5–7 h. The diluted mixture with water (120 ml) was extracted with *n*-hexane or ether (4 × 30 ml). The combined extracts were dried (Na_2SO_4) and evaporated to afford crude product which was purified by distillation under reduced pressure (Table II).

Method B. Instead of aqueous KOH in method A, powdered solid KOH was used. As an example, the reaction of butadiene is described. To a magnetically stirred and cooled (−78 °C) mixture of powdered KOH (85% purity, 4.20 g, 63.6 mmol), dicyclohexyl-18-crown-6 (0.27 g, 0.72 mmol), and butadiene (6.50 g, 120 mmol) was added **1a** (2.06 g, 20.0 mmol) slowly over 2 h under nitrogen. After stirring was continued for a further 15 h at the same temperature, the mixture was allowed to warm to room temperature in order to remove the excess butadiene and an oily residue was purified by distillation to afford **6** (1.40 g, 58.0%). Analytical and physical data of all new compounds are summarized in Tables II and III.

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Phosphonic Acid Chemistry. 1. Synthesis and Dienophilic Properties of Diethyl 2-Formylvinylphosphonate and Diethyl 2-Formylethynylphosphonate[1a,b]

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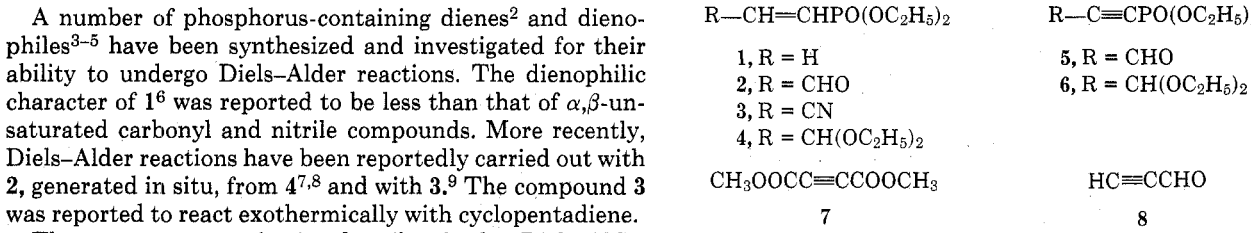
The synthesis of the title compounds, **5** and **11**, was accomplished from diethyl 3,3-diethoxy-1-propyn-1-ylphosphonate (**6**). A reported synthesis of diethyl 3,3-diethoxy-1-propen-1-ylphosphonate (**4**) from PCl_5 and ethyl allyl ether was investigated and found not to give **4** as claimed. The isomeric phosphonyl dichloride (**17**) and the isomeric vinylphosphonates, **18** and **19**, were obtained instead. The dienophiles, **5**, **11**, dimethyl acetylenedicarboxylate (**7**), and propiolaldehyde (**8**), were treated with isoprene and the order of reactivity for these dienophiles was found to be **5** > **7** > **11** > **8**. The resultant cycloadducts **21** and **23** were obtained in good yield and the structure of **23** was established unambiguously by conversion to the known xylenylphosphonic acid (**28**). This latter compound and its isomer (**30**) were prepared using photochemical Arbuzov reaction methods. The increased dienophilic reactivity of **5** and **11** as compared to **7** and **8**, respectively, was in accord with published data that the diethyl phosphonyl group exerts an activating effect on the dienophilic character of an olefin.

A number of phosphorus-containing dienes[2] and dienophiles[3–5] have been synthesized and investigated for their ability to undergo Diels–Alder reactions. The dienophilic character of **1**[6] was reported to be less than that of α,β-unsaturated carbonyl and nitrile compounds. More recently, Diels–Alder reactions have been reportedly carried out with **2**, generated in situ, from **4**[7,8] and with **3**.[9] The compound **3** was reported to react exothermically with cyclopentadiene.

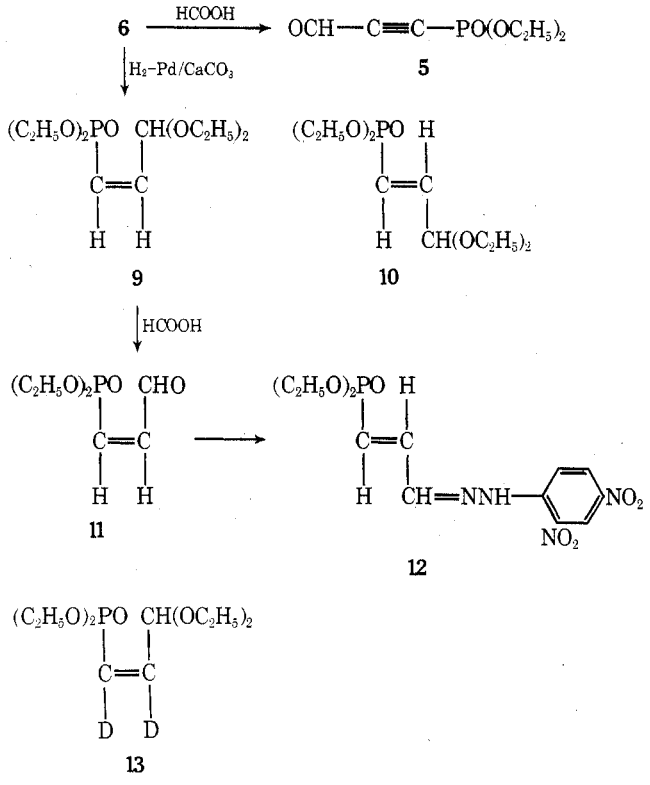
The present communication describes further Diels–Alder studies, involving the dienophiles **5** and **11** (the pure cis isomer of **2**) and their synthesis from **6**. The dienophile **5** is shown to be more reactive toward isoprene than **11**, **7**, and **8**. The communication also presents evidence that the reported synthesis of **4**, which was used to generate **2**, in situ, for Diels–Alder reactions was in error. Compounds **11** and **5** were of interest because of their potential usefulness in the preparation of new and novel alicyclic analogues of pyridoxal phosphate.[1a]



Synthesis. The synthesis of **5** was done from **6**, whose preparation has been described.[1a] The acetal **6** was hydrolyzed with 97% HCOOH to give **5** in quantitative yield. The compound was isolated by fractional distillation and proved to be a stable, colorless liquid which when stored for several months at 0 °C under N_2 showed no decomposition.

The synthesis of **11** was done from **6** also. Catalytic hydrogenation of **6** using 5% $Pd/CaCO_3$, poisoned with quinoline, gave a mixture of acetals **9** and **10**, from which the cis isomer

Chart I



9 was isolated by distillation in 60% yield. Formolysis of pure 9 using 97% HCOOH gave a mixture of cis and trans aldehydes from which *cis*-11 was isolated in 60% yield by distillation. Compound 11 was characterized by ir and NMR, elemental analysis, and by its conversion to a *trans*-dinitrophenylhydrazone (DNPH) 12.

GLC analysis of the reduction reaction mixture, obtained by the reduction of 6 in C_5H_5N solution with 10% $Pd/CaCO_3$, revealed the presence of 6, 9, and 10 in 20, 70, and 8.3% yields, respectively. These GLC results were confirmed by the TLC isolation of 6, 9, and 10 in 19, 55, and 8% yields, respectively. The structure of the isomeric trans acetal 10 was established by ir and NMR and was supported by synthesis from pure 9. Formolysis of 9 gave crude 11, which when refluxed with C_2H_5OH, $CH(OC_2H_5)_3$, and HCOOH gave 9 and 10 in 13 and 23% yields, respectively. These compounds were isolated by TLC and exhibited ir and NMR spectra the same as those of 9 and 10 obtained from reduction of 6.

The deuterated acetal 13 was prepared by hydrogenation of 6 with deuterium. The compound was isolated in the same manner as was 9 and had the same TLC mobility as 9. The mass spectrum of 13 showed no molecular ion, but the mass fragmentation pattern was similar to that of 9 and was consistently 2 mass units higher than that for 9.

The stereochemistry of 9–13 was established by NMR. The chemical shift and proton coupling constants for 9–13 are summarized in Table I. The *cis*-vinylphosphonate geometry was assigned 9 because of the larger coupling constant, J_{bx} = 50 Hz, that was observed for this compound as compared to that found in 10 (J_{bx} = 21 Hz). This result is in accord with published findings[10-12] that *cis*-vinylphosphonates have larger coupling constants (J_{bx} = 30–50 Hz) than do *trans*-vinylphosphonates (J_{bx} = 10–30 Hz). The stereochemical assignment of a cis geometry to 9 and a trans geometry to 10 was also supported by chemical shift data of the acetal *methine* protons of 9, 10, and 13. These protons were considerably more deshielded in 9 and 13 (by 1.22 and 1.1 ppm) than the acetal methine proton found in 10. The γ protons in cis olefins are known[13,14] to resonate at lower field than the corresponding ones in the trans isomer.

The crude formolysis product 11 was found to show two NMR aldehyde absorptions, one at 9.33 ppm (d), the other at 11.1 ppm (d) in the ratio of 1:9. The lower field absorption was attributed to *cis*-11. The coupling constants obtained for 12 were consistent with a trans geometry for the compound, indicating that an isomerization of the double bond had occurred during hydrazone formation.

Reaction of PCl_5 with 14 and 20. During the preparation of 9, the reported[7,8] synthesis of 4 of unspecified geometry was repeated to better establish the structure of 9 and 10. The synthesis was found to give products completely different from those claimed.[7,8] Thus 14 reacted with PCl_5 to give a

Chart II

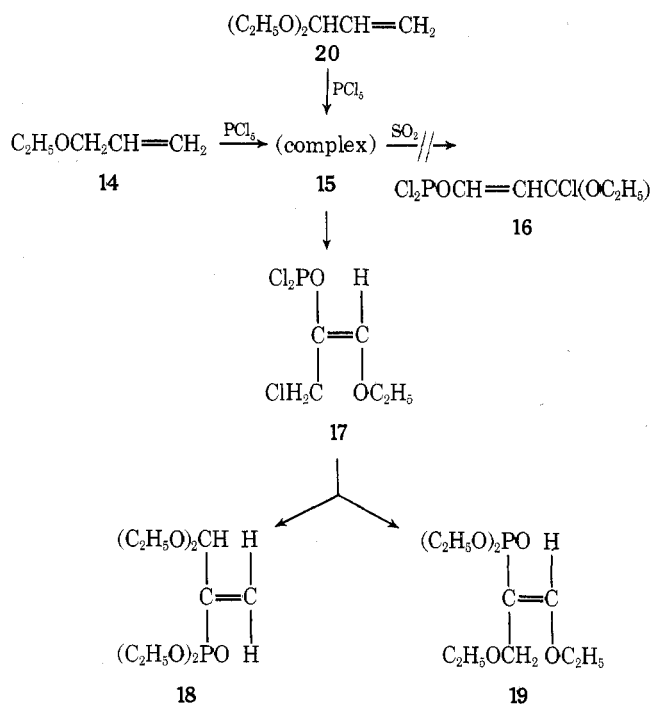


Table I. Chemical Shifts and Coupling Constants of Vinyl and α-Methine Protons of 9, 10, 11, 12, and 13

$CH_c—CH_b=CH_a—P_x$

Compd (solvent)	Chemical shifts, ppm			Coupling constants, Hz					
	a	b	c	ab	ac	bc	ax	bx	cx
9 ($CDCl_3$)	5.90	6.57	5.93	13	~1	7.5	18	50	~2.5
(C_6D_6)	5.68	6.53	6.30						
10 ($CDCl_3$)	6.20	6.80	5.13	18	~1	3.5	21	21.5	Not detn
(C_6D_6)	6.23	6.85	5.08						
13 (C_6D_6)			6.18						
11 (C_6D_6)	6.27	6.29	11.10	13		7	11	52	
12 ($CDCl_3$)	7.36	6.16	7.83	16.8		8.8	20.5	17.2	Not detn

Table II. NMR Chemical Shifts and Coupling Constants for 17, 18, and 19

Compd	Solvent C_6D_6	Solvent $CDCl_3$	
17[a]	0.73	1.43	t, J = 7 Hz, CH_3
	3.33	4.33	q, J = 7 Hz, CH_2O
	4.02	4.33	d, J = 27 Hz, CH_2Cl
	7.12	7.46	d, J = 10 Hz, CH=C
18	1.13	1.25	t, J = 7 Hz, CH_3
		1.35	t, J = 7 Hz, CH_3
	3.52	3.63	AB q, J = 7 Hz, CH_2O
	4.05	4.15	2 q, J = 7, 8 Hz, CH_2OP
	5.32	5.13	m, J = 0.6, 0.8, 4 Hz, CH
	6.30	6.24	2 m, J = 0.8, 2.4, 22 Hz, CH=C
	6.35	6.28	2 m, J = 0.6, 2.4, 43 Hz, CH=C
19	0.85		3 t, J = 7 Hz, CH_3
	1.07		
	1.20		
	3.44		q, J = 7 Hz, CH_2O
	4.08		2 q, J = 7, 8 Hz, CH_2OP
	4.28		d, J = 18 Hz, CH_2O
	7.28		d, J = 10 Hz, CH=C

[a] The reported spectrum[15] run on a 40-MHz Ya MR-5535 spectrophotometer was listed as 1.35 (t), 4.00 (q), 3.91 (d, J = 23 Hz), and 6.85 ppm (d, J = 12 Hz). No solvent was indicated.

Table III. Diels–Alder Reaction of Isoprene with Various Dienophiles

Compd	Percentage yields: Neat[a]	0.5 M benzene[b] solution	Reported
5	c	62	86
7	58	12	90[d]
8	63	2[e]	76[f]
11	55	7 (61[g])	86[h]

[a] No solvent, allowed to react for 70 h at room temperature. [b] Both reactants were present in 0.5 M concentrations in the reaction solution and were allowed to react under nitrogen for 70 h at room temperature. [c] Reaction was too violently exothermic and caused the carbonization of the reaction contents when reactants were mixed neat at room temperature. [d] Reported by V. F. Kucheron and N. Ya. Grigor'eva;[22] obtained by heating 7 with isoprene in benzene solution, 4 h at 130–140 °C. [e] The 2% yield represents the residue after removal of the volatiles which by NMR was predominantly the cycloadduct. [f] Reported by Petrov and Sopov;[23] obtained by heating 8 for 5 h at 110 °C in a bomb in toluene. [g] The yield obtained by heating 11 with isoprene in benzene solution in a Parr bomb for 19 h at 100 °C. [h] Reported by Tsivunin et al.;[7] obtained by heating 4, water, concentrated HCl, and isoprene at 100 °C for 10 h.

complex (**15**) which precipitated from solution. However, treatment of this complex **15** with SO_2 gave a product in the reported yield which (vide infra) was **17** and not **16** as claimed.[7] The ir spectrum of **17** was remarkably similar to that published for **16**. The published spectrum differed from that observed for **17** only in the presence of an additional ir absorption at 13.3 μ. The product **17** was treated with NaOEt in Et_2O in the manner described for the synthesis of **4** to give two vinylphosphonates (proved to be **18** and **19**) in 8.5 and 34.5% yields, respectively, and no **4**. The compound **17** was known[15] and the reported synthesis of **17** from **20** and PCl_5 was also repeated so that the structure of **17** could be established in a definative manner. Acreolin diethyl acetal (**20**) was found to react with PCl_5 to give **17** which was the same as **17** obtained above from **14** and PCl_5 (as judged by ir and NMR).

The NMR spectra of **17, 18,** and **19** are presented in Table II. The reported NMR spectrum of **17** was found to be at variance with that observed by the present authors. Differences in the chemical shift and coupling constants were observed. Although the chemical shift differences can probably be attributed to solvent effects (present spectra were run in C_6D_6 and $CDCl_3$ while the reported spectrum appears to have been run neat since no solvent was specified), the differences in the coupling constants (especially the vinyl proton one) are more difficultly explainable and may be due to experimental error (published spectrum run on a 40-MHz spectrophotometer).[15]

The NMR spectra listed in Table II for **17, 18,** and **19** are in complete accord with the structures assigned these compounds. The cis stereochemistry of the vinyl proton–phosphorus atom assigned **17** and **19** is supported by the small vinyl proton–phosphorus coupling constant ($^3J_{PH}$ = 10 Hz). A trans stereochemistry would require a larger coupling constant ($^3J_{PH}$ = 30–50 Hz).[10-12] The presence of two vinyl proton–phosphorus coupling constants in **18**, one large ($^3J_{PH}$ = 43 Hz), the other small ($^3J_{PH}$ = 22 Hz), is consistent with the vinyl methylene structure assigned this compound. Spin decoupling (irradiation of the acetal methine proton) was used to determine the vinyl proton coupling constant ($^2J_{HH}$ = 2.4 Hz) and to provide proof that the smaller coupling constants ($^4J_{HH}$ = 0.6 and 0.8 Hz) were due to allylic coupling with the acetal methine proton. The allyl proton–phosphorus coupling constants ($^3J_{PH}$ = 27 and 18 Hz in **17** and **19**, respectively) are in the expected range[10,16] and also support the structural assignments of **17** and **19**. The unusually small acetal methine–phosphorus proton coupling constant ($^3J_{PH}$ = 4 Hz) in **18** is due to stereochemistry. The coupling constant ($^3J_{PH}$) has been reported[10,16] to vary as a function of the dihedral angle ϕ (the angle formed by the intersection of the planes $H_{acetal}C_1C_2$ and C_1C_2P), and was reported to be 14.5–20 Hz for ϕ = 0°, 7–9 Hz for ϕ = 30°, 5–7 Hz for ϕ = 60°, 0.5 Hz for ϕ = 90°, 5.5–8.6 Hz for ϕ = 120°. The small coupling ($^3J_{PH}$ = 4 Hz) observed for the acetal methine proton in **18** would therefore suggest that this proton spends a considerable amount of time in a conformation which has a dihedral angle $\phi > 60° < 120°$.

The structural assignment of **18** is also supported by a correct elemental analysis and by mass spectrometry. The mass spectrum of **18** exhibited three principal modes of fragmentation, all of which were consistent with structure **18**. The mass spectrum showed (a) a progressive loss of fragments C_2H_5O (*m/e* 221), C_2H_4 (193), C_2H_4 (165) (this fragmentation pattern was supported by the metastable ions, *m/e* 168.5, 141, and 113.5); (b) the formation of fragments $CH(OC_2H_5)_2$, $CH(OC_2H_5)OH$, $CH(OH)_2$, the transformation $CH(OC_2H_5)_2 \rightarrow CH(OC_2H_5)OH$ being supported by a metastable ion (*m/e* 54.6); (c) the formation of phosphorus-containing fragments such as $HPO(OC_2H_5)_2$, $PO(OC_2H_5)_2$, $PO(OH)OC_2H_5$. The above fragmentation pattern is clearly consistent with the structure of **18** and is similar to the isomeric product (**9**).

The reported[7,8] synthesis of **4** had also indicated that this compound reacted in dilute aqueous HCl with isoprene at 100 °C to give the Diels–Alder adduct, formulated as **21**, and characterized by its DNPH **22**. The compound **21** was prepared from **11** by reaction with isoprene and was converted to **22** which was found to have a different melting point from that reported.[7]

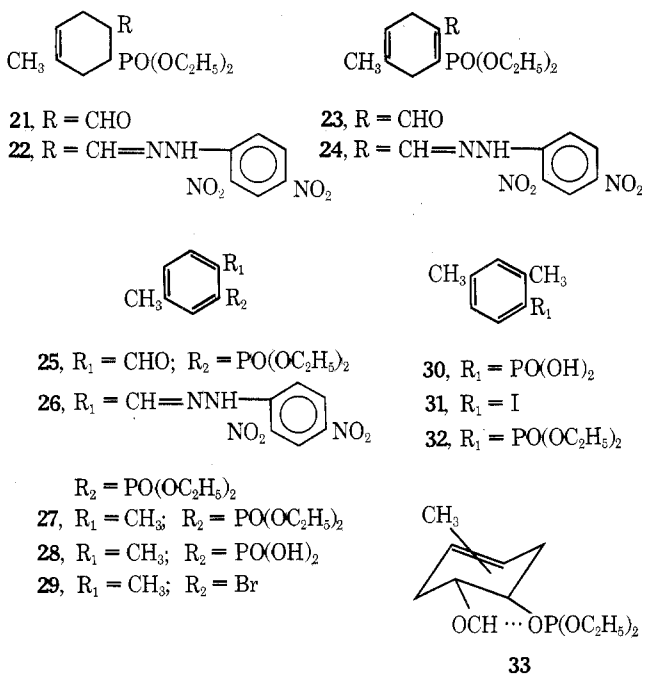
Diels–Alder Reactions. The Diels–Alder reactions of **5** and **11** with isoprene were examined and compared to those of **7** and **8**. The results are summarized in Table III.

A violent exothermic reaction occurred when **5** was mixed neat with isoprene. The heat of the reaction carbonized the contents of the flask. In benzene solution, however, **5** reacted

with isoprene to give **23** in 62% yield (room temperature, 70 h).

The structure of **23** was established by conversion into the known **28**. The cycloadduct **23** (Chart III) was dehydrogenated

Chart III



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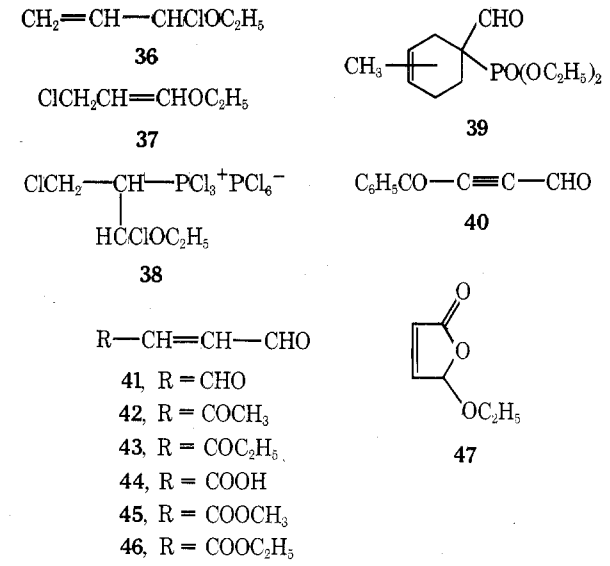
with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give **25** in 56% yield. This compound was characterized by its 2,4-dinitrophenylhydrazone **26**, because distillation of **25** always resulted in some decomposition. Catalytic hydrogenolysis of **25** gave **27** in a near-quantitative yield. The product was converted into **28** using the Rabinowitz method[17] of dealkylation of phosphonate esters. The melting point of phosphonic acid **28** was identical with that reported[18] for **28**. An authentic sample of **28** was prepared from **29** by photolysis[19] of this compound in triethyl phosphite solution at 2537 nm. The compound **27** was isolated in 66% yield and converted into **28** by hydrolysis with refluxing HCl. The product thus obtained was identical in all respects, ir, NMR, melting point, and mixture melting point, with that obtained by transformation of **23**. The known[20] isomeric phosphonic acid **30** was prepared in the same way[19] from **31** and was shown to be different from **28**, obtained by degradation.

The aldehyde **11** reacted with isoprene neat at room temperature *without* the evolution of heat to give **21** in 55% yield. The reaction carried out in benzene solution at room temperature yielded **21** in only 7% yield, but required heating at 100 °C for 19 h to give 61% yield. The position of the methyl group in this cycloadduct was not established. The NMR spectrum of **21**, obtained from the reaction done at 100 °C in benzene solution, showed two broad aldehyde absorptions, one at 10.1 ppm, the other at 9.67 ppm, in a ratio of 1:3. The lower field absorption was attributed to **33** in which the phosphorus and aldehyde groups could assume a coplanar geometry, and would be capable of interacting to give a lower field resonance for the aldehyde proton.[21] The cycloadduct gave a single 2,4-DNPH **22** which had a different melting point from that reported[7] for **22**.

The reaction of **7** and **8** with isoprene gave the known cycloadducts, **34**[22] and **35**.[23] The yield of the adducts from **7** and **8** was low (12 and 2%, respectively) when the reactions were carried out at room temperature in benzene solution. In the case of **8** some polymerization was observed which probably lowered the yield of **35**, because of the long reaction time.

Discussion

The formation of **17** from the reaction of PCl_5 and **14** can be explained in terms of the reaction scheme, **14** → **36** → **37** → **38** → **17**. In this scheme PCl_5 is postulated to react with **14** to give the α-halo ether **36** which undergoes an allylic rearrangement to **37**. The product (**37**) then reacts with PCl_5 ($PCl_4^+PCl_6^-$) to give the adduct **38**, which when treated with SO_2 gives **17**. The above reaction scheme is supported by the known[24] ability of PCl_5 to react with vinyl ethers to give after workup the corresponding vinyl ether phosphonic acid derivatives. Also similar reaction mechanisms proceeding through α-halo ethers have been proposed to explain the formation of vinylphosphonate products from reactions of ethers, acetals, and ketals with PCl_5.[25-28]



The experimental results presented in this paper, as (a) the isolation of **17** in place of **16** in the reported yield, (b) the close similarity of the ir spectrum of **17** with that reported for **16**, and (c) the inability to obtain the same physical characteristics (melting point) for the 2,4-DNPH (**22**) reportedly used to characterize the cycloadduct (**21**) derived from **4** (in this case the cycloadduct **21** was prepared from the well-characterized **11**) are strongly indicative of erroneous structural assignment for **16**. Structural data as ir, molecular rotation, elemental analysis, the ability to undergo transformation to a product with a molecular formula $C_{11}H_{23}O_5P$ (assigned structure **4**), and the ability of the latter (**4**) to react in a Diels–Alder manner with isoprene under acidic conditions are not sufficient to distinguish between the isomeric compounds **16** and **17**. The reported cycloadduct may in fact be **39**.

The findings presented in this communication on the dienophilic reactivity of **5** and **11** confirm the previously reported observations[3-6] that the introduction of a phosphonyl group into olefins enhances their dienophilic character. The results in Table III allow a rough qualitative ordering of the dienophilic reactivity of these compounds: **5** > **7** > *cis*-**11** > **8**. The observation that *cis*-**11** is less reactive than **5** is consistent with published findings[29] that cis olefin dienophiles are usually less reactive than their acetylene counterparts. Since analogues of **5** in which the diethyl phosphonyl moiety of **5** has been replaced by CHO, COR, COOR, or CN are for the most part unknown or, as in the case of **40**, the Diels–Alder reactions have been done under different conditions and with different dienes, a more precise evaluation of the activating ability of the diethyl phosphonyl group cannot be made at this time. In the case of **40**, the compound was reported to react with cyclopentadiene,[30] neat at room temperature, to give good yield of adduct. These reaction conditions suggest that

40 may be more similar in its reactivity to 11, than to 5, which would be expected to react violently with cyclopentadiene in the light of the present findings with isoprene.

A similar situation exists with analogues related to 11. Many of these compounds (41–46) have been prepared but only a few[31] (44, 45, and the pseudoester 47) have been studied for the Diels–Alder reaction and these under reaction conditions not strictly comparable to the ones used in this study for 5 and 11. The dienophilic reactivity of esters of 44 was reported[31] to be comparable with those of maleic acid.

Experimental Section

The melting points were taken on a Fisher-Johns melting point block and are uncorrected. The infrared spectra were determined in KBr disks for solids and as smears on NaCl plates for liquids, using a Perkin-Elmer 237 grating spectrophotometer. The NMR spectra were determined in the solvents indicated using Varian A-60 and T-60 spectrophotometers. The chemical shifts are reported in parts per million (ppm) downfield from the internal standard tetramethylsilane. Mass spectra were obtained on a Hitachi Perkin-Elmer RMV-6D mass spectrophotometer. GLC analyses were performed on Varian Aerograph Hi Fi and Model 90 gas chromatographs using analytical columns specified. Elemental analyses were performed by Galbraith Laboratories, Nashville, Tenn.

Diethyl 2-Formylethynylphosphonate (5). A solution of 25.63 g (0.1 mol) of 6 in 125 ml of 97% HCOOH was heated at 60 °C for 0.5 h. The HCOOH was evaporated under reduced pressure and the remaining traces of acid removed by azeotroping with toluene. Distillation of the residue yielded 18.0 g (97%) of 5: bp 83–91 °C (0.02 Torr); ir (neat) 4.50, 5.94, 7.98, 9.75 μ; NMR (CCl_4) δ 1.40 (t, J = 7 Hz, CH_3), 4.16 (2 q, J = 7, 9 Hz, CH_2OP), 9.3 (s, CHO); mass spectrum m/e 191 (0.17, M + 1), 190 (0.17, M), 163 (25), 161 (17), 147 (16), 145 (19), 135 (100), 134 (48), 133 (38), 118 (18), 117 (59), 89 (28), 82 (27), 81 (32), 70 (29), 65 (33), metastable ions m/e 111.5, 101.5, 61.5, 35.5.

Anal. Calcd for $C_7H_{11}O_4P$: C, 44.21; H, 5.83; P, 16.27. Found: C, 44.09; H, 5.85; P, 16.23.

Diethyl 3,3-Diethoxy-1-*cis*-propen-1-ylphosphonate (9). A mixture of 1.32 g of 6, 0.0314 g of 5% Pd/$CaCO_3$, and 20 ml of EtOH containing 0.0088 g of quinoline was hydrogenated at atmospheric pressure until a theoretical amount of H_2 was taken up. The catalyst was filtered, and the EtOH was evaporated under reduced pressure to yield a residue which was distilled giving 0.778 g (60%) of 9, bp 99–101 °C (0.008 Torr). An analytical sample of 9 was prepared by preparative TLC using silica gel G plates and EtOAc as the developing solvent. In this way 0.454 g of pure 9 was obtained: bp 100 °C (0.01 Torr); ir (neat) 6.06, 7.98, 9.45, 9.72, 10.35 μ; NMR (C_6D_6) δ 1.07 (t, J = 7 Hz, CH_3), 1.15 (t, J = 7 Hz, CH_3), 3.63 (AB q, J = 7 Hz, CH_2O), 3.90 (2 q, J = 7, 9 Hz, CH_2OP), 5.68 (m, J = 1, 13, 18 Hz, POCH=C), 6.53 (m, J = 7.5, 13, 50 Hz, POCH=C**H**), 6.30 [m, J = 1, 2.5, 7.5 Hz, C**H**$(OR)_2$]; NMR ($CDCl_3$) δ 1.23 (t), 1.35 (t), 3.74 (AB q), 4.13 (2 q), 5.9 (m), 5.93 (m), 6.57 (m); mass spectrum m/e 265 (0.5, M + 1), 237 (58), 221 (98.9), 209 (18), 193 (34), 181 (46), 165 (30), 163 (25), 153 (39), 147 (48), 137 (51), 136 (17), 135 (78), 129 (43), 120 (23), 119 (100), 109 (12), 103 (37), 82 (24), 81 (24), 75 (25), metastable ions m/e 184.5, 168.5, 156.5, 141, 113.5.

Anal. Calcd for $C_{11}H_{23}O_5P$: C, 49.62; H, 8.74; P, 11.63. Found: C, 49.75; H, 8.57; P, 11.40.

Diethyl 3,3-Diethoxy-1-*trans*-propen-1-ylphosphonate (10). A solution of 0.52 g of 9 in 5 ml of HCOOH (97%) was heated at 60 °C for 15 min. The HCOOH was evaporated under reduced pressure to yield an oil which by GLC was free of starting material. This oil was dissolved in 1.6 g (2 ml) of anhydrous EtOH and 7.2 g (8 ml) of triethyl orthoformate containing a drop of HCOOH and was heated at reflux for 70 min. The solvents were evaporated under reduced pressure and the residue was submitted to preparative TLC on silica gel GF plates using EtOAc to develop the chromatograms. Three TLC fractions were obtained, two of which were isolated: 9 (0.07 g, 13.4%) and 10 (0.12 g, 23%). The third fraction appeared to be unreacted aldehyde. GLC of the crude reaction mixture before TLC indicated the presence of three components in the ratio of 1:1:1.

For 10: ir (neat) 6.07, 7.97, 9.49, 9.77, 10.37 μ; NMR (C_6D_6) δ 1.13, 1.21 (2 t, J = 7 Hz, CH_3), 3.88 (AB q, J = 7 Hz, CH_2O), 4.08 (2 q, J = 7 Hz, CH_2OP), 5.08 [t, J = ca. 3 Hz, C**H**$(OEt)_2$], 6.23 (m, J = 1, 18, 21 Hz, PCH=C), 6.85 (m, J = 3.5, 18, 21.5 Hz, PC=CH; NMR ($CDCl_3$) δ 1.3 (t), 1.4 (t), 3.7 (AB q), 4.22 (2 q), 5.13 (t), 6.20 (m), 6.80 (m).

Analysis of the Reaction Mixture Obtained from the Reduction of 6. A mixture of 1.05 g of 6 and 0.01 g of 10% Pd/$CaCO_3$ in 10 ml of C_5H_5N was hydrogenated at atmospheric pressure. The hydrogenation was stopped after 1 equiv of H_2 had been absorbed. The catalyst was filtered and the C_5H_5N evaporated under reduced pressure. The residue was submitted to preparative TLC on silica gel GF plates using EtOAc to develope the chromatograms. Three fractions were isolated and were identified as 6 (0.2 g, 19%), 9 (0.58 g, 55%), and 10 (0.08 g, 8%). GLC analysis of the crude reaction mixture on a 4-ft UCW 3.8% column indicated a 20:70:8.3 product distribution of the three components. The ir, GLC, TLC, and NMR data were those obtained previously for these compounds.

Diethyl 2-Formylvinylphosphonate (11) and Its 2,4-DNPH (12). A solution of 3.98 g (0.15 mol) of 9 in 37 ml of 97% HCOOH was kept at room temperature for 30 min and heated for 10 min at 70 °C. The HCOOH was evaporated under reduced pressure and the residue was distilled to give 2.04 g (70%) of 11, bp 70–74 °C (0.06 Torr). Redistillation through a 15-cm Vigreux column yielded 1.75 g (60%) of 11: bp 62–66 °C (0.07 Torr); ir (neat) 5.86, 6.19, 7.95, 9.50, 9.74, 10.25 μ; NMR (C_6D_6) δ 1.03 (t, J = 7 Hz, CH_3), 3.9 (2 q, J = 7, 8 Hz, CH_2OP), 6.27 (m, J = 11, 13 Hz, POC**H**=CH), 6.29 (m, J = 7, 13, 52 Hz, PO-CH=C**H**), 11.10 (d, J = 7 Hz, CHO).

Anal. Calcd for $C_7H_{13}O_4P$: C, 43.76; H, 6.82; P, 16.12. Found: C, 43.57; H, 6.68; P, 16.30.

A solution of 1.45 g (0.0076 mol) of 11 in 30 ml of 2,4-DNPH reagent[32] was allowed to stand for 5 min at room temperature. Water (6 ml) was added and the solution kept for 30 min at room temperature to allow complete crystallization of the hydrazone. The mixture was filtered to yield 1.82 g of crude 12 which was recrystallized from EtOH to yield pure 12: mp 160.5–161.5 °C; ir (KBr) 6.21, 6.28, 6.37, 6.55, 6.65, 8.0, 9.51, 9.67 μ; NMR ($CDCl_3$) δ 1.37 (t, J = 7 Hz, CH_3), 4.17 (2 q, J = 7, ca. 8.5 Hz, CH_2OP), 6.16 (overlapping d, J = 17.2, 16.8 Hz, POC**H**=CH), 7.25 (m, J = 8.8, 16.8, 20.5 Hz, POCH=C**H**), 7.85 (d, J = ca. 9 Hz, CH=N), 7.95 (d, J = ca. 9.5 Hz), 8.35 (2 d, J = ca. 2.5, 9.5 Hz), 9.13 (d, J = ca. 2.5 Hz), 11.28 (bs, NH); NMR (C_6D_6) δ 1.13 (t), 4.0 (2 q), 5.87 (2 d), 6.40 (2 bm), 6.92–7.13 (olefin H), 7.25 (d), 7.80 (2 d), 8.78 (d), 10.55 (bs).

Anal. Calcd for $C_{13}H_{17}N_4O_7P$: C, 41.93; H, 4.60; N, 15.05; P, 8.32. Found: C, 42.02; H, 4.45; N, 14.93; P, 8.17.

Diethyl 3,3-Diethoxy-1-*cis*-propen-1-ylphosphonate-*1,2-d*$_2$ (13). This was obtained by hydrogenation of 6 using D_2, 5% Pd/$BaSO_4$, and C_5H_5N as the solvent. GLC of the product on a 15% SE-30 (5 ft × 0.125 in. column) at 170 °C indicated it to be a mixture of at least two substances. The product was purified in the same way as that described for the nondeuterated material, cf. 9: ir (neat) 6.18, 7.95, 9.4, 9.70, 10.30 μ; NMR (C_6D_6) δ 1.11, 1.15 (2 t, J = 7 Hz, CH_3), 3.95 (2 q, J = 7, 9 Hz, CH_2OP), 3.65 (AB q, J = 7 Hz, CH_2O), 6.18 [s, C**H**$(OEt)_2$]; mass spectrum m/e 239 (40.9), 224 (15), 223 (80), 222 (20), 211 (13), 195 (33), 194 (10), 193 (12), 167 (27), 165 (26), 164 (8), 155 (25), 149 (44), 148 (13), 139 (75), 138 (33), 137 (77), 136 (20), 135 (10), 131 (31), 130 (10), 129 (16), 123 (12), 122 (28), 121 (100), 120 (30), 111 (25), 110 (15), 109 (16), 103 (39), 100 (12), 94 (16), 93 (26), 87 (16), 84 (11), 83 (28), 82 (53), 81 (46), 75 (30).

3-Chloro-1-ethoxy-1-propen-2-ylphosphonyl Dichloride (17). Method A. Using the method of Tsivunin[7] a solution of 50 g (0.59 mol) of 14 in 335 ml of C_6H_6 was treated with 241 g of PCl_5 to give, after workup and distillation, 60 g (42%) of 17: bp 147–152 °C (5 Torr) [lit.[7] yield 41%, bp 134–135 °C (4 Torr)]; ir (neat) 6.20, 7.9, 8.15 μ; NMR (C_6D_6) δ 0.73 (t, J = 7 Hz, CH_3), 3.33 (q, J = 7 Hz, CH_2O), 4.02 (d, J = 26 Hz, CH_2Cl), 7.12 (d, J = 10 Hz, OCH=C). The literature ir spectrum for the product formulated as 16 was essentially identical with that found for 17, except for an additional ir absorption at 13.3 μ.

Method B. Using the method of Moskva[15] a solution of 12 g (0.09 mol) of 20 in 80 ml of C_6H_6 was treated with 42 g of PCl_5 to give after workup and distillation 17, bp 133.5–135 °C (6 Torr). The ir and NMR spectra of this product were identical with those obtained in method A. The literature NMR [δ 1.35 (t), 3.91 (d, J = 23 Hz), 4.00 (q), 6.85 (d, J = 12 Hz)] differed in its shift values and its coupling constants from that of 17 prepared and observed by the present authors.

Diethyl 1,3-Diethoxy-1-*cis*-propen-2-ylphosphonate (19) and Diethyl 1,1-Diethoxy-2-propen-2-ylphosphonate (18). This was prepared according to the procedure described by Tsivunin[7] for the preparation of 4. Thus 14.2 g (0.06 mol) of 17 was treated with 12.5 g of NaOEt (prepared from EtOH and NaH) in 75 ml of ether. The mixture was processed as described[7] and the solution distilled to give 12.7 g of crude product, bp 83–101 °C (0.02 Torr). Careful repeated fractional distillation yielded two products.

For 18: bp 46–48 °C (0.85 Torr); 1.36 g (8.5%) yield; ir (neat) 3.32, 3.40, 3.43, 7.95, 9.45, 9.74, 10.35 μ; NMR (C_6D_6) δ 1.13 (t, J = 7 Hz, CH_3), 3.5 (m, J = 7 Hz, CH_2O), 4.05 (2 q, J = 7, 9 Hz, CH_2OP), 5.31 [m, J = 0.6, 0.8, 4 Hz, C**H**$(OEt)_2$], 6.28 (2 m, J = 0.6, 2.4, 43.2 Hz, POC=CH), 6.33 (2 m, J = 0.8, 2.4, 22.0 Hz, POC=CH); mass spec-

trum *m/e* 266 (0.1), 221 (40), 193 (60), 165 (30), 137 (88), 135 (10), 119 (37), 109 (11), 103 (100), 81 (23), 75 (48), 65 (18), 55 (20), metastable ions *m/e* 168.5, 141, 113.5, 54.6.

Anal. Calcd for $C_{11}H_{23}O_5P$: C, 49.62; H, 8.71; P, 11.63. Found: C, 49.40; H, 8.74; P, 11.51.

For **19:** bp 115–117 °C (0.9 Torr) [lit. bp 148–149 °C (7 Torr)]; 5.5 g (34.5%) yield; ir (neat) 3.38, 3.43, 3.48, 3.53, 6.15, 8.05, 8.30, 9.15, 9.50, 9.75, 10.45 μ; NMR (C_6D_6) δ 0.83, 1.07, 1.20 (3 t, J = 7 Hz, CH_3), 3.44 (q, J ≈ 7 Hz, CH_2O), 4.08 (2 q, J = 7, 8 Hz, CH_2OP), 4.28 (d, J = 18 Hz, CH_2OEt), 7.28 (d, J = 10 Hz, CH=C).

Diethyl 5-Methyl-2-formyl-1,4-cyclohexadien-1-ylphosphonate (23) and Its 2,4-DNPH (24). A solution of 5.0 g (0.026 mol) of **5** and 2.11 g (0.031 mol, 2.64 ml) of isoprene in 50 ml of C_6H_6 was kept for 70 h at room temperature. Evaporation of the volatiles under reduced pressure and distillation of the residue yielded 4.2 g (62%) of **23,** bp 100–118 °C (0.04 Torr). Redistillation of the liquid through a 15-cm Vigreux column yielded 3.28 g of **23:** bp 98–103 °C (0.02 Torr); ir (neat) 5.94, 6.18, 8.15, 9.6, 9.7, 9.95, 10.5 μ; NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, CH_3), 1.73 (s, CH_3), 2.97 (s, CH_2C=C), 4.18 (2 q, J = 7, 7.75 Hz, CH_2OP), 5.46 (s, CH=C), 10.67 (s, CHO); mass spectrum *m/e* 258 (6), 257 (12), 230 (24), 229 (85), 201 (37), 184 (12), 183 (32), 173 (80), 169 (17), 155 (18), 120 (35), 119 (29), 109 (12), 93 (62), 92 (36), 91 (100), metastable ions *m/e* 204.5, 176.5, 148.5, 139, 46.5.

Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.80; H, 7.41; P, 11.99. Found: C, 55.77; H, 7.35; P, 11.79.

Treatment of 0.95 g (0.0037 mol) of **23** with 10 ml of 2,4-DNPH reagent[32] gave 0.8 g of hydrazone. Recrystallization of the solid from EtOH yielded an analytical product: mp 150–152 °C; ir (KBr) 6.18, 6.29, 6.37, 6.60, 6.65, 7.43, 7.50, 8.03, 9.42, 9.80, 10.40 μ; NMR (C_6D_6) δ 1.11 (t, J = 7 Hz, CH_3), 1.60 (s, CH_3), 3.05 (m, CH_2C=C), 4.00 (m, J = 7, 8 Hz, CH_2OP), 5.4 (s, HC=C), 7.31 (d, J ≈ 9 Hz), 7.84 (2 d, J ≈ 3, 9 Hz), 8.78 (d, J = 3 Hz), 9.55 (s, CH=N), 11.0 (bs, NH); NMR ($CDCl_3$) δ 1.4 (t), 1.8 (bs), 3.13 (m), 4.16 (2 q), 5.53 (bs), 7.9 (d), 8.29 (2 d), 9.12 (d), 9.32 (bs), 11.23 (bs).

Anal. Calcd for $C_{18}H_{23}N_4O_7P$: C, 49.31; H, 5.28; N, 12.78; P, 7.06. Found: C, 49.19; H, 5.16; N, 12.53; P, 6.89.

Diethyl 5-Methyl-2-formylphenylphosphonate (25) and Its 2,4-DNPH (26). A solution of 4.2 g (0.016 mol) of **23** and 3.7 g (0.016 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 50 ml of C_6H_6 was stirred under N_2 for 42 h. The precipitate was filtered and the solution concentrated to yield a residue. Distillation yielded 2.34 g (55.7%) of **25** (considerable superheating was required to vacuum distill the product): ir (neat) 3.3, 5.9, 6.24, 7.95, 9.57, 9.75, 10.25 μ; NMR (CCl_4) δ 1.33 (t, J = 7 Hz, CH_3), 2.5 (bs, CH_3), 4.2 (2 q, J = 7, 8 Hz, CH_2OP), 7.36 (bd, J = 8 Hz, aromatic H), 7.52 (bd, J = 12 Hz), 7.85 (2 d, J = 6, 8 Hz), 10.63 (d, J = 2 Hz, CHO).

A solution of 1.29 g (0.005 mol) of **25** and 1.15 g of DDQ in 50 ml C_6H_6 was stirred under N_2 for 42 h. The precipitate was filtered and the solution concentrated to yield an oily residue. This was treated with 20 ml of 2,4-DNPH reagent.[32] The solution was heated at 50 °C for 1–2 min, then left overnight at room temperature. The precipitate was filtered and recrystallized from EtOH to yield an analytical sample: mp 169–171 °C; ir (KBr) 6.16, 6.26, 6.31, 6.60, 7.4, 7.5, 8.03, 9.76, 10.23 μ; NMR ($CDCl_3$) δ 1.37 (t, J = 7 Hz, CH_3), 2.47 (s, CH_3), 4.18 (2 q, J = 7, 8 Hz, CH_2OP), 7.45 (d), 7.72 (d, J = 8, 14 Hz), 8.06 (d, J = 9.5 Hz), 8.33 (2 d, J = 2, 9.5 Hz), 8.4 (d), 8.9 (bs, NH), 9.08 (d, J = 2 Hz), 11.30 (s, b, NH).

Anal. Calcd for $C_{18}H_{21}N_4O_7P$: C, 49.54; H, 4.87; N, 12.84; P, 7.09. Found: C, 49.36; H, 4.77; N, 12.74; P, 7.05.

Diethyl 2,5-Dimethylphenylphosphonate (27). Method A. A solution of 4.45 g (0.017 mol) of **25** in 90 ml of EtOH containing 0.89 g of 5% Pd/C was hydrogenated at an initial pressure of 50 psi until a theoretical amount of H_2 was absorbed. The catalyst was filtered, the solvents evaporated, and the residue distilled to give **27,** bp 92–94 °C (0.025 Torr), in an almost quantitative yield. GLC using a 15% SE-30 column, 5 ft × 0.125 in., indicated the presence of a second component, but the concentration appeared to be <8%: ir (neat) 6.20, 8.0, 9.55, 9.75, 10.42 μ; NMR (neat) δ 1.27 (t, J = 7 Hz, CH_3), 2.28 (s, CH_3), 2.56 (s, CH_3), 4.12 (2 q, J = 8 Hz, CH_2OP), 7.25 (m), 7.81 (d, J = 14.8 Hz); mass spectrum *m/e* 242 (29), 186 (35), 185 (14), 170 (17), 169 (15), 168 (15), 167 (14), 133 (21), 105 (29), 104 (17), 103 (15), 90 (10), 76 (18), 31 (34), 28 (10), 27 (100).

Method B. A solution of 37 g (0.2 mol) of 2-bromo-*p*-xylene and 166 g of triethyl phosphite was placed in a quartz vessel. The solution was degassed by passing argon through it for 5 min. Photolysis was done using a Rayonet-Srinivasin-Griffin photochemical reactor RPR-100 with 16 lamps of 2537-nm wavelength. Distillation of the reaction solution yielded 32 g (66%) of **27,** bp 99–103 °C (0.04 Torr). The ir and NMR spectra were the same as those obtained for the product derived from **23.**

2,5-Dimethylphenylphosphonic Acid (28). Method A. A solution of 1 g of **27** (obtained by degradation) in 10 ml of TMSCl was heated in a Parr bomb for 6 days at 100 °C. Evaporation of the volatiles yielded a residue that was dissolved in EtOH. The EtOH was film evaporated and the process of dissolution and evaporation was repeated again. The solid was recrystallized from H_2O to give **28:** mp 179–180 °C (lit.[18] mp 179–180 °C); ir (KBr) broad absorption band λ_{max} at 3.5 and 4.4, 6.18, 6.35, 8.0, 9.1, 9.92, 10.75, 12.2, 14.0, 14.35 μ; NMR (CD_3COCD_3) δ 2.33 (s, CH_3), 2.58 (s, CH_3), 7.15 (m, aromatic, 2 H), 7.61 (bd, J = 14 Hz, *o*-H), 10.63 (s, POH).

Method B. A mixture of 5 g (0.02 mol) of synthetic **27** and 20 ml of HCl was heated at reflux for 10 h. The reaction mixture was cooled and the crystalline solids filtered to yield 3.3 g of **28,** mp ca. 170 °C. Recrystallization from H_2O yielded **28,** mp 179–180 °C; mixture melting point with the product obtained from the degradation of **23** showed no melting point depression. The ir and NMR spectra of the two products were also identical.

Diethyl 2,4-Dimethylphenylphosphonate (32) and 2,4-Dimethylphenylphosphonic Acid (30). A solution of 2.51 g (0.01 mol) of **31** and 8.52 g (0.05 mol) of triethyl phosphite was placed in a quartz test tube and degassed by flushing with Ar for 5 min. Photolysis at 37 °C for 24 h using a Rayonet Srinivasin-Griffin photochemical reactor RPR-100, using 16 lamps of 2537 nm, yielded upon distillation 2.6 g (100%) of **32,** bp 89 °C (0.005 Torr). This material was contaminated with a small amount of impurity which was visible in the NMR and could not be removed by distillation or acid washing (0.1 M HCl): ir (neat) 6.23, 8.0, 9.54, 9.75, 10.40 μ; NMR (C_6D_6) δ 1.07 (t, J ≈ 7 Hz, CH_3), 2.07 (s, CH_3), 2.63 (s, CH_3), 4.00 (2 q, J = 7, 8 Hz, CH_2OP), 6.91 (bd, J = 5 Hz), 8.13 (2 d, J = 8, 14 Hz). GLC using 15% SE-30 column indicated this compound to be different from the product obtained in the previously described Diels–Alder degradation schema.

Anal. Calcd for $C_{12}H_{19}O_3P$: C, 59.50; H, 7.91; P, 12.79. Found: C, 59.89; H, 7.60; P, 13.66.

A mixture of 1.0 g (0.0041 mol) of **32** and 10 ml of concentrated HCl was refluxed for 9 h to give 0.24 g (31%) of **30,** recrystallized from H_2O, mp 194 °C (lit.[20] mp 194 °C).

Diethyl 6-Formyl-3-methyl-3-cyclohexen-1-ylphosphonate (21) and Its 2,4-DNPH (22). Method A. A solution of 3.6 g (0.019 mol) of **11** and 1.36 g (0.02 mol) of isoprene was heated in a Parr bomb at 100 °C for 19 h. Distillation of the reaction solution yielded 3.0 g (61%) of **21:** bp 109–112 °C (0.07 Torr) [lit.[7] yield 86%, bp 129–130 °C (2 Torr)]; ir (neat) 5.78, 8.0, 9.48, 9.75, 10.4 μ (lit.[7] ir 5.78, 6.12 μ); NMR (C_6D_6) δ 1.10 (t, J = 7 Hz, CH_3), 1.53 (s, CH_3), 1.76–3.0 (m, cyclohexene H hump), 4.0 (2 q, J = 7, 8 Hz, CH_2OP), 5.28 (bs, CH=C), 9.67, 10.1 (ratio 3:1) (bs, CHO).

A solution of 1.0 g of **21** and 16 ml of 2,4-DNPH reagent[32] was allowed to stand at room temperature for several hours. The solvent was evaporated and the residue crystallized on standing. Recrystallization from EtOH yielded **22:** mp 155–156 °C; ir (KBr) 6.15, 6.30, 6.56, 6.64, 7.42, 7.78, 8.19, 9.45, 9.55, 9.68, 10.24 μ; NMR ($CDCl_3$) δ 1.33 (t, J = 7 Hz, CH_3), 1.73 (s, CH_3), 2.0–3.1 (m, cyclohexene protons), 4.13 (2 d, J = 7, 8 Hz, CH_2OP), 5.47 (bs, CH=C), 7.61 (d, J = 2.4, 9.6 Hz), 7.9 (d, J = 9.6 Hz), 8.03 (2 d, J = 2.4, 9.6 Hz), 9.33 (d, J = 2.4 Hz), 11.23 (bs, NH).

Anal. Calcd for $C_{18}H_{25}N_4O_7P$: C, 49.09; H, 5.72; N, 12.72; P, 7.03. Found: C, 48.96; H, 5.83; N, 12.60; P, 7.00.

Method B. A solution of 3.84 g (0.02 mol) of **11** and 1.36 g (0.02 mol) of isoprene was kept neat at room temperature under N_2 for 70 h. Distillation of the reaction mixture yielded 2.85 g (55%) of **21,** bp 108–111 °C (0.07 Torr). The product by NMR appeared to be 1:1 mixture of two isomers which were isomeric in the CHO absorption.

Method C. A solution of 3.84 g (0.02 mol) of **11** and 1.36 g (0.02 mol) of isoprene in 40 ml of C_6H_6 was kept at room temperature for 70 h. Distillation gave 3.5 g of unreacted **11,** bp 72–86 °C (0.25 Torr). The residue weighing 0.38 g (7%) was found to be **21,** as indicated by NMR and GLC.

Dimethyl 5-Methyl-1,4-cyclohexadiene-1,2-dicarboxylate (34). Method A. A solution of 1.95 g (0.014 mol) of **7** and 1.02 g of isoprene was kept neat at room temperature for 70 h. Distillation of the reaction mixture yielded 0.46 g of **7,** bp 78–80 °C (3 Torr) [lit.[33] bp 98 °C (20 Torr)], and 1.71 g (58%) of **34:** bp 129–132 °C (3.5 Torr) [lit.[22] bp 122.5–124 °C (3 Torr)]; ir (neat) 5.8, 6.04, 7.9 μ; NMR ($CDCl_3$) δ 1.73 (s, CH_3), 2.97 (bs, CH_2C=C), 3.81 (s, CH_3O), 5.47 (bs, J = ca. 1 Hz, CH=C).

Method B. A solution of 3.9 g (0.027 mol) of **7** and 2.04 g (0.03 mol) of isoprene in 60 ml of C_6H_6 was kept at room temperature for 70 h. Distillation of the reaction mixture yielded 3.32 g of **7,** bp 78 °C (3.1 Torr) [lit.[33] bp 98 °C (20 Torr)], and 0.69 g (12%) of **34,** bp 128 °C (3.4 Torr) [lit.[22] bp 122.5–124 °C (3 Torr)].

4-Methyl-1,3-cyclohexadiene-1-carboxaldehyde (35). Method A. A solution of 1.4 g (0.026 mol) of propiolaldehyde[34] and 1.8 g (0.026 mol) of isoprene was kept neat at room temperature for 70 h. Distillation of the reaction mixture yielded 2.0 g (63%) of **35**, bp 84–87 °C (10 Torr) [lit.[23] bp 95.5–96 °C (20 Torr)].

Method B. A solution of 2.8 g (0.052 mol) of **8** and 3.6 g (0.053 mol) of isoprene in 100 ml of Et_2O was kept at room temperature for 70 h. The volatiles were removed in vacuo and the residue weighing 0.34 g was distilled to give 0.14 g of **35**, bp 84–86 °C (11 Torr) [lit.[23] bp 95.5–96 °C (20 Torr)].

Registry No.—**5**, 58983-02-1; **6**, 58983-03-2; **7**, 762-42-5; **8**, 624-67-9; **9**, 58983-04-3; **10**, 58983-05-4; **11**, 58983-06-5; **12**, 58983-07-6; **13**, 58983-08-7; **14**, 557-31-3; **17**, 58983-09-8; **18**, 58983-10-1; **19**, 58983-11-2; **20**, 3054-95-3; **21**, 58983-12-3; **22**, 58983-13-4; **23**, 58983-14-5; **24**, 58983-15-6; **25**, 58983-16-7; **26**, 58983-17-8; **27**, 58983-18-9; **28**, 58983-19-0; **31**, 4214-28-2; **32**, 58983-20-3; **34**, 58983-21-4; PCl_5, 10026-13-8; triethyl phosphite, 122-52-1; isoprene, 78-79-5.

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Electron Impact Induced Fragmentations and Rearrangements of Aliphatic, Heterocyclic Phosphine Oxides[1]

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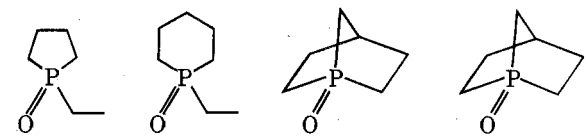
Common electron impact induced fragmentations and rearrangements of 1-ethylphospholane 1-oxide (**1**), 1-ethylphosphorinane 1-oxide (**2**), 1-phosphabicyclo[2.2.1]heptane 1-oxide (**3**), and 1-phosphabicyclo[2.2.2]octane 1-oxide (**4**) were investigated, and the nature of the fragments were compared with those resulting from similar decompositions of trimethylphosphine oxide (**5**), triethylphosphine oxide (**6**), quinuclidine (**7**), and quinuclidine *N*-oxide (**8**). Details of ethylene loss from and concomitant rearrangement of **1** were investigated using specifically deuterium-labeled derivatives. Possible structures for some of the major fragments and rearrangement products are proposed.

Reports of the consequences of electron impaction upon carbonyl-containing organic compounds abound in the chemical literature.[4] In contrast, only a few reports have appeared concerning analogous studies on phosphoryl-containing organic substances; mass spectral studies on the simplest class within this series, aliphatic phosphine oxides, have been even scarcer,[5–8] and these reports have dealt almost exclusively with acyclic phosphine oxides. No systematic studies of the mass spectral behavior of aliphatic, heterocyclic phosphine oxides have appeared up to this time.

We have recently synthesized monocyclic and bicyclic phosphine oxides containing five- and six-membered rings, namely compounds **1–4**.[9] In order to confirm these structural



1 **2** **3** **4**

assignments, these compounds were subjected to electron impaction and the ions generated analyzed.[9] In this paper we present much more detailed observations on the fragmentations of **1–4**. Particular attention has been given to molecular rearrangements induced by electron impaction. The fragmentation patterns of trimethylphosphine oxide (**5**), trieth-