fairly rapidly to a stirred suspension of NaH (4.35 g of a 57% dispersion in mineral oil) in 80 ml of monoglyme at room temperature. After completing the addition, the reaction mixture containing a grayish-white solid was heated at 50° for 1 hr and then cooled to room temperature. A solution of chloromethyl methyl ether (8.86 g, 0.11 mol) in 20 ml of monoglyme was added dropwise with stirring to the reaction mixture and, upon completing the addition, the reaction mixture was heated at 50° for 2.5 hr.

After cooling to room temperature, the reaction mixture was filtered and the filter cake was washed with monoglyme. The monoglyme was evaporated off using a rotary evaporator. The liquid residue was subjected to vacuum distillation and yielded 9.7 g (80.5%) of *N*-methoxymethyl-2-oxazolidone (**4**), bp 80–81° (0.07 mm). Another distillation yielded an analytical sample.

Anal. Calcd. for $C_5H_9NO_3$: C, 45.79; H, 6.92; N, 10.68. Found: C, 45.92; H, 7.08; N, 10.77.

***N*-Methoxymethyl-5-phenyl-2-oxazolidone (3).**—The experimental procedure is similar to that described previously. A solution of 5-phenyl-2-oxazolidone (8.1 g, 0.05 mol) in 100 ml of monoglyme was added to a stirred suspension of NaH (2.18 g of 57% dispersion in mineral oil) in 75 ml of monoglyme at room temperature. After addition, the reaction mixture was heated at 50° for 1 hr and then cooled to room temperature. A solution of chloromethyl methyl ether (4.43 g, 0.055 mol) in 25 ml of monoglyme was added dropwise with stirring to the reaction mixture. Upon completing the addition, the reaction mixture was heated at 50° for 1 hr. After cooling to room temperature, the reaction mixture was filtered, the filter cake was washed with monoglyme, and the monoglyme was evaporated off using a rotary evaporator, yielding 8.5 g (82%) of crude **3** melting at 38–39°. One recrystallization from benzene–cyclohexane gave an analytical sample, mp 41–42°.

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; H, 6.76. Found: C, 64.04; H, 6.25; N, 6.67.

***N*-Methoxymethylene-5-phenoxymethylene-2-oxazolidone (1).**

A. From 5-Phenoxymethylene-2-oxazolidone and Chloromethyl Methyl Ether.—The experimental procedure was the same as that described above. A solution of 5-phenoxymethylene-2-oxazolidone (9.6 g, 0.05 mol) in 150 ml of monoglyme was added to a stirred suspension of NaH (2.18 g of 57% dispersion in mineral oil) in 75 ml of monoglyme at room temperature. After addition, the reaction mixture was heated at 50° for 1 hr and then cooled to room temperature. A solution of chloromethyl methyl ether (4.43 g, 0.055 mol) in 25 ml of monoglyme was added dropwise to the stirred reaction mixture. After the addition was complete, the reaction mixture was heated at 50° for 1 hr, cooled to room temperature, and filtered, and the monoglyme filtrate was evaporated on a rotary evaporator. There was obtained 10.2 g (86% yield) of crude **1** with mp 55–61°. Recrystallization from CCl_4–pentane raised the mp to 64–67°.

B. From Phenyl Glycidyl Ether and Methoxymethyl Isocyanate.—We have previously reported[1] the preparation of **1** from reaction of phenyl glycidyl ether and methoxymethyl isocyanate using a hydrocarbon-soluble tributylphosphine oxide–lithium bromide adduct. The material isolated had mp 69.5–70.5°.

Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90; mol wt, 237. Found: C, 60.57; H, 6.41; N, 6.06; mol wt, 253.

Spectral data and mixture melting point indicated that this material was the same as that prepared from 5-phenoxymethylene-2-oxazolidone and chloromethyl methyl ether.

***N*-*p*-Toluenesulfonyl-5-phenoxymethylene-2-oxazolidone (5).**—A solution of 5-phenoxymethylene-2-oxazolidone (0.6 g, 0.05 mol) in 100 ml of monoglyme was added as described above to a stirred mixture of NaH (2.18 g, 57% in mineral oil) in 50 ml of monoglyme at room temperature. After addition, the reaction was heated at 40° for 0.5 hr and then cooled to room temperature. A solution of *p*-tolylsulfonyl chloride (9.5 g, 0.05 mol) in 50 ml of monoglyme was added dropwise to the stirred reaction mixture. After addition, the reaction mixture was heated at 50–55° for 2.5 hr.

After cooling to room temperature, the reaction mixture was filtered, the filter cake was washed with monoglyme, and the monoglyme was evaporated using a rotary evaporator. There was obtained 11.5 g (66%) of crude **5**. Recrystallization from benzene yielded an analytical sample, mp 156.5–157.5°.

Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.77; H, 4.93; N, 4.03; S, 9.23; mol wt, 347. Found: C, 58.76; H, 4.94; N, 4.01; S, 9.19; mol wt, 350.

This material was also prepared in 83.7% yield by using the solubilized lithium bromide–tributylphosphine oxide catalyst with phenyl glycidyl ether and *p*-toluenesulfonyl isocyanate.[3]

Registry No. —**1**, 34277-53-7; **2**, 17539-83-2; **3**, 34277-55-9; **4**, 34277-56-0; **5**, 34277-57-1.

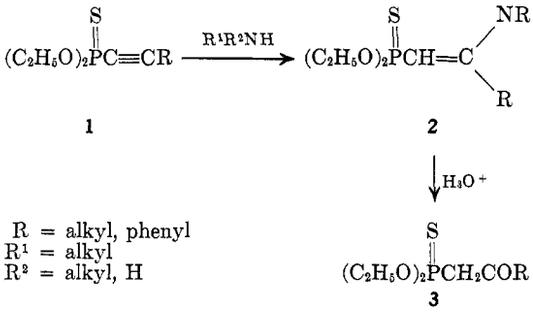
Organophosphorus Enamines. VI. Use of Enamine Thiophosphonates in the Synthesis of Diethyl β-Ketothiophosphonates

MOHINDER S. CHATTHA AND ADAM M. AGUIAR*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received November 5, 1971

Recently we reported a general preparation of dialkyl alkynyl-1-thiophosphonates (**1**).[1] We also found that the addition of amines to the alkynyl-1-thiophosphonates **1** is rather facile giving enamine thiophosphonates **2** in excellent yields.[2] We now wish to report that enamine thiophosphonates **2** can be very conveniently hydrolyzed with aqueous oxalic acid to afford diethyl β-ketothiophosphonates **3** in good to excellent yields (eq 1).



Diethyl β-ketothiophosphonates (**3**) represent a new class of phosphorus(V) esters which have not been described in the literature to date. Our method affords a very simple and high-yield preparation of these compounds **3**. The success of this method is based upon the fact that the enamine moiety in **2** is much more readily hydrolyzed as compared to the ester function. Also, it is interesting to note that the rate of addition of amine to the triple bond in **1** is much faster than the rate of displacement of the ethoxy groups.

The compounds **3** prepared by this method are listed in Table I together with their boiling points and yields.

Because of their similarity to the Emmons reagents, compounds **3** should be useful in the synthesis of α,β-unsaturated ketones[3] and cyclopropyl ketones.[4] Compounds **3** also seem to be potentially important ligands; work in that direction is in progress.

The ir spectra ($CHCl_3$) of all the compounds **3a–e** show strong absorption in the region of 5.80–5.87 μ (C=O). In the nmr spectra of **3a–e**, the *P*-methylene protons exhibit a doublet (J_{PH} = 20 Hz) in the region of δ 3.21–3.34. The methylene protons from the *O*-

(1) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, **36**, 2720 (1971).
(2) M. S. Chattha and A. M. Aguiar, *ibid.*, **36**, 2892 (1971).
(3) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).
(4) H. Normant and G. Sturts, *C. R. Acad. Sci.*, **256**, 1800 (1963).

TABLE I
DIETHYL β-KETOTHIOPHOSPHONATES 3[a]

Series	R	Bp, °C (mm)	Yield,[b] %
a	CH_3	70–71 (0.12)	85
b	n-C_3H_7	101 (0.50)	92
c	n-C_4H_9	96–97 (0.10)	93
d	n-C_6H_{13}	140 (0.76)	87
e	$C_6H_5CH_2CH_2$	157–158 (0.10)	71

[a] Satisfactory analytical values (±0.4% for C, H, P, S) were obtained for all compounds. [b] This is the per cent yield of the distilled material based on the starting alkynyl-1-thiophosphonates 1.

ethyl groups display two quartets (J_{PH} = 7.5, J_{PH} = 10.5 Hz) at δ ~4.15. However, at 100 MHz, further resolution into four quartets occurs. This splitting pattern is apparently due to the magnetic nonequivalence of these methylene protons.

Experimental Section

The nmr spectra were determined on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. The chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N.J.

Preparation of Diethyl β-Ketothiophosphonates 3a–e. General Procedure.—The diethyl alkynyl-1-thiophosphonates 1 (0.025 mol) were refluxed with a 10–12 molar excess of n-butylamine. The reflux was continued for 2–3 days until the ir spectra of a test portion of the reaction mixture showed complete disappearance of the absorption band in the region of 4.52–4.56 μ (C≡C).[2] The excess amine was evaporated *in vacuo* at aspirator pressure. The resulting adduct was dissolved in ether (100 ml) and 100 ml of 1% aqueous solution of oxalic acid was added. The two-layer reaction mixture was stirred for 4–5 hr at room temperature and then transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted twice with 25-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and filtered, and ether was distilled off. The resulting oil was short path distilled under reduced pressure.

Registry No.—**3a**, 1067-72-7; **3b**, 34281-17-9; **3c**, 34297-64-8; **3d**, 34281-18-0; **3e**, 34281-19-1.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739. We also wish to thank Dr. Joseph D. Wander for the 100-MHz spectra.

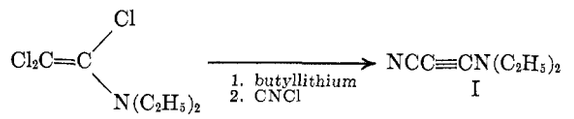
Preparation of *N*,*N*-Diethylcyanoynamine and Its Reactions with Phenyl Isocyanate and Phenylsulfene

MARTIN E. KUEHNE* AND HAROLD LINDE

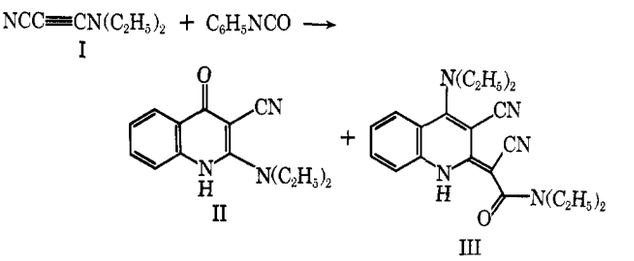
Department of Chemistry, University of Vermont, Burlington, Vermont 05401

Received October 1, 1971

In a previous investigation of ynamine chemistry[1] we had prepared *N*,*N*-diethylcarbomethoxyethynylamine by a reaction of methyl chlorocarbonate with the lithium salt of *N*,*N*-diethylethynylamine. Similarly, the cyanoynamine I could be prepared in 63% yield from *N*,*N*-diethyltrichlorovinylamine, n-butyllithium, and cyanogen chloride.[2,3]



While our earlier study had shown that phenyl isocyanate adds to ynamines with methyl, phenyl, and carbomethoxy substituents to give 4-amino-2-quinolones and 2-amino-4-quinolones, we have now found that the cyanoynamine I reacts with phenyl isocyanate to produce a 2-amino-4-quinolone II and a 2:1 adduct of ynamine and phenyl isocyanate as the major product. Spectroscopic evidence indicated a conjugated dinitrile diethylamide with four aromatic protons and one NH proton [ir 3420, 2205, 2180, 1612 cm^{-1}; nmr δ 1.29 (t, 12 H), 3.6 and 3.8 (q, 8 H), 7.6 (m, 4 H), 15.0 (s, 1 H); m/e 363 (parent), 100 (100%, diethyl amide)]. A 4-amino-2-quinolone methine or a 2-amino-4-quinolone methine structure was thus possible for the 2:1 adduct. The first alternative, III, could be established by single-crystal X-ray analysis.[4]



The formation of the new product does not seem to be due to reaction of an initially formed 4-amino-2-quinolone with a second equivalent of ynamine, since attempts to add the cyanoynamine I to 3-phenyl or 3-carbomethoxy-4-amino-2-quinolones led only to recovered starting materials. Furthermore, very slow addition of the cyanoynamine to 2 equiv of phenyl isocyanate again gave only the initially observed products and unreacted phenyl isocyanate, but no 4-amino-2-quinolone.

These results demonstrate a third reaction pathway for the addition of phenyl isocyanate to an ynamine. In addition to the initially observed six-center reaction (path a, stepwise or concerted) leading directly to 4-amino-2-quinolones and the β-lactam formation (path b) as intermediate to 2-amino-4-quinolones, one now encounters addition of the ynamine to the carbonyl double bond of phenyl isocyanate (path c), followed by ring opening and addition of a second equivalent of ynamine to the keteneimine.[5,6] An alternative scheme, where the four-membered intermediate of path b is

(1) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4407 (1968).

(2) The principle of this reaction was first described by J. Ficini and C. Barbara, *Bull. Soc. Chim. Fr.*, 2787 (1965).

(3) An alternative route to cyanoynamines from chlorocyanoacetylene and secondary amines has since been described: T. Sasaki and A. Kojina, *J. Chem. Soc. C*, 476 (1970).

(4) We thank Drs. J. A. Lerbscher and J. Trotter of the University of British Columbia, Vancouver, Canada, for the results of this study which will be published separately.

(5) Reactions of *N*-phenylketeneimines with ynamines have been found to produce 2-alkyl-4-aminoquinolines: L. Ghosez and P. de Perez, *Angew. Chem., Int. Ed. Engl.*, **10**, 184 (1971).

(6) Alkyl isocyanates and diethylamino-1-propyne gave keteneimines: J. U. Piper, M. B. Allard, and V. Lee, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, ORGN 103.