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.

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

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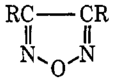
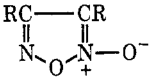
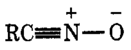
The 1,2,5-oxadiazoles **1** can be made[3a,b] by dehydration of 1,2-dioximes and by deoxygenation[4] of 1,2,5-oxadiazole 2-oxides **2**. The latter are obtained[3] from 1,2-dioximes by oxidation and from nitrile oxides **3** by dimerization.[5]



1



2



$RC{\equiv}\overset{+}{N}{-}\overset{-}{O}$

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.

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[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).

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

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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

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