

Neutral Conversion of Aldoximes into Nitriles at Low Temperature

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Summary (*E*)- and (*Z*)-Aldoximes can be induced to lose water to yield nitriles at, or slightly above, room temperature in dichloromethane solution by treatment with 1,1'-dicarbonylbi-imidazole.

THE dehydration of aldoximes to nitriles often involves heating and/or acidic or basic catalysis, which may be detrimental to complex molecules.

In the course of our investigations on the structures of some unusual nitrones¹ we examined the reaction between (*E*)- and (*Z*)-aldoximes and 1,1'-dicarbonylbi-imidazole. When, for example, one equivalent of the carbonylbi-imidazole in dichloromethane solution was added to one equivalent of (*Z*)-*p*-chlorobenzaldoxime in the same solvent at room temperature, immediate vigorous evolution of carbon dioxide occurred and, after extraction of the

TABLE

Nitriles obtained from selected oximes on treatment with carbonylbi-imidazole

	Oxime ^a	Nitrile	Yield (%)
(1)	(<i>E</i>)- <i>p</i> -Nitrobenzaldoxime ^b	<i>p</i> -Nitrobenzonitrile	99
(2)	(<i>E</i>)- <i>p</i> -Chlorobenzaldoxime	<i>p</i> -Chlorobenzonitrile	95
(3)	(<i>Z</i>)- <i>p</i> -Chlorobenzaldoxime ^c	<i>p</i> -Chlorobenzonitrile	98
(4)	2,2-Dimethylpropanaldoxime ^d	2,2-Dimethylpropionitrile	95

^a The oximes were prepared by standard procedures. ^b Heated under reflux for 6 h in dichloromethane. ^c Prepared according to the method of C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, 1955, **20**, 1491. ^d This mixture of (*E*)- and (*Z*)-oximes reacted explosively with carbonylbi-imidazole when mixed neat. The crude mixture of oximes was used directly.

imidazole (or filtration through an alumina column), *p*-chlorobenzonitrile was isolated as the only product. On the other hand, (*E*)-*p*-methoxybenzaldoxime required, for 75% conversion into the corresponding nitrile, heating under reflux in dichloromethane solvent for 3 h; conditions which we consider mild.

been successfully converted, by the method indicated, into the corresponding nitriles in the isolated yields shown.[†]

One of us (H.G.F.) acknowledges financial aid from the Fund for Scientific Education, Inc., Philadelphia, Pennsylvania.

The Table presents a series of typical oximes which have

(Received, 1st June 1973; Com. 790.)

[†] The products were compared to known materials. Satisfactory analyses have been obtained. The yields reported have been obtained more than once for each compound shown in the Table.

¹ D. R. Dalton, K. N. Trueblood, and M. R. Murphy, *Tetrahedron Letters*, 1973, 779.