced pressure. The second fraction was the desired product in each case.

n-Butylphenylphenylethynylphosphine (9a) had bp 170° (0.07 mm); yield 53%; ir ($CHCl_3$) 4.61 μ (C≡C); nmr ($CDCl_3$) δ 7.90–7.15 (m, 10 H, phenyl), 2.1–1.15 (m, 6 H, methylenes), 0.85 (t, J = 6.5 Hz, 3 H, methyl).

Anal. Calcd for $C_{18}H_{19}P$: C, 81.18; H, 7.19; P, 11.63. Found: C, 80.99; H, 7.11; P. 11.71.

n-Butylphenylpentynyl-1-phosphine (9b) had bp 143° (0.1 mm); yield 61%; ir ($CHCl_3$) 4.56 μ (C≡C); nmr ($CDCl_3$) δ 7.9–7.2 (m, 5 H, phenyl), 2.38 (close pair of t, J = 6.5 Hz, 2 H, C≡CCH_2), 1.85–1.25 (m, 8 H, methylenes), 1.02 (close pair of t, J = 6.9 Hz, 6 H, methyl).

n-Butylphenylhexynyl-1-phosphine (9c) had bp 159–160° (0.1 mm); yield 60%; ir ($CHCl_3$) 4.59 μ (C≡C); nmr ($CDCl_3$) 7.82–7.18 (m, 5 H) phenyl), 2.35 (close pair of t, 2 H, C≡CCH_2), 1.82–1.2 (m, 10 H, methylenes), 0.95 (crude pair of t, 6 H, methyl).

Anal. Calcd for $C_{16}H_{23}P$: C, 78.02; H, 9.41; P, 12.57. Found: C, 77.56; H, 9.38; P, 12.61.

Preparation of 8, 10, and 11a,b. General Procedure.—The alkynyl-1-phosphine (0.01 mol) was dissolved in 75 ml of acetic acid and a slow stream of HCl was passed through the solution for 1 hr. Owing to heat of solution of HCl, the reaction mixture started boiling. The reaction flask was cooled to room tempera-

ture, stoppered, and kept overnight. The acetic acid was distilled off under reduced pressure. The pale-white solid residue was washed twice with 25-ml portions of acetone and crystallized from mixed acetone–methanol solvent.

1,1,4,4-Tetraphenyl-2,5-di-*tert*-butyl-1,4-diphosphoniacyclohexadiene 2,5-dichloride (8) had mp 285–287°; yield 73%; ir (KBr) 6.12 (C=C), 6.95 μ (PC_6H_5); nmr (TFA) δ 8.45 (t, J = 28 Hz, 2 H, vinyl), 7.94 (m, 20 H, phenyl), 1.33 (s, 18 H, *tert*-butyl groups).

A methanol solution of **8** on treatment with a methanol solution of sodium picrate produced an orange, crystalline precipitate of dipicrate. The precipitate was recrystallized from methanol, mp 278–279°.

Anal. Calcd for $C_{48}H_{44}N_6O_{14}P_2$ (picrate): C, 57.60; H, 4.43; N, 8.40; P, 6.19. Found: C, 58.00; H, 4.54; N, 8.35; P, 5.96.

1,4-Di-*n*-butyl-1,2,4,5-tetraphenyl-1,4-diphosphoniacyclohexadiene 2,5-dichloride (10) had mp 257–259°; ir (KBr) 6.48 (C=C), 6.96 μ (PC_6H_5); nmr (TFA) 8.17 (t, J = 29 Hz, 2 H, vinyl), 7.21–8.65 (m, 20 H, phenyl), 3.11 (m, 4 H, PCH_2), 1.69 (m, 8 H, methylenes), 1.01 (t, J = 7 Hz, 6 H, methyl). The dipricrate of **10** was prepared as described under **8**, mp 265–267°.

Anal. Calcd for $C_{48}H_{44}N_6O_{14}P_2$: C, 57.60; H, 4.43; N, 8.40; P, 6.19. Found: C, 57.76; H, 54.2; N, 8.46; P, 6.33.

1,4-Di-*n*-butyl-1,4-diphenyl-1,4-diphosphonia-2,5-dipropylidenecyclohexane dichloride (11a) had mp 240–241°; yield 32%; ir 6.19 (C=C), 6.96 μ (PC_6H_5); nmr δ 7.10 (2 H, vinyl), 4.27 (t, J = 13 Hz, 4 H, ring methylenes), 3.02 (m, 4 H, PCH_2), 2.49 (d, J = 7 Hz, 4 H, allylic), 1.58 (m, 8 H methylenes), 1.22 (two t, J = 7.5 Hz, 12 H, methyl).

1,4-Di-*n*-butyl-1,4-diphenyl-1,4-diphosphonia-2,5-dibutylidenecyclohexane dichloride (11b) had mp 249–251°; yield 27%; ir 6.20 (C=C), 7.01 μ (PC_6H_5); nmr (TFA) δ 7.95 (m, 10 H, phenyl), 7.08 (crude d of t, J_{PH} = 20, J_{HH} = 7 Hz, 2 H, vinyl), 4.25 (t, J = 13 Hz), 4 H, ring methylenes), 2.98 (m, 4 H, PCH_2), 2.48 (d, J = 7 Hz, 4 H, allylic), 1.56 (m, 12 H, methylenes), 1.02 (12 H, methyls).

1,4-Di-*n*-butyl-1,4-diphenyl-2,5-di-*n*-propyl-1,4-diphosphoniacyclohexadiene 2,5-Dichloride (12).—*n*-Butylphenylpentynyl-1-phosphine (1.16 g, 0.005 mol) was dissolved in 25 ml of glacial acetic acid and cooled to 0°. A slow stream of HCl was passed through the solution for 1 hr with continuous stirring while the temperature was kept at 0°. The acetic acid was stripped off under reduced pressure at room temperature. The residue on trituration with acetone gave the desired product in 20% yield, melting at 229–235°. The ir spectrum (KBr) showed characteristic absorption bands of 6.21 (C=C) and 6.98 μ (PC_6H_5) and the nmr spectrum (AcOH) exhibited the characteristic pseudotriplet (J = 27 Hz) at δ 8.24 and all the other proton resonance signals also checked with the assigned structure. Similarly, the nmr spectrum in methanol was found to be in agreement with the structure. However, nmr spectrum in TFA showed that **12** had isomerized to **11a**. Also when **12** was refluxed with acetic acid for 1 hr, the nmr spectra in all the three solvents, AcOH, TFA, and methanol, showed that **12** had isomerized to the exocyclic form **11a**. Compounds described here are available from Strem Chemical Co., Danvers, Mass.

Registry No.—**7,** 33730-51-7; **8,** 38565-20-7; **8** dipicrate, 38565-21-8; **9a,** 38592-33-5; **9b,** 38565-22-9; **9c,** 38565-23-0; **10,** 38565-24-1; **10** dipicrate, 38565-25-2; **11a,** 38565-26-3; **11b,** 38565-27-4; **12,** 38565-28-5; 3,3-dimethylbutyryllithium, 37892-71-0; diphenylphosphinous chloride, 1079-66-9; phenylethyne, 536-74-3; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739. We also wish to thank Hoffmann-La Roche, Inc., Nutley, N. J., for their unrestricted grant which helped to complete the work.

The Reaction of Phenylphosphonic Dichloride with Dimethyl Sulfoxide[1]

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Received November 28, 1972

Dimethyl sulfoxide (DMSO) will convert chlorides of pentavalent phosphorus into their acids.[2] To date this reaction has been used only with monochlorides, but we find it to be a convenient method for the single-step conversion of phenylphosphonic dichloride (I) into methyl phenylphosphonate (II).

$$\underset{\text{I}}{\text{PhPOCl}_2} \xrightarrow[2.\ \text{MeOH}]{1.\ \text{DMSO}} \underset{\text{II}}{\text{PhPO(OH)OMe}}$$

Experimental Section

DMSO (2 g, 0.0256 mol) in CH_2Cl_2 (15 ml, dried over CaH_2) was added to stirred phenylphosphonic dichloride (5 g, 0.0256 mol) in dry CH_2Cl_2 (100 ml) during a period of 5 min. The reaction was followed by ir spectroscopy using matched NaCl cells and CH_2Cl_2 as a reference. After *ca.* 30 min, the absorptions at 1258 (P=O) and 1110 cm^{-1} (PPh) due to the phosphonic dichloride had reached a minimum and a new absorption at 1230 cm^{-1} (P=O) had reached a maximum. A fivefold excess of MeOH was then added and after several hours the solvent was removed on a rotary evaporator. The residue, dissolved in dry Me_2CO, was neutralized with cyclohexylamine (Congo Red). The cyclohexylammonium salts of II and phenylphosphonic acid precipitated. (A small amount of dimethyl phenylphosphonate remained in solution, and was identified by nmr.)

Cyclohexylammonium methyl phenylphosphonate (III) was extracted with hot Me_2CO, in which the salt of the diacid is insoluble. The cyclohexylammonium methyl phenylphosphonate (III) had mp 156–158° after recrystallization from Me_2CO, and the overall yield was 52%. *Anal.* Calcd: C, 57.5; H, 8.2; N, 5.2. Found: C, 57.4; H, 8.4; N, 5.0. It had a strong P=O stretch at 1188 cm^{-1}, and the barium salt had a P=O stretch at 1220 cm^{-1}. [That of barium phenylphosphonate is at 1258 cm^{-1}, and that of the free acid is at 1145 cm^{-1}, and the dichloride shows strong absorptions at 1258, 1110, and 580 cm^{-1} (PCl)]. The 60-MHz nmr spectrum of III (in D_2O, Varian T-60) had a multiplet (cyclohexyl) at δ 0.86–1.96 (10.9), a doublet (OMe) at 3.22 and 3.40 (J = 11 Hz, 3.0),[5] and a multiplet (phenyl) at 7.31–7.76 (5.2). The values in parentheses are peak areas. Dimethyl phenylphosphonate in $CDCl_3$ had a doublet (methoxy) at δ 3.69 and 3.87 (J = 11 Hz) and a multiplet (phenyl) at 7.41–8.08.

In an initial experiment the reaction mixture was left for 1 hr after addition of DMSO under N_2 and the yield of III was 40% after recrystallization, but only the salt of the diacid was isolated from an experiment using an twofold excess of DMSO.

Results

This reaction appears to provide a simple alternative to the usual method of dealkylation with halide ion for the preparation of monomethyl phosphates or

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(5) This $^{31}P-^{1}H$ coupling is typical of compounds of this general structure.[6]

(6) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **22**, 565 (1966).