Registry No.—**2a**, 34220-09-2; **2b**, 34220-10-5; **2c**, 34220-11-6; **3a**, 34226-07-8; **3b**, 34220-12-7; **3c**, 34220-13-8; **4**, 34226-08-9; lithium aluminum hydride, 16853-85-3.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

Preparation of Nitriles from 1,2,5-Oxadiazoles by Reduction with Triphenyl Phosphite[1,2]

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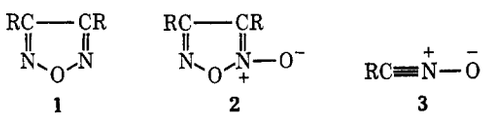
The 1,2,5-oxadiazoles **1** can be made[3a,b] by dehydration of 1,2-dioximes and by deoxygenation[4] of 1,2,5-oxadiazole 2-oxides **2**. The latter are obtained[3] from 1,2-dioximes by oxidation and from nitrile oxides **3** by dimerization.[5]



1 **2** **3**

The present note reports our results on the conversion of 1,2,5-oxadiazoles (and their 2-oxides) to nitriles. We heated a number of the oxadiazoles with triphenyl phosphite (chosen for cost and convenient boiling point) and were pleased to find that nitriles were produced in preparatively useful amounts. Since the 1,2,5-oxadiazole 2-oxides are reduced to the 1,2,5-oxadiazoles under much milder conditions[4] than ours, we believe that the reactions we report here are all conversions of 1,2,5-oxadiazoles to nitriles.

After the completion of our study a note without experimental details appeared[6] describing the cleavage and reduction to dicyano compounds of the 1,2,5-oxadiazole 2-oxides prepared from acenaphthylenequinone dioxime and camphorquinone dioxime. These workers used trimethyl phosphite and attributed the easy reduction to ring strain because the oxadiazole ring is fused to another 5-ring in each of their examples. We find their argument convincing as a reason for the ease of the reaction in the cases they report, but our findings indicate that under more strenuous conditions this reductive cleavage is general.

The ultimate utility of this sequence in preparative chemistry remains to be worked out. We note, however, that the overall conversion of a ketone with an adjacent CH_2 group to two cyano groups may be a useful alternative to other cleavage schemes.

Our results are too fragmentary to support any speculations about the effects of substituents on yield. Much of the difference in yields reported here can be accounted for by higher losses in isolation and purification of very volatile or very soluble nitriles. The yields are collected in Table I and a typical experiment is described in the Experimental Section.

TABLE I

R in **1** or **2**	Ref	RCN, %	Notes
Phenyl **1**	*a*	79	*f*
Phenyl **2**	*b*	87.4	*f*
4-Methoxyphenyl **2**	*c*	31.4	*g*, *h*
2-Furyl **2**	*d*	22.3	*g*
Ethyl **2**	*e*	65.2	*g*
Methyl **2**	*e*	38.7	*g*

[a] K. Auwers and V. Meyer, *Ber.*, **22**, 714 (1889). [b] J. H. Boyer and U. Toggweiler, *J. Amer. Chem. Soc.*, **79**, 895 (1957). [c] G. Ponzio, *Gazz. Chim. Ital.*, **36**, 596 (1906). [d] H. Rheinboldt, *Justus Liebigs Ann. Chem.*, **451**, 167 (1926). [e] T. Mukaiyama and T. Hoshino, *J. Amer. Chem. Soc.*, **82**, 5339 (1960). [f] Reaction mixture was yellow-orange. [g] Reaction mixture was black. [h] Nitrile mp 57–58° (EtOH) [lit. mp 59°: W. Reinder and W. E. Ringer, *Recl. Trav. Chim. Pays-Bas*, **18**, 328 (1899)].

Experimental Section

It is advisable to use triphenyl phosphite that has been washed with alkali and then water and has been thoroughly dried.

Benzonitrile from 3,4-Diphenyl-1,2,5-oxadiazole 2-Oxide.—To 26.0 g (0.084 mol) of triphenyl phosphite preheated to 270° in a flask equipped with a stirrer, a thermometer in the liquid, and a reflux condenser was added a mixture of 10.00 g (0.042 mol) of 3,4-diphenyl-1,2,5-oxadiazole 2-oxide and 26.0 g of triphenyl phosphite. The reaction mixture, which heated up spontaneously and turned light yellow-orange, was kept under reflux by external heating for 15 min longer and was then fractionated in vacuum to give 7.57 g (87.4%) of benzonitrile identical (infrared) with an authentic sample.

Registry No.—Benzonitrile, 100-47-0; 3,4-diphenyl-1,2,5-oxadiazole-2-oxide, 5585-14-8; triphenyl phosphite, 101-02-0.

Nonequivalency of *exo*-*N*-Methylene Protons of Some 2-Oxazolidones

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Received August 13, 1971

A previous publication[1] reported the preparation of 2-oxazolidones in excellent yields using a hydrocarbon-soluble catalyst composed of lithium bromide and tributylphosphine oxide. The cycloaddition reaction of methoxymethyl isocyanate with phenyl glycidyl ether in benzene gave *N*-methoxymethylene-5-phenoxymethylene-2-oxazolidone (**1**), mp 69.5–70.5°.

Nmr analysis of this compound in *o*-dichlorobenzene and deuteriochloroform indicated that the *exo*-*N*-methylene protons were nonequivalent. We would like to report some additional nmr studies which further

(1) Taken from the Ph.D. Dissertation of Stanley M. Katzman, University of Missouri—Kansas City, January 1967.

(2) Support by the National Science Foundation under Grant No. G10031 is gratefully acknowledged.

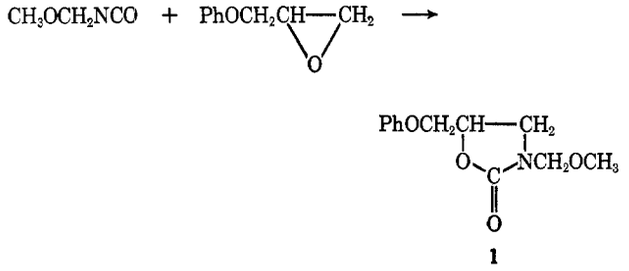
(3) (a) J. Doeuvre in "Traité de Chimie Organique," Vol. 21, V. Grignard, G. Dupont, and R. Locquin, Ed., Masson et Cie, Paris, 1953. (b) L. C. Behr in "Heterocyclic Compounds," Vol. 17, A. Weissberger and R. H. Wiley, Ed., Wiley-Interscience, New York, N. Y., 1962. (c) J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, **59**, 429 (1959).

(4) (a) T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962); (b) Ch. Grundmann, *Chem. Ber.*, **97**, 575 (1964); (c) A. S. Bailey and J. M. Evans, *Chem. Ind. (London)*, 1424 (1964).

(5) Ch. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer Verlag, West Berlin and Heidelberg, 1971.

(6) Altaf-Ur-Rahman and A. J. Boulton, *Chem. Commun.*, 73 (1968).

(1) J. E. Herweh and W. J. Kauffman, *Tetrahedron Lett.*, 809 (1971).



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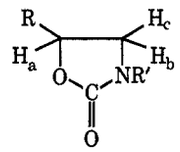
elucidate the factors affecting the nonequivalency of the *exo*-*N*-methylene protons.

A number of 2-oxazolidones have been prepared and their nmr spectral characteristics are tabulated in Table I. The compounds investigated were designed



to determine the effect of the asymmetric center and the methoxy group on the nonequivalency of the *exo*-*N*-methylene protons.

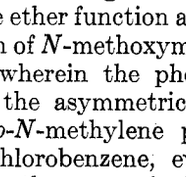
Nmr analysis of *N*-methoxymethylene-2-oxazolidone (**4**) in *o*-dichlorobenzene to −10° and deuteriochloroform to −30°, with and without europium shift reagents (see Experimental Section), indicated that the *exo*-*N*-methylene protons were equivalent.

Low-temperature analysis of *N*-butyl-5-phenoxymethylene-2-oxazolidone (**2**) in *o*-dichlorobenzene to −10° and deuteriochloroform to −30°, with and without spin decoupling of the adjacent butyl methylenes, indicated nonequivalency of the *exo*-*N*-methylene protons. However, in no case did the nonequivalency become large enough to cause sharp splitting of the nmr signals. In order to more clearly demonstrate this nonequivalency, the effect of a europium shift reagent on the *exo*-*N*-methylene protons was examined. The addition of $Eu(fod)_3$ to **2** (10%, $CDCl_3$) in calculated small amounts resulted in resolution of the *N*-butyl group and simultaneously the *exo*-*N*-methylene protons became nonequivalent. Enough shift reagent was added to shift the signals and enable spin decoupling to be accomplished. The results are shown in Table II.

Spin decoupling the $H_{e\beta}$ butyl methylene protons produced an AB quartet for the H_d *exo*-*N*-methylene protons and verfiied their assignment. The data (Table II) show that the *exo*-*N*-methylene protons shift much faster than the adjacent ring methylene protons, which shift at about the same rate as the β methylene protons of the butyl group. The data also indicate that the shift reagent is coordinating with the 2-oxazolidone function and not the ether function at ring position 5.

Nmr investigation of *N*-methoxymethylene-5-phenyl-2-oxazolidone (**3**), wherein the phenyl moiety is attached directly to the asymmetric carbon, indicated again that the *exo*-*N*-methylene protons were nonequivalent in *o*-dichlorobenzene, even at room temperature. However, the nonequivalency of the *exo*-*N*-methylene protons were not manifested at room temperature in deuteriochloroform as the solvent. In the case of compound **3** the magnitude of the nonequivalency at room temperature was not so great as in the

TABLE I
NMR SPECTRAL DATA[a]

Compd	R	R′	Chemical shifts, δ ppm (TMS = 0) H_a	H_b	H_c	$H_{dd'}$	H_e	$H_{ff'}$
1[b]	$PhOCH_2$	CH_3OCH_2	4.80 (m)	3.77 (t, J_{ba} = J_{bc} = 8.50 Hz)	3.62 (dd, J_{cb} = 8.50, J_{ca} = 6.50 Hz)	4.15, 5.23 (q, $J_{dd'}$ = 10.75 Hz)[c]	3.35 (s)	4.49, 3.73 (dq, J_{fa} = $J_{f'a}$ = 4.00, $J_{ff'}$ = 10.50 Hz)
2[b]	$PhOCH_2$	$CH_3(CH_2)_2CH_2$	5.05 (m)	3.86 (t, J_{ba} = J_{bc} = 8.50 Hz)	3.70 (dd, J_{ca} = 6.50 Hz)	3.42 (t, J_{de} = 7.00 Hz)	1.50 (m)	4.07, 4.53 (dq, J_{fa} = $J_{f'a}$ = 4.00, $J_{ff'}$ = 10.50 Hz)
3[b]	Ph	CH_3OCH_2	5.50 (dd, J_{ab} = 9.00, J_{ae} = 7.50 Hz)	3.99 (t, J_{bc} = J_{ba} = 9.00 Hz)	3.32 (dd, J_{cb} = 9.00, J_{ca} = 7.50 Hz)	4.41, 4.89 (q, $J_{dd'}$ = 10.75 Hz)[d]	3.30 (s)	
4	H_I	CH_3OCH_2	4.55 (m)	3.68 (m)	3.68 (m)	4.64 (s)	3.28 (s)	4.55 (m)
5[c]	$PhOCH_2$		5.05 (m)	4.27 (t, J_{bc} = J_{ba} = 9.00 Hz)	3.98 (dd, J_{ca} = 6.25 Hz)	7.92 (d, J_{de} = 8.25 Hz)	7.50 (d)	4.15 (m, obscured)

[a] The nmr spectra were determined in *o*-dichlorobenzene (20–30%) at 25°, except compound **5** which was determined in DMSO-d_6. A comparison with spectra in deuteriochloroform indicated very little change in chemical shifts. [b] The phenyl absorptions for compound **1** occurred at δ 7.40–6.90 (m); compound **2**, 7.80–7.20 (m); compound **3**, 7.32 (s). [c] The H_D protons were also nonequivalent in $CDCl_3$ at room temperature.[1] [d] The H_D protons were equivalent in $CDCl_3$ at room temperature. [e] The ortho, meta, and para protons of the phenoxy group appear as multiplets at δ 7.25, 6.72, and 6.95, respectively. The meta absorptions were unusually shifted upfield in comparison with other 5-phenoxy-2-oxazolidones. The assignments were made by comparison with spectra of other compounds and integration of peak areas. Decoupling experiments on the H_{de} protons of **5** determined the location of the H_e protons. At 100° the meta protons were observed to shift downfield 0.1 ppm and remained constant at 150°. The ortho and para protons were unaffected by temperature changes.

TABLE II
SHIFTS AND GRADIENTS OBSERVED FOR COMPOUND 2[a]

	Shift[b]	Gradient[c]
H_a	0.7	2.6
H_b, H_c [d]	1.0	3.5
H_d	1.9	7.0
$H_{d'}$	1.6	5.8
$H_{e\beta}$	0.95	3.5
$H_{e\gamma}$	0.56	2.0
H_f	0.32	1.2
H_g	0.28	1.1

[a] A 10% solution of **2** in $CDCl_3$ with 0.27 molar equiv of Eu(fod)$_3$ per mol of substrate. [b] Expressed in parts per million downfield from the position of resonance in the absence of Eu(fod)$_3$. [c] Expressed in parts per million per mol of Eu(fod)$_3$ per mol of substrate. [d] Data undiscernible due to complexity, but both shifted approximately as described.

N-methoxymethylene-5-phenoxymethylene-2-oxazolidone (**1**). However, in both compounds the nonequivalency of the *exo*-*N*-methylene protons disappeared at the same temperature, namely at 100–120°. The temperature required for equivalency of these *exo*-*N*-methylene protons is quite high and is higher than that observed for the phenoxymethylene protons which are adjacent to the asymmetric center. In all the compounds containing the 5-phenoxymethylene protons, the methylene protons became equivalent on heating to 80° in *o*-dichlorobenzene. From considerations of Dreiding models, it can be seen that for free rotation to occur, the methoxy oxygen must eclipse the carbonyl group in position 2 and the lone pair of electrons on nitrogen. It has been reported[2] that acyclic urethanes possess the same dipolar resonance interactions as observed in amides and an energy of activation on the same order of magnitude. No such dipolar resonance has been reported in cyclic urethanes (2-oxazolidones) because of the inability to use nmr techniques as in the acyclic systems. However, this possibility cannot be discounted. Any dipolar resonance structures would increase the magnitude of the eclipsed polar interaction with the methoxyl oxygen and decrease the eclipsed interaction with the lone pair.

The temperature effect on the spectra indicates that the conformer interconversions are fast on the nmr time scale, and that the nonequivalency must be due to unequal conformer populations. The influence of the asymmetric center on the various conformers gives rise to the magnitude of the nonequivalency of the *exo*-*N*-methylene protons. The nonequivalency of these protons in the *N*-methoxymethylene-2-oxazolidones is greater than in the *N*-butyl-2-oxazolidones owing to a larger inequality in conformer population. This is caused by a greater difference in conformation energies owing to the electronic interactions of the methoxy group.

An interesting observation is that the nonequivalency of the *exo*-*N*-methylene protons is greater for **1** than for **3**. Consideration of Dreiding models indicates that in **1** the phenoxymethylene group can be oriented so that the *exo*-*N*-methylene protons are affected more strongly by the phenyl moiety.

An indication that this could be the case can be seen in the nmr spectrum of *N*-*p*-tolylsulfonyl-5-phenoxymethylene-2-oxazolidone (**5**). In this compound we observed that the meta protons on the phenoxy ring were *unusually* shifted upfield (see Table I).[3]

This upfield shift indicates a possible interaction with the *N*-sulfonyl group. The meta protons were observed to shift as a function of temperature. Nmr data indicate that the meta protons reach a constant chemical-shift value at approximately the same temperature that the phenoxymethylene protons become equivalent. At this point free rotation about the carbon–carbon bond, to which the phenoxy group is attached, occurs and any conformation preference of the phenoxy group is overcome.

In summary, we have demonstrated that the nonequivalency of the *exo*-*N*-methylene protons in *N*-methoxymethylene-2-oxazolidones is caused by unequal conformer populations, possibly owing to electronic interactions of the methoxy group. The temperature effect on the spectra indicate that the *exo*-*N*-methylene nonequivalency is not due to chirality (intrinsic nonequivalence). The equivalency of *exo*-*N*-methylene protons in compound **4** is probably accidental[4] and can best be rationalized by stating that the environment of the different conformers is not sufficiently different to allow for observation of nonequivalency. Furthermore, indications are that the nonequivalency is greater for **1** than for **3** because of increased interaction of the phenyl ring with the N substituent.

Experimental Section

General.—Phenyl glycidyl ether, *n*-butyl isocyanate, and chloromethyl methyl ether were distilled prior to use. 2-Oxazolidone was purchased from Aldrich Chemical Co. *N*-Butyl-5-phenoxymethylene-2-oxazolidone (**2**) was prepared as previously reported.[5] Solvents used as reaction media were dried by appropriate means. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared absorption spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer. The nmr spectra were determined on a Japan Electron Optics Lab 4H-100 spectrometer using TMS as an internal standard and solvents as indicated. The chemical shift work was accomplished with Eu(fod)$_3$ in $CDCl_3$ at 25°.

5-Phenyl-2-oxazolidone (**6**).—Compound **6** was prepared (70.5%) according to the procedure of Poos[6] and coworkers. The crude product **6**, melting at 88–91° (lit. mp 88.5–89.5°), was used without further purification.

5-Phenoxymethylene-2-oxazolidone (**7**).—The procedure of Oda and Hata[7] was used with some modification, the latter being that a mixture of urea (120 g 2.0 mol) and phenyl glycidyl ether (171.7 g, 1.28 mol) was heated to 150°. At *ca.* 150° a relatively violent exothermic reaction occurred and the temperature rose to 215° with frothing. The reaction mixture was left to cool and then extracted with 1600 ml of hot chloroform. Enough pentane was added to produce turbidity. The resulting mixture was cooled to ice-bath temperature and the precipitate was filtered. One recrystallization of the dried filter cake from ethyl acetate gave 5-phenoxymethylene-2-oxazolidone, mp 121.5–123° (lit.[7] mp 124°).

N-**Methoxymethyl-2-oxazolidone** (**4**).—A solution of 2-oxazolidone (8.71 g, 0.1 mol) in 150 ml of monoglyme was added

(2) W. E. Stewart and T. H. Siddall, *Chem. Rev.*, **70**, 550 (1970).

(3) J. E. Herweh and W. J. Kauffman, *J. Heterocycl. Chem.* **8**, 983 (1971).

(4) We would like to acknowledge the reviewer's comments concerning this interpretation.

(5) J. E. Herweh, T. A. Foglia, and D. Swern, *J. Org. Chem.*, **33**, 4029 (1968).

(6) G. Poos, J. Carson, J. Rosenau, A. Roszkowski, N. Kelley, and J. McGowin, *J. Med. Chem.*, **6**, 266 (1963).

(7) R. Oda and M. Hata, *Nippon Kaguku Zasski*, **82**, 1426 (1962); *Chem. Abstr.*, **58**, 3337 (1963).

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

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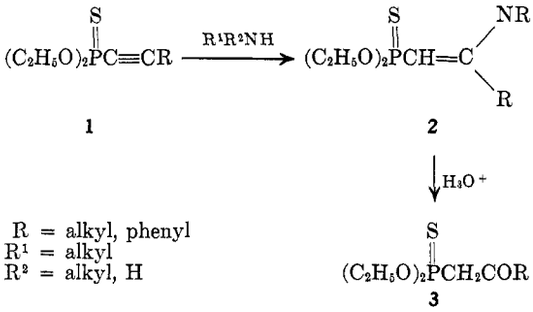
Received November 5, 1971

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).