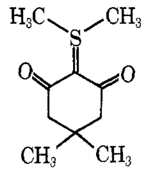
deep red color is produced immediately. A wine-red crystalline compound, formulated as **2** from analytical evidence (*vide infra*), can be isolated from the mixture in moderate yield. The formation of **2** can be regarded as proceeding by nucleophilic addition of the ylide to picryl chloride, followed by elimination of hydrogen chloride. For the elimination step, either the tertiary amine or a second equivalent of ylide can serve as the base. Compound **2** is stable in air and in aqueous solution and can be protonated by dilute mineral acids to produce the colorless conjugate acid **3** of **2**. The pK_a of **3** is 1.8, qualifying it as an unusually strong organic acid. The color change can be reversed by the addition of base to an acidified solution of **2**. The formation of a very stable "anion" in which charge is delocalized over the entire aromatic ring as well as over the sulfuranylidene skeleton is undoubtedly responsible for the acid strength of **3**.

$$\underset{\mathbf{3}}{2H^+X^-} \rightleftharpoons \mathbf{2} + HX$$



4

A similar color is produced when **1** is mixed with *sym*-trinitrobenzene or with trinitrotoluene. Systematic study of these colored complexes[4] is hampered by their propensity toward decomposition and by their apparent lack of simple stoichiometry. Aromatic solvents in general, and nitroaromatic solvents in particular, produce a large downfield shift in the methinyl proton resonance signal of **1**, suggesting that a weak charge transfer interaction may be operating in these cases as well.[5] However, no color was produced when 2-dimethylsulfuranylidene-5,5-dimethylcyclohexane-1,3-dione (**4**)[6] was mixed with *sym*-trinitrobenzene. Beyond these observations, the scope of the substitution reaction remains to be explored, as does the possibility of a parallel reaction in ylides of other elements.

Experimental Section

Ethyl Dimethylsulfuranylidene-2,4,6-trinitrophenylacetate (2).—Ethyl dimethylsulfuranylidenylacetate[3a] (2.25 g, 15 mmol), dissolved in 10 ml of acetone, was mixed with a solution of picryl chloride (1.88 g, 7.6 mmol) in 15 ml of acetone under a nitrogen atmosphere. An intense red color developed immediately. The mixture was refluxed for 90 min, cooled, and evaporated to a small volume. Chromatography in benzene on 300 g of alumina (grade II) caused the product to separate into three colored bands. The first band, eluted rapidly by ether, was evaporated to give a deep red semisolid, 1.41 g. Recrystallization of this material from benzene, ether–petroleum ether, or ethanol–water (best) afforded small deep red prisms: 0.76 g (28%); mp 176° dec (Koeffler block; the melting point varied with heating rate); ir ($CHCl_3$) 1639 (C=C aliphatic), 1600, 1522 (C=C arom), 1515 (CNO_2 asym), 1319 cm^{-1} (CNO_2 sym); nmr ($CDCl_3$) δ 8.73 (s, 2, arom H), 4.07 (q, 2, J = 7.8 Hz, OCH_2CH_3), 3.08 (s, 6, $S^+(CH_3)_2$), 1.19 (t, 3, J = 7.8 Hz, OCH_2CH_3); uv max (CH_3CN) 234 nm (ϵ 10,200), 380 sh (2460), 474 (5240); uv max (95% C_2H_5OH) 230 sh nm (ϵ 29,900), 368 (4410), 469 (8500); pK_a[7] (50% C_2H_5OH) = 1.8.

Anal. Calcd for $C_{12}H_{13}O_8N_3S$: C, 40.11; H, 3.65; N, 11.70; S, 8.93. Found: C, 40.1; H, 3.68; N, 11.7; S, 9.14.

Complex of Ethyl Dimethylsulfuranylidenylacetate with *sym*-Trinitrobenzene.—Equimolar solutions of ylide **1** and *sym*-trinitrobenzene in either cyclohexane, benzene, chloroform, ether, acetonitrile, dioxane, or alcohol gave a deep red color immediately upon mixing, detectable below 5×10^{-5} *M*: uv max (CH_3CN) 220 nm (ϵ 23,600), 438 (13,900), 557 (9110), which changed slowly over 1 hr. No isosbestic point was apparent. A plot of molar absorptivity *vs.* molar concentrations of donor/donor + acceptor for the two longer wavelength maxima showed no maximum between 0.25 and 0.80. An equimolar mixture of ylide **1** and *sym*-trinitrobenzene, 2 *M* in CDCl , displayed a proton resonance spectrum with very broad, undistinguishable signals which changed slowly with time. The spectrum was not sharpened noticeably upon cooling the sample to −35°. No electron spin resonance spectrum could be detected. After 1 hr a sharp proton resonance signal due to dimethyl sulfide became apparent, as did the odor of this compound.

Registry No.—**2**, 29765-36-4.

Acknowledgment.—The authors are indebted to the Department of Organic Chemistry, University of Lund, for elemental analysis.

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[4] E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968).

[5] J. Casanova and R. A. Felix, unpublished observations.

[6] A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968).

[7] C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London, 1967, p 77.

Organophosphorus Enamines. IV.[1] Enamine Thiophosphonates: Preparation and Their Attempted Use in the Synthesis of α,β-Ethylenic Ketones

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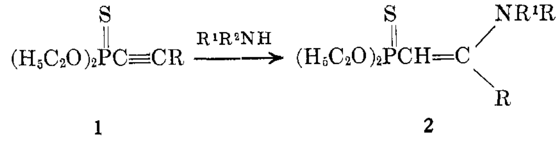
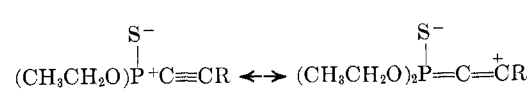
Recently we reported a general synthesis of dialkyl alkynyl-1-thiophosphonates (**1**) which in themselves constitute a new class of phosphorus(V) esters.[3] We now wish to report that addition of amines to the carbon–carbon triple bond in **1** is rather facile, giving enamine thiophosphonates **2** in essentially quantitative yields (eq 1).



$$\underset{\mathbf{1}}{(H_5C_2O)_2\overset{\overset{S}{\|}}{P}C\equiv CR} \xrightarrow{R^1R^2NH} \underset{\mathbf{2}}{(H_5C_2O)_2\overset{\overset{S}{\|}}{P}CH=C\begin{matrix}\diagup NR^1R^2\\ \diagdown R\end{matrix}} \quad (1)$$

R = alkyl, phenyl
R^1 = alkyl, cycloalkyl
R^2 = alkyl, H

No doubt there is some contribution of phosphine-methylene to the transition state of the addition.



$$(CH_3CH_2O)\overset{\overset{S^-}{|}}{P}{}^+C\equiv CR \longleftrightarrow (CH_3CH_2O)_2\overset{\overset{S^-}{|}}{P}=C=\overset{+}{C}R$$

Enamine thiophosphonates **2** produced in this manner are listed in Table I together with their boiling points, yields and chemical analyses.

Enamines **2** (R^1 = alkyl; R^2 = H) have been found to react with NaH to give anions **3** which, when treated

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[1] Parts I, II, and III, Organophosphorus Enamines: A. M. Aguiar, *et al.*, *Tetrahedron Lett.*, 1397, 1401, 1419 (1971).

[2] Awarded Cities Service Award for Excellence in Teaching, 1969.

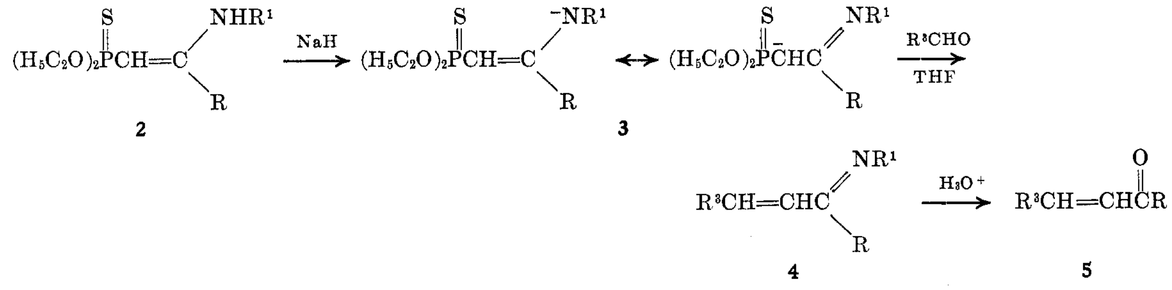
[3] M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, **36**, 2720 (1971).

TABLE I

ENAMINE THIOPHOSPHONATES 2

	R	R¹	R²	Bp, °C (mm)	Yield, %	Calcd, % C	H	N	P	S	Found, % C	H	N	P	S
a	n-C_4H_9	n-C_4H_9	H	121 (0.06)	84	54.70	9.84	4.55	10.07	10.43	54.68	9.78	4.60	10.08	10.49
b	n-C_6H_{13}	n-C_4H_9	H	137 (0.05)	83	57.28	10.22	4.17	9.23	9.56	57.49	10.09	4.03	9.30	9.50
c	n-C_5H_{11}	*tert*-C_4H_9	H	122 (0.04)	82	56.05	10.03	4.36	9.64	9.97	56.03	10.02	4.47	9.77	10.12
d	n-C_6H_{13}	*tert*-C_4H_9	H	137 (0.10)	81	57.28	10.22	4.17	9.23	9.56	56.99	10.37	4.47	8.99	9.74
e	n-C_3H_7	C_6H_{12}	H	134 (0.10)	81	56.40	9.47	4.38	9.69	10.04	56.20	9.57	4.31	9.70	10.11
f	C_6H_5	C_6H_{12}	H	163 (0.09)	79	61.17	7.98	3.96	8.76	9.07	61.41	8.08	4.06	8.67	9.13
g	n-C_7H_{15}	C_2H_5	C_2H_5	141 (0.03)	72	58.42	10.38	4.01	8.86	9.17	58.62	10.40	4.29	8.93	9.35
h	C_6H_5	C_2H_5	C_2H_5	139 (0.04)	85	58.69	8.01	4.28	9.46	9.79	58.68	7.86	4.36	9.39	9.82

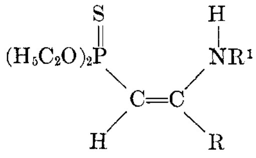
SCHEME I



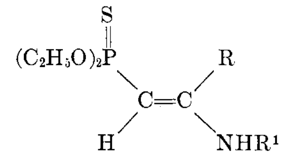
$R = n$-C_3H_7, n-C_6H_{13}
$R^1 = n$-C_4H_9
$R^3 = C_6H_5$, p-$CH_3OC_6H_4$

with aldehydes, produce α,β-ethylenic imines **4**. Imines **4** have been hydrolyzed with 1% aqueous oxalic acid solution to produce α,β-ethylenic ketones **5** (Scheme I).

The ir spectra of **2a–h** show a strong absorption band in the region of 6.25–6.55 μ (C=C). The nmr spectra of each of the enamines **2a–f** (R^1 = alkyl; R^2 = H) display the amino proton signal at two different chemical shifts (δ ~7.40 and ~4.50) which indicates that **2a–f** (R^1 = alkyl; R^2 = H) exist as cis–trans mixtures as shown below.



cis-2



trans-2

Taking into account the deshielding due to the thiophosphonate group, the lower field proton has been assigned to the cis isomer and the higher field to the trans isomer.[4] Two different vinyl protons in the cis–trans mixture of **2a–f** (R^1 = alkyl; R^2 = H) could not be identified because their signals occur in the same general region as the methylene signals of the *O*-ethyl groups (δ 4.35–3.75) and as a rule are obscured by overlapping. Application of a strong magnetic field (100 MHz) produced no practical improvement in the solution of the problem of overlapping, and, as the NH resonances are broad and not generally well separated to permit reliable integration of relative intensities, the quantitative determination of the cis/trans ratio is not possible by this method.

However, enamines **2g, h** (R^1 = alkyl; R^2 = alkyl), resulting from the addition of secondary amines to **1**, are found to exist only in one isomeric form as shown by the presence of one doublet (J_{PH} = 16 Hz, δ 4.52) assigned to the vinyl proton in the nmr of **2h**. This has been assigned a trans configuration because the most stable configuration should have the donor and the acceptor group trans to each other.[4–6] In enamines **2a–f** (R^1 = alkyl; R^2 = H) the cis isomer also exists because of the stability gained by it through hydrogen bonding between the amino proton and the sulfur atom. Steric hindrance no doubt plays a role.

The trans addition of amines to a carbon–carbon triple bond activated by the phosphoryl group has been described.[6] Conceivably in **2**, post-isomerization results in the trans product. This is in accordance with the concept that electron-withdrawing substituents on one end and electron-releasing substituents on the other end of the double bond favor cis–trans isomerization.[7] The excess of amine in the reaction mixture may also be playing some part in the cis–trans isomerization.

The addition of amines to **1** is found to be slower than the addition of amines to diphenyl alkynyl-1-phosphine sulfides.[8] This rate difference is probably due to greater electron withdrawal from the triple bond by the thiophosphoryl group as compared to the thiophosphonate group. This is probably true because in the latter, the lone pairs of electrons on the two oxygen atoms are partially donated to the d orbitals of the phosphorus, thus reducing its net positive charge.

For the synthesis of α,β-ethylenic ketones, enamine phosphonates have been found to be better than the corresponding thiophosphonates **2** (R^1 = alkyl; R^2 = H). These results will be reported shortly.

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(4) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(5) B. C. Saunders and P. Simpson, *J. Chem. Soc.*, 3351 (1963).

(6) W. Hagens, H. J. T. Bos, W. Voskuil, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **88**, 71 (1969).

(7) G. Isaksson, J. Sandström, and I. Wennerbeck, *Tetrahedron Lett.*, 2233 (1967).

(8) C. J. Morrow, Ph.D. Dissertation, Tulane University, 1970.

Experimental Section

The amines were dried over potassium hydroxide pellets and the thiophosphonates **1** were redistilled before use. Acetonitrile was distilled from P_2O_5. The nmr spectra were determined on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N. J.

Preparation of Enamines Thiophosphonates 2a–h. General Procedure.—The diethyl alkynyl-1-thiophosphonates **1** were refluxed with a 10–12 molar excess of the amines. The reflux was continued for 2–4 days until the ir spectra of a test portion of the reaction mixture showed almost complete disappearance of the absorption band in the region of 4.52–54.6 μ (C≡C). In the case of cyclohexylamine, the reaction solution was diluted by the addition of a volume of acetonitrile equal too ne-fourth the original reaction volume. This addition was necessary to keep the reflux temperature low. The solvent and the excess amines were evaporated *in vacuo* at aspirator pressure. The resulting adducts were short path distilled at reduced pressure from anhydrous potassium carbonate.

Diethyl 2-*n*-Butylaminohexenyl-1-thiophosphonate (2a).—The ir spectrum (CHCl$_3$) displayed short absorption bands at 2.92 and 3.08 μ and strong bands at 3.41, 6.25, 9.75, and 10.54 μ: nmr 4.09 (m, 5 H, -CH$_2$OP, PCH=), 3.08 (m, 2 H, NCH$_2$), 2.51 (m, 2 H, =CCH$_2$), 1.21 (m, containing t, J = 6.8 Hz, 20 H, the remaining methyl and methylene protons; the amino proton was observed as low multiplets at 7.35 and 4.45 ppm.

Diethyl 2-*n*-Butylaminooctenyl-1-thiophosphonate (2b).—The ir spectrum (CHCl$_3$) showed short bands at 2.92 and 3.08 μ and strong bands at 3.42, 6.25, 9.65, and 10.55 μ: nmr 7.40 and 4.81 (two low m, 1 H, amino), 4.08 (m, 5 H, CH$_2$OP and PCH=), 3.02 (m, 2 H, (NCH$_2$), 2.50 (m, 2 H, =CCH$_2$), 1.24 ppm (m containing t, J = 6.9 Hz), 24 H, the remaining methyls and methylenes.

Diethyl 2-*tert*-Butylaminoheptenyl-1-thiophosphonate (2c).—The ir spectrum (CHCl$_3$) showed short bands at 2.85 and 3.05 μ and strong bands at 3.38, 6.24, 9.74 and 10.47 μ: nmr 4.12 (m, 5 H, CH$_2$OP and PCH=), 2.41 (m, 2 H, =CCH$_2$), 1.32 (m, 24 H, the remaining methyl and methylene), 7.40 and 4.35 (two low m, 1 H, NH).

Diethyl 2-*tert*-butylaminooctenyl-1-thiophosphonate (2d).—The ir spectrum (CHCl$_3$) displayed a short band at 2.91 μ and strong bands at 3.41, 6.26, 9.74, and 10.56 μ: nmr 4.16 (m, 5 H, CH$_2$OP and PCH=), 2.41 (m, 2 H, =CCH$_2$), 1.25 (m containing t, J = 6.5 Hz), 26 H, the remaining methyls and methylenes; the amino proton was observed as two low multiplets at 7.35 and 4.41 ppm.

Diethyl 2-Cyclohexylaminopentenyl-1-thiophosphonate (2e).—The ir spectrum (CHCl$_3$) displayed short bands at 2.95 and 3.10 μ and strong bands at 3.46, 6.30, 9.76 and 10.56 μ: nmr 4.08 (m, 5 H, CH$_2$OP and PCH=), 3.48 (m, 1 H, NCH), 2.48 (m, 2 H, =CCH$_2$, 1.27 (m containing t, J = 6.7 Hz), 21 H, the remaining methyl and methylenes; the amino proton showed two low multiplets at 7.31 and 4.65 ppm.

Diethyl 2-Cyclohexylamino-2-phenylethenylthiophosphonate (2f).—The ir spectrum (CHCl$_3$) showed short bands at 2.92 and 3.08 μ and strong absorption bands at 3.41, 6.31, 9.75, 10.55, and 11.81 μ: nmr 7.41 (br s, 5 H, phenyl), 4.11 (m, 5 H, (CH$_2$OP and PCH=), 2.88 (m, 1 H, NCH), 1.32 (m containing t, J = 6.8 Hz), 16 H, the remaining methyls and methylenes; 7.30 and 4.65 ppm, two low multiplets, 1 H, amino.

Diethyl 2-Diethylaminononenyl-1-thiophosphonate (2g).—The ir spectrum (CHCl$_3$) displayed strong absorption bands at 3.44, 6.50, 9.75, and 10.58 μ: nmr 4.12 (m, 5 H, CH$_2$OP and PCH=), 3.26 (q, J = 7.2 Hz, 4 H, NCH$_2$), 2.63 (m, 2 H, =CCH$_2$), 1.24 ppm (m containing a t, (J = 6.6 Hz), 25 H, the remaining methyls and methylenes.

Diethyl 2-Diethylamino-2-phenylethenylthiophosphonate (2h).—The ir spectrum (CHCl$_3$) displayed strong absorptions at 3.42, 6.55, 9.76, 10.54, and 12.15 μ: nmr 7.36 (s, 5 H, phenyl), 4.52 (d, J = 16 Hz, 1 H, PC*H*=), 3.79 (two crude q, 4 H, CH$_2$OP), 3.17 (q, J = 7 Hz, 4 H, NCH$_2$), 1.13 ppm (t, J = 7.2 Hz, 12 H, methyls).

Preparation of α,β-Ethylenic Ketones. General Procedure.—Diethyl alkynyl-1-thiophosphonate (0.01 mol) was dissolved in a 10 molar excess of *n*-butylamine and refluxed for 2 days. The excess amine was evaporated on an aspirator and its last traces were removed on a vacuum pump. The resultant adduct was dissolved in 100 ml of tetrahydrofuran and was cooled to 0°. To this THF solution 0.01 mol of NaH was added and stirred for 0.5 hr, 0.01 mol of the aldehyde was added, and the reaction mixture was stirred at 0° for 1 hr and then at room temperature for 6 hr. The solvent was evaporated, and the residue was stirred well with 100 ml of ether and filtered. The ether solution was stirred for 6–7 hr with 100 ml of 1% aqueous solution of oxalic acid. The two phases were separated, and the ether layer was washed with water, dried (MgSO$_4$), filtered, and evaporated. The resulting oil was distilled at reduced pressure to obtain the α,β-ethylenic ketones.

1-(4-Methoxyphenyl)-3-one-1-hexene gave the following data: bp 124–127° (0.05 mm); mp 38–40° (lit.[9] mp 40–41°); yield 34%; the ir spectrum (CHCl$_3$) showed strong absorption bands at 6.07 (C=O) and 6.25 μ (C=C); nmr 7.54 (d, J = 15.5 Hz, 1 H, ArCH=), 7.56–6.78 (m, 4 H, aromatic), 6.62 (d, J = 15.5 Hz, 1 H, =CHCO), 3.76 (s, 3 H, CH$_3$O), 2.62 (t, J = 7.5 Hz, 2 H, OCCH$_2$), 1.68 (m, 2 H, OCCCH$_2$), 0.96 ppm (t, (J = 7.5 Hz, the terminal methyl).

1-Phenyl-3-one-1-nonene gave the following data: bp 118–120° (0.05 mm); mp 42–43° (lit.[10] mp 44°); yield 37%; the ir spectrum displayed strong absorptions at 6.05 (C=O) and 6.22 μ (C=C); nmr 7.59 (d, J = 15 Hz), 1 H, ArCH=), 7.38 (m, 5 H, phenyl), 6.73 (d, J = 15 Hz, 1 H, =CH-CO), 2.61 (t, J = 7.5 Hz, 2 H, -COCH$_2$), 1.62–0.64 ppm (multiplet, the remaining protons).

Registry No.—**2a**, 30669-38-6; **2b**, 30669-39-7; **2c**, 30669-40-0; **2d**, 30669-39-7; **2e**, 30669-42-2; **2f**, 30669-43-3; **2g**, 30669-44-4; **2h**, 30669-45-5; 1-(4-methoxyphenyl)-3-one-1-hexene, 30669-46-6; 1-phenyl-3-one-1-nonene, 30669-47-7.

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[9] E. Friedmann, *J. Prakt. Chem.*, **145**, 321 (1936).

[10] I. M. Heilbron and F. Irving, *J. Chem. Soc.*, 2323 (1928).

Electric Discharge Reactions of C$_1$ to C$_3$ Hydrocarbons[1a]

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The effects of various electric discharges on simple hydrocarbons have been subjected to extensive investigations.[2] Most of these investigations have been concerned with the formation of the low molecular weight products; methane, ethane, ethylene, and actylene have been formed in almost every reported electric discharge reaction on any hydrocarbon. However, a detailed analysis of the higher molecular weight products have not been reported, although a few individual compounds have been identified.[3]

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[1] (a) Supported by NSF Grant GB-8056. (b) University of California, San Diego.

[2] G. Glockler and S. C. Lind, "Electrochemistry of Gases and other Dielectrics," Wiley, New York, N. Y., 1939; G. C. Akerlof and E. Wills, "Bibliography of Chemical Reactions in Electric Discharges," Office of Technical Services, Department of Commerce, Washington, D. C., 1951; B. D. Blaustein, Ed., "Chemical Reactions in Electric Discharge," Advances in Chemistry Series, No. 80, American Chemical Society, Washington, D. C., 1969.

[3] C. Ponnamperuma and F. Woeller, *Nature*, **203**, 272 (1964); C. Ponnamperuma and K. Pering, *ibid.*, **209**, 979 (1966).