(1 H, m), 3.20–3.24 (1 H, d, J = 15 Hz), 4.01 (3 H, s), 4.05 (2 H, AB q, J_{AB} = 20 Hz, $\Delta\nu$ = 210 Hz, δ_A 4.47, δ_B 3.63), 4.07 (3 H, s), 4.11 (3 H, s), 7.20 (1 H, d, J = 10 Hz), 7.26 (1 H, s), 7.80 (1 H, d, J = 10 Hz), 7.91 (2 H, s); UV λ_{max} 259 nm (ϵ 47 170), 287 (28 740), 302 (sh), 312 (sh), 344 (1260); mass spectrum. m/z (relative intensity) 377 (M^+, 24), 294 (100); $[\alpha]^{23}_D$ +106° (c 1.0, $CHCl_3$); $[\theta]_{285}$ +16 000° (c 2.8 × 10^{-3}, EtOH).

Registry No. (*S*)-(+)-**1**, 482-20-2; (*S*)-(+)-**2**, 87302-53-2; **3a**·HCl, 30061-20-2; **3a** (benzyl ester), 30061-09-7; **5a**, 87227-00-7; **5b**, 87227-01-8; **6a**, 87227-03-0; **6b**, 87227-04-1; **7**, 35676-02-9; **8**, 30062-15-8; **9**, 30062-19-2; **10**, 71779-56-1; **11**, 30062-39-6; **12**, 30062-14-7; **13**, 33329-56-5; (*Z*)-**14**, 37629-72-4; **15**, 87226-94-6; **16**, 87226-96-8; **17**, 87226-95-7; **18a**, 87226-97-9; **18a** (aminal), 87226-98-0; **19**, 87226-99-1; **20a**, 87227-10-9; **20b**, 87227-11-0; **22a**, 87227-05-2; **22a** (acetate), 87227-06-3; **22b**, 87227-07-4; **23a**, 87302-54-3; **23a** (acetate), 87302-55-4; **23b**, 87302-56-5; **24a**, 87302-57-6; **24b**, 87302-59-8; **25a**, 87302-58-7; **25b**, 87302-60-1; **26**, 87302-61-2; **28** (β-iodo), 87227-12-1; **28** (α-iodo), 87302-63-4; **29**, 87302-62-3; (*E*)-2-(3,4-dimethoxyphenyl)-3-(2-nitro-4,5-dimethoxyphenyl)cinnamic acid, 87227-08-5; (*E*)-2-(3,4-dimethoxyphenyl)-3-(2-amino-4,5-dimethoxyphenyl)cinnamic acid, 87227-09-6; (*E*)-2-(4-methoxyphenyl)-3-(2-nitro-4,5-dimethoxyphenyl)cinnamic acid, 68742-13-2; (*E*)-2-(4-methoxyphenyl)-3-(2-amino-4,5-dimethoxyphenyl)cinnamic acid, 68742-17-6; veratraldehyde, 120-14-9; (3,4-dimethoxyphenyl)acetonitrile, 93-17-4; (*S*)-(+)-*N*-[(3,4-dimethoxyphenyl)methyl]glutamic acid, 87249-38-5; (*S*)-(+)-glutamic acid, 56-86-0; benzyl prolinate, 41324-66-7; diisopropyl glutamate, 25975-47-7; (*S*)-α-aminoadipic acid, 1118-90-7; diisopropyl (*S*)-α-aminoadipate, 87227-02-9.

Dialkyl (3-Aryl-1,2,4-oxadiazol-5-yl)phosphonates: Synthesis and Thermal Behavior—Evidence for Monomeric Alkyl Metaphosphate

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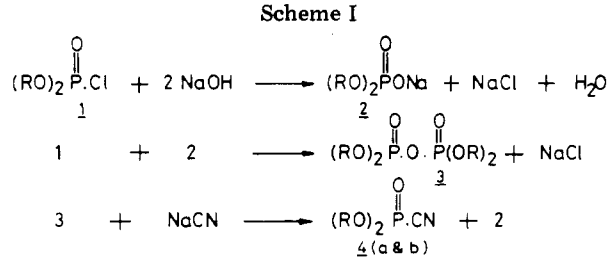
Dialkyl (3-aryl-1,2,4-oxadiazol-5-yl)phosphonates **6a–h** have been obtained by 1,3-dipolar cycloaddition of arenenitrile oxides **5a–f** to dialkyl phosphorocyanidates (**4a** and **4b**) in yields ranging between 30% and 58%. A standardized method for obtaining cyanidates **4a** and **4b** has been established. The diethyl thiophosphorocyanidate (**4c**) is less reactive than **4a** and **4b**, only the 3-(4′-nitrophenyl) derivative **6i** being obtainable. While the IR and NMR spectra of **6a–i** were unexceptional, their UV spectra showed evidence of conjugative interaction in high degrees between the phosphonate and heterocyclic moieties as well as a varying conjugative interaction between the heterocyclic and aryl moieties. The oxadiazoles **6a–h** are thermally labile and yield trialkyl phosphates **7** as the only identifiable products. A mechanism based on the intermediacy of monomeric alkyl metaphosphate **11** in the formation of trialkyl phosphate was postulated, and supportive evidence in the form of trapping the metaphosphate with acetophenone has been obtained.

Even though a number of reports have described the cycloaddition of 1,3-dipolar species to phosphorus(V) activated multiple bonds, such as those in olefinic,[1] acetylenic,[2] or allenic[3] groups, the potential of the method has scarcely been exploited—an enormous range of variation in structural or substitution patterns is possible even if only a perfunctory list of the potentially accessible phosphonates (e.g., heteroaryl phosphonates) is drawn up.

The present paper describes the synthesis, spectral properties, and thermal behavior of several hitherto unknown dialkyl (3-aryl-1,2,4-oxadiazol-5-yl)phosphonates **6a–h** prepared by 1,3-dipolar cycloaddition of arenenitrile oxides **5** to dialkyl phosphorocyanidates **4a,b**. The synthesis of one thiophosphonate (**6i**) by a similar reaction is also described. In the methods employed for the isolation of oxadiazolylphosphonates, the concomitant and somewhat unexpected formation of trialkyl phosphates was noticed. The complicity of thermal decomposition was suspected, and the thermal behavior of the phosphonates **6** was investigated in some detail. Chemical evidence which confirms the role of thermally generated monomeric alkyl metaphosphate in the formation of trialkyl phosphates has been obtained.

Scheme I



Results and Discussion

Dialkyl Phosphorocyanidates 4a,b. The phosphorus–carbon bond forming reaction in the synthesis of oxadiazolylphosphonates **6** described here depends on the availability of dialkyl phosphorocyanidates **4**. The first reported synthesis of **4b** employed a reaction between

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(2) B. C. Saunders and P. Simpson, *J. Chem. Soc.*, 3351 (1963); D. Seyferth and J. D. H. Paetsch, *J. Org. Chem.*, **34**, 1483 (1969); A. N. Pudovik, N. G. Khusainova, Z. A. Bredikhina, and E. A. Berdnikov, *Dokl. Akad. Nauk SSSR*, **226**, 364 (1976); *Chem. Abstr.*, **84**, 163982*v* (1976); N. G. Khusainova, Z. A. Bredikhina, A. I. Konovalov, and A. N. Pukovik, *Zh. Obshch. Khim.*, **47**, 1456 (1977); *Chem. Abstr.*, **84**, 117452*m* (1977); T. M. Balthazor and R. A. Flores, *J. Org. Chem.*, **45**, 529 (1980).

(3) A. N. Pudovik, N. G. Khusainova, T. V. Tumosiva, and O. E. Raevskaya, *Zh. Obshch. Khim.*, **41**, 1476 (1971); A. N. Pudovik, N. G. Khusainova, and T. V. Tumosiva, *ibid.*, **42**, 2159 (1972).

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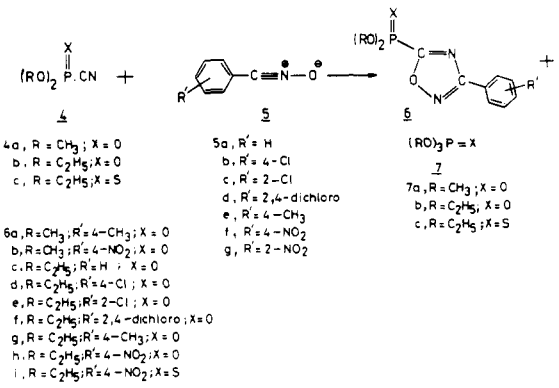
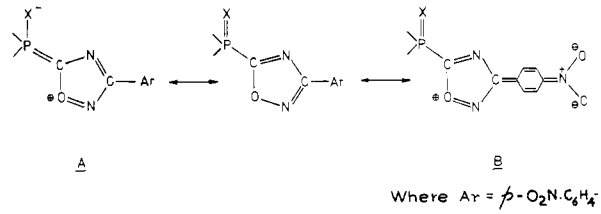
Scheme II



Scheme III



cyanogen iodide and triethyl phosphite;[4] a variation of this was the use of cyanogen bromide.[5] An alternative approach employed the reaction of diethyl phosphite and an alkali cyanide using carbon tetrachloride as the solvent under "appropriate conditions".[6] An attempt to repeat this preparation, following the information provided in the abstract,[6] failed. We now report a convenient method for the preparation of **4a** and **4b** from the corresponding chloridates **1**.

Since diethyl phosphorochloridate was stated[4] to be unreactive toward sodium cyanide when used directly, the reaction was attempted in the presence of a phase-transfer catalyst (benzyltriethylammonium chloride) in benzene, but the results were negative. However, a facile reaction ensued when an aged sample of sodium cyanide was employed in one experiment. This suggested that sodium hydroxide, formed by partial hydrolysis of sodium cyanide in the old sample, might have catalyzed the reaction. When the experiment was repeated with fresh sodium cyanide mixed with a small amount of sodium hydroxide, consistent yields of the cyanidates **4** (up to 46%) were obtained. The catalytic role of sodium hydroxide suggested the mechanism of Scheme I, involving the intermediacy of tetraalkyl pyrophosphate **3**. The inclusion of a phase-transfer catalyst did not improve the yield, and employment of polar aprotic solvents such as CH_3CN, DMF, or Me_2SO was found to supress the reaction totally.

Freshly prepared and fractionally distilled dialkyl phosphorocyanidates **4** show sharp bands of medium intensity at ca. 2200 and 2085 cm^{-1}. The band at the longer wavelength had been attributed[7] in the case of **4b** to the presence of isomeric isocyanidate and not to that of free hydrogen cyanide formed by hydrolysis. Redistillation of our materials after allowing them to stand for 10 weeks afforded pure colorless cyanidates having a single absorption band at ca. 2200 cm^{-1}. An attempt to separate the cyanidates by allowing the isocyanidate present to react with bromine in CCl_4 failed.

Dialkyl (3-Aryl-1,2,4-oxadiazol-5-yl)phosphonates 6. (a) Synthesis. The cyanidates **4** were found to be excellent dipolarophiles and to react smoothly with arenenitrile oxides (**5**), giving moderate to good yields of dialkyl (3-aryl-1,2,4-oxadiazol-5-yl)phosphonates **6a–h** (Scheme II). *o*-Nitrobenzenenitrile oxide (**5f**), however, reacted with diethyl phosphorocyanidate (**4b**) to yield only triethyl phosphate (**7b**). In five cases (**6a–d** and **6f**), TLC of the reaction mixture revealed the presence of the corresponding 3,4-diarylfuroxan, which undoubtedly resulted from unavoidable dimerization of the nitrile oxide formed in situ.

Since 3,5-disubstituted (e.g., diaryl) 1,2,4-oxadiazoles had been reported to be fairly stable systems,[8] fractional distillation was used to isolate the products from the cycloaddition reactions. Even though oxadiazolylphosphonates **6a,c–h** were isolated without difficulty, a lower boiling fraction, later identified as trialkyl phosphates **7a,b**, always accompanied the products.

Diethyl thiophosphorocyanidate (**4c**),[9] however, showed considerably less dipolarophilic activity than the corresponding oxo analogues **4a,b**. The cycloaddition could be effected only with the most stable nitrile oxide **5f**; even in this case a considerable amount of the corresponding 3,4-diarylfuroxan formation was noticed and the yield of the thiophosphonate **6i** was limited to 20%. Interestingly, triethyl thiophosphate (**7c**) was detected by GC of the mother liquor after the isolation of the thiophosphonate **6i**. With other nitrile oxides, only the corresponding furoxans could be isolated, together with the unreacted **4c**. Use of $BF_3{\cdot}Et_2O$ to enhance the electrophilicity of the cyanidate moiety[10] did not alter the situation.

(b) Spectral Properties. Spectral data of the phosphonates **6a–h** and the thiophosphonate **6i** are summarized in Table I, together with other physical characteristics.

The phosphonates **6a–h** exhibit characteristic bands in the regions 1590–1570 and 1280–1240 cm^{-1} due, respectively, to the C=N and P=O groupings in the systems;[11,12] the thiophosphonate **6i** showed bands at 820 and 650 cm^{-1} due to P=S grouping.[12]

3-Aryl-5-alkyl, 3-alkyl-5-aryl, and 3,5-diaryl 1,2,4-oxadiazoles have been reported to exhibit a strong absorption band ($\epsilon > 10000$) in the region 238–252 nm.[10,13] Replacement of the 5-alkyl group by a phosphonate or thiophosphonate moiety in the 3-arylated oxadiazoles (**6**) shifts the main maximum to ca. 270 nm and somewhat lowers the strength of the absorption (ca. ϵ 9000); a shoulder is seen at ca. 287 nm. The bathochromic shift of the main maximum indicates a high degree of conjugative interaction between the phosphonate or thiophosphonate and the heterocyclic moieties.

The band at ca. 270 nm, common to all the 3-arylated systems **6a,c,g,h** and **i**, may be ascribed, in the main, to

(4) B. C. Saunders, G. T. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).
(5) A. Takamizawa, Y. Sato, and S. Tanaka, *Yakugaku Zasshi*, **85**, 298 (1965) (cited in S. Yamada, Y. Kasai, and T. Shioiri, *Tetrahedron Lett.*, 1595 (1973)).
(6) T. S. Tung and C. S. Tai, *Hua Hsuch Pao*, **31**, 199 (1965); *Chem. Abstr.*, **63**, 16380*a* (1965).
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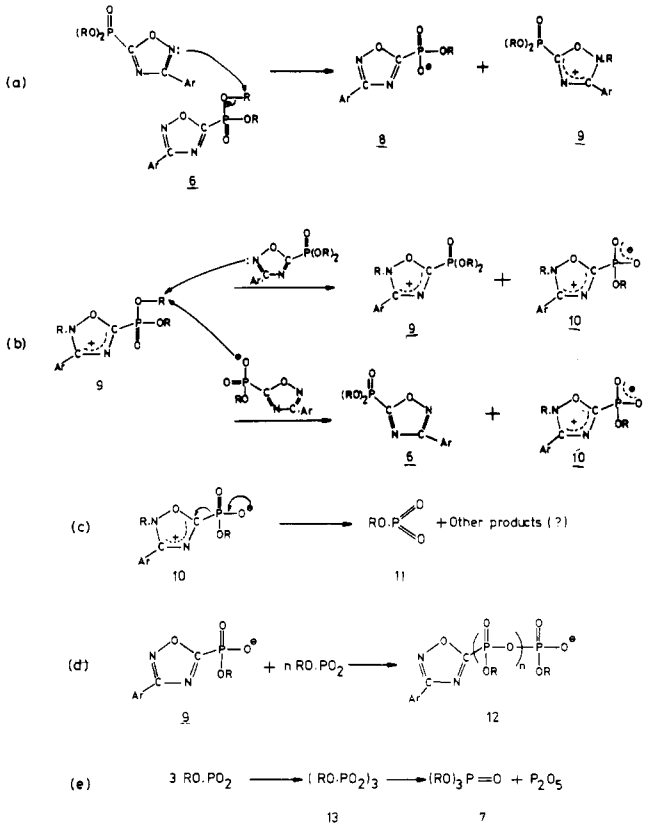
(8) L. B. Clapp, in "Advances in Heterocyclic Chemistry", A. R. Katritzky and A. J. Boulton, eds., 1966, Vol. 25, p 65.
(9) Details of preparation and some of the interesting reactions exhibited by diethyl thiophosphorocyanidate (**4c**) will be published shortly.
(10) S. Morrocchi, A. Rica, and L. Velo, *Tetrahedron Lett.*, 331 (1967).
(11) J. Barrans, *C. R. Hebd. Seances. Acad. Sci.*, **249**, 1096 (1959); H. Goncalves and F. Mathis, *ibid.*, **259**, 1819 (1964); K. Blast, M. Christe, R. Huisgen, and W. Mach, *Chem. Ber.*, **105**, 2825 (1972).
(12) L. C. Thomas "The Identification of Functional Groups in Organophosphorous Compounds", Academic Press, London, 1974, Chapters 3 and 9.
(13) C. Moussebois and J. F. M. Oth, *Helv. Chim. Acta*, **47**, 942 (1964).

Table I. Yields, Physical Constants, and Spectral Characteristics of Heterocyclic Phosphonates 6a–h and Thiophosphonate 6i

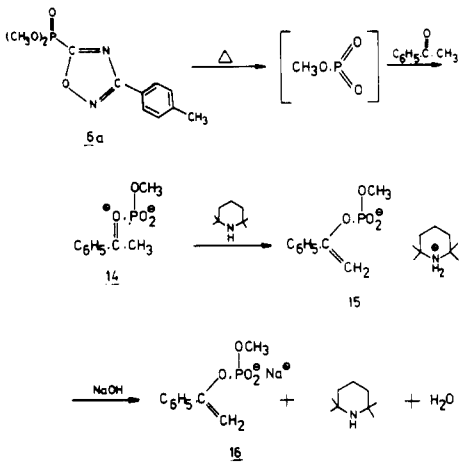
phosphonates	R	R′	X	yield,[a] %	mp, °C	bp (torr), °C	yield of $(RO)_3P{=}X$,[c] %	yield of 3,4-diaryl-furoxan,[a] %	UV λ_{max}, nm (log ϵ)	IR, cm^{-1}	^1H NMR, δ	*m/e* ($M^{+\cdot}$)
6a	CH_3	4-CH_3	O	30		91–94 (0.5)	11	detected[e]	271 (s, 3.81), 287 (sh, 3.75)	3040, 2990–2920, 1595, 1280, 1025, 975	2.41 (s, 3 H), 3.76 (d, J = 11 Hz, 6 H), 7.54 (m, 4 H)	268
6b	CH_3	4-NO_2	O	31[b]	110–112 (from benzene–petroleum ether)			8		3050, 2995–2920, 1570, 1520, 1345, 1275, 1025, 975	4.02 (d, J = 11 Hz, 6 H), 8.10 (m, 4 H)	
6c	C_2H_5	H	O	31		104–107 (0.5)	19	detected[e]	271 (s, 3.885), 286 (sh, 3.84)	3040, 2990–2920, 1590, 1280, 1025, 970	1.32 (t, 6 H), 4.19 (m, 4 H), 7.46 (m, 5 H)	282
6d	C_2H_5	4-Cl	O	56		130–133 (0.5)	20	detected[e]		3030, 2990–2915, 1590, 1260, 1040, 970, 800	1.23 (t, 6 H), 4.00 (m, 4 H), 7.59 (m, 4 H)	316
6e	C_2H_5	2-Cl	O	50		115–117 (0.5)	22			3030, 2990–2910, 1590, 1265, 1030, 970, 800	1.25 (t, 6 H), 4.02 (m, 4 H), 7.52 (m, 4 H)	
6f	C_2H_5	2,4-dichloro	O	46		138–142 (0.3)	17	10		3030, 2990–2905, 1585, 1240, 1025, 970, 805	1.32 (t, 6 H), 4.06 (m, 4 H), 7.57 (m, 3 H)	
6g	C_2H_5	4-CH_3	O	32		110–112 (0.5)	18		272 (s, 3.87), 2.87 (sh, 3.835)	3040, 2990–2910, 1595, 1275, 1020, 975	1.31 (t, 6 H), 2.40 (s, 3 H), 4.15 (m, 4 H), 7.52 (m, 4 H)	296
6h	C_2H_5	4-NO_2	O	58	86–87 (from benzene–petroleum ether)		10		267 (s, 4.44), 300 (sh, 4.20)	3045, 2995–2910, 1570, 1525, 1340, 1270, 1030, 975	1.89 (t, 6 H), 4.30 (m, 4 H), 8.07 (m, 4 H)	327
6i	C_2H_5	4-NO_2	S	20	60 (from methanol)		detected by GC[d]	31	270 (s, 4.22), 276 (sh, 4.20)	3100, 2995–2920, 1610, 1520, 1340, 1010, 965, 820, 805, 725, 650	1.50 (t, 6 H), 4.47 (m, 4 H), 8.37 ("s", 4 H)	343

[a] Yields refer to pure isolated compounds. [b] Isolated by preparative TLC (C_6H_6:$CHCl_3$, 9:1, v/v), R_f 0.18–0.10. The corresponding furoxan (R_f 0.80–0.72) was also isolated in this case. [c] P content of product isolated/P content of the starting material taken × 100. [d] GC analyses were carried out with Perkin-Elmer 3920 gas chromatograph equipped with FID, on OV-17 (1.5% on Chromosarb W, 120 mesh) column (6 ft × 1/8 in.) at 110 °C. Temperature of the detector and injector were set at 200 °C. Nitrogen flow rate used was 30 mL/min. Peaks were identified by comparing the retention times with those of authentic samples. [e] Not isolated. R_f values (TLC) were same as those of authentic samples.

Scheme IV



Scheme V



the charge distribution A (Scheme III) in which the aryl group is relatively isolated. The longer wavelength, less intense, absorption that occurs at ca. 286 nm in the phenyl or 4-tolyl cases (**6a** or **6c** and **6g**) suffers a bathochromic shift (to 300 nm) in the phosphonate **6h** and a hypsochromic shift (to 276 nm) in the thiophosphonate **6i**. This is consistent with a high degree of nitrophenyl participation, as would be apparent from the charge distribution B, indicated for the phosphonate **6h**. The hypsochromic shift in the thio case **6i** shows that the electron distribution changes back to being more like A, probably primarily due to the greater ability of sulfur to hold a negative charge.

(c) Thermal Behavior. Because partial thermal decomposition, during isolation, of the phosphonates **6** was the likely source of the trialkyl phosphates **7** (in reaction monitored by TLC, the formation of trialkyl phosphates could not be detected), samples of purified **6a** and **6d** were subjected to conditions taken as conducive to thermolysis, and the respective formation of trimethyl and triethyl phosphates was confirmed.

A possible mechanism for the formation of trialkyl phosphates **7** from the phosphonates **6** is depicted in Scheme IV. In this, an intermediary role has been assigned to monomeric alkyl metaphosphate for the transfer of alkoxy groups via the formation of a trimer. Initially, a nucleophilic attack[14] by N-2[15] of one oxadiazole ring on C-α of another generates the ion pair **8** and **9** (a). This is followed by the loss of an alkyl group from the ester moiety of cation **9**, resulting in the dipolar species **10** (b), which decomposes to yield the monomeric alkyl metaphosphate **11** (c). Depending on rate differentials, the latter can either phosphorylate **9** to yield **12** (d) or polymerize to yield linear branched polymers or cyclic systems, probably mainly the trimer **13** (e). It is believed that trialkyl phosphates are formed, together with phosphorus pentoxide, chiefly by the rearrangement and cleavage of **13** in a manner analogous to the thermal decomposition of "Langheld esters".[16] The residue from thermolysis was soluble in water and gave a positive reaction for orthophosphate after digestion with 2 N H_2SO_4. It was immobile in TLC under all conditions tried; this result was taken to indicate the presence of polymerized (polyphosphate) material.

The intermediacy of monomeric alkyl metaphosphate has a precedence in the postulated mechanism for the decomposition of 1-dialkylphosphorylimidazoles.[17] Also, involvement of monomeric alkyl metaphosphate in the gas-phase as well as in liquid-phase reactions has been demonstrated.[18,19]

In an attempt to demonstrate the intermediacy of monomeric alkyl metaphosphate **11**, the thermolysis of **6a** was carried out in the presence of an excess of acetophenone containing a small amount of 2,2,6,6-tetramethylpiperidine. The latter is required for abstraction of a proton from the dipolar species **14**, postulated[18] to be formed from the reaction of metaphosphate with acetophenone (Scheme V). The enol phosphate **16** was found among the reaction products in this experiment. An alternative mechanism for the formation of **16**, involving phosphorylation of the enol form of acetophenone by metaphosphate species has recently been proposed.[19]

The method described here for the synthesis of phosphonates **6a–h** and thiophosphonate **6i** by 1,3-dipolar cycloaddition of phosphorocyanidates **4** would seem to be superior to other conceivable methods such as Michaelis–Arbuzov or Michaelis–Baker reactions starting with halogenated derivatives. This should be especially so when the products are thermally labile since the former involves exposure to high temperature.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Model 577 spectrophotometer using liquid films or, with solid compounds, KBr pellets. ^1H NMR spectra were registered either with a Perkin-Elmer R-32 or with a Varian HA-100D spectrometer, using

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(16) G. Burkhardt, M. P. Klein, and M. Calvin, *J. Am. Chem. Soc.*, 87, 591 (1965).

(17) N. Ranganathan and W. S. Brinigar, *J. Org. Chem.*, 43, 4853 (1978).

(18) F. H. Westheimer, *Chem. Rev.*, 81, 313 (1981) and references therein.

(19) F. Ramirez, J. F. Marecek, and S. S. Yemul, *J. Am. Chem. Soc.*, 104, 1345 (1982) and references therein.

CCl_4 or $CDCl_3$ as solvents, as specified, with Me_4Si as the internal standard. Ultraviolet spectra were recorded with a Pye-Unicam SP-500 (series 2) spectrophotometer using spectroscopic-grade methanol. Mass spectra were obtained with either an AEI MS-702 or a JEOL DX-300 spectrometer operating at 70 eV. Melting and boiling points are uncorrected. TLC analyses and separations were carried out with SISCO silica gel. Petroleum ether refers to petroleum fraction boiling in the range 60–80 °C. Solvents used were purified and dried by standard procedures.

Dialkyl Phosphorocyanidates 4a and 4b. To a stirred suspension in benzene (50 mL) of finely powdered sodium cyanide (0.15 mol) and sodium hydroxide (0.005 mol) was added a solution of dialkyl phosphorochloridate (0.10 mol) in benzene (20 mL). After the addition was complete (15 min) the mixture was refluxed with stirring for 10 h. Filtration and removal of the solvent gave a reddish brown liquid. Distillation yielded a colorless liquid, which turned brown on standing. Redistillation after 10 weeks gave pure cyanidates **4a** and **4b**. There IR spectra were identical with those of samples prepared by the reported procedure.[5]

Dimethyl phosphorocyanidate (4a): yield 30%; bp 90–91 °C (17 mm); IR (neat) 2200 ($\nu_{C\equiv N}$); 1290 ($\nu_{P=O}$); ^1H NMR (CCl_4) δ 3.95 (d, J = 12 Hz). Anal. Calcd for $C_3H_6NO_3P$: C, 26.67; H, 4.44; N, 10.37. Found: C, 26.61; H, 4.08; N, 10.31.

Diethyl phosphorocyanidate (4b): yield 46%; bp 104–106 °C (14 mm) (lit.[4] bp 90–96 °C (14 mm)); IR (neat) 2200 ($\nu_{C\equiv N}$), 1280 ($\nu_{P=O}$); ^1H NMR (CCl_4) δ 1.35 (t, 3 H), 4.12 (m, 2 H).

Dialkyl (3-Aryl-1,2,4-oxadiazol-5-yl)phosphonates 6a–h and the Thiophosphonate 6i. General Procedure. To a cooled (−5 to 0 °C) stirred solution of the cyanidates **4** (15 mmol) and the required arylhydroxamyl chloride[20] (15 mmol) in ether or THF (100 mL) was added triethylamine (15 mmol). After being stirred for 3–4 h at low temperature, the reaction mixture was kept overnight at room temperature, followed by heating under reflux for 0.5 h (water bath). Filtration and removal of the solvent gave light yellow to reddish oils.

All but three of the oxadiazoles were liquids that could be purified by fractional distillation. In all these cases an initial low-boiling fraction consisting of trialkyl phosphates was obtained. Two of the crystalline oxadiazoles (**6h** and **6i**) were obtained by triturating the oils with suitable solvents, while **6b** was obtained by preparative TLC (Table I; footnote b). They were crystallized from the solvents indicated in Table I. The mother liquor after the isolation of **6h**, on concentration and distillation under vacuum, yielded triethyl phosphate (**7b**) and in the case of **6i**, an analysis by GC showed the presence of triethyl thiophosphate (**7c**).

(20) R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

In most cases the corresponding furoxans were either detected by TLC of the original reaction mixture or isolated and characterized by comparison with authentic samples.[20,21]

Thermolysis of Phosphonates 6a and 6d. Purified samples of each of the two systems (ca. 700 mg) were heated in a sealed tube placed in an oil bath. In the case of **6a** the temperature was maintained between 100 and 110 °C for 45 min, and in the case of **6d** it was maintained between 140 and 145 °C for 30 min. Kugelrohr distillation of the residues afforded trimethyl phosphate (**7a**, 58–60 °C (bath temperature) (3 mm); 10%, footnote c, Table I) from **6a** and triethyl phosphate (**7b**, 68–70 °C (bath temperature) (0.5 mm); 21%, footnote c, Table I) from **6d**; both were characterized spectroscopically.

Thermolysis of 6a in the Presence of Acetophenone. Trapping of Monomeric Methyl Metaphosphate. A reaction mixture consisting of the phosphonate **6a** (1.00 g), acetophenone (10 mL), and 2,2,6,6-tetramethylpiperidine (0.2 mL) was heated in a flask, protected from moisture, at 100 °C for 4 h. The resulting product was partitioned between CH_2Cl_2 (100 mL) and 0.1 N NaOH (100 mL). The aqueous layer was extracted twice with 25-mL portions of CH_2Cl_2 and concentrated in vacuo. The residual wine-red liquid was analyzed by TLC (CH_3OH:CH_3CN, 1:1, v/v). A band with R_f 0.20–0.14 was extracted out with CH_3OH–CH_3CN. Removal of the solvent at reduced pressure yielded the enol phosphate **14** (25 mg; ≃2%; footnote c, Table I): ^1H NMR (D_2O; internal DSS) δ 3.45 (d, 3 H, $^3J_{P-H}$ = 10 Hz; OCH_3; lit.[22] 3.65, d, $^3J_{P-H}$ = 10.8 Hz), 5.24 and 5.10 (two multiplets, each 1 H, H_A and H_B of vinylic group), 7.80–7.40 (m, 5 H, aromatic).

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Registry No. **1a**, 813-77-4; **1b**, 814-49-3; **4a**, 3583-90-2; **4b**, 2942-58-7; **4c**, 87174-50-3; **5a**, 873-67-6; **5b**, 15500-74-0; **5c**, 49660-38-0; **5d**, 37737-65-8; **5e**, 13820-14-9; **5f**, 2574-03-0; **6a**, 87174-51-4; **6b**, 87174-52-5; **6c**, 87174-53-6; **6d**, 87174-54-7; **6e**, 87174-55-8; **6f**, 87174-56-9; **6g**, 87174-57-0; **6h**, 87174-58-1; **6i**, 87174-59-2; **7a**, 512-56-1; **7b**, 78-40-0; **7c**, 126-68-1; **14**, 87174-60-5; bis(4-nitrophenyl)furoxan, 31562-30-8; bis(2,4-dichlorophenyl)-furoxan, 54696-53-6; acetophenone, 98-86-2.

(21) C. Grundmann, *Fortschr. Chem. Forsch.*, 7, 62 (1966); "The Chemistry of the Cyano Group", Z. Rappoport, ed., Wiley-Interscience, New York, 1970, Chapter 14, p 791.

(22) A. C. Satterthwait and F. H. Westheimer, *J. Am. Chem. Soc.*, **102**, 4464 (1980).

Palladium-Catalyzed Conjugate Addition Type Reaction of Aryl Iodides with α,β-Unsaturated Ketones

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Aryl iodides have been found to react with α,β-unsaturated ketones in the presence of catalytic amounts of palladium, an excess of formic acid, and triethylamine, giving rise to conjugate addition type products. The electron-withdrawing power of the group attached to the olefinic double bond, the substituent β to the carbonyl group, and the basic reaction medium appear to affect greatly the conjugate addition/vinylic substitution ratio.

In previous papers[1] we have reported the reaction of arylmercury compounds with α,β-enones in the presence of catalytic amounts of palladium(II) to give conjugate addition type products through in situ generated arylpalladium intermediates. As arylmercury compounds can

Scheme I

(a) $ArH + PdX_2 \longrightarrow ArPdX + HX$

(b) $ArX + Pd(0) \longrightarrow ArPdX$

tolerate a wide variety of functional groups, the reaction allows an easy synthesis of β-aryl ketones and provides an improvement of the conjugate addition methodology. Unfortunately mercurials, even though usually high

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