COMMUNICATIONS

Pyrolysis of Oxime Carbonates: Novel Conversion of Aldehydes into Nitriles under Mild Conditions

J. M. PROKIPCAK AND P. A. FORTE
Department of Chemistry, University of Guelph, Guelph, Ontario

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A new synthesis of nitriles is reported based on the pyrolysis of oxime carbonates.

On rapporte une nouvelle synthèse des nitriles qui fait appel à la pyrolyse de carbonates d'oximes.

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Recently there have been reports for preparing nitriles using dialkyl hydrogen phosphonates (1), 3-chloro-1,2-benzisothiazole-*S*,*S*-dioxide (2), and chlorothionoformate (3) derivatives of oximes. Other methods generally used involve more vigorous fragmentation of oxime esters under a variety of conditions (4). We wish to report a new relatively mild method of effecting this conversion of aldehydes to nitriles without use of any acidic or basic reagents.

Various aldoximes **1** which were readily available from the aldehydes were treated with phenyl chloroformate to yield the desired oxime carbonate **2**. Thermal decomposition of these oxime carbonates produced high yields of the corresponding nitriles. A typical transformation is depicted in Scheme 1.

The method seems applicable to both aliphatic and aromatic systems. A summary of our results to date is given in Table 1.

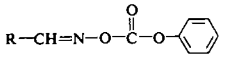
Although the mechanistic details of the reaction are not yet understood, a possible six-centered transition state **3** could be involved.

TABLE 1. Preparation and pyrolysis* of oxime carbonates†

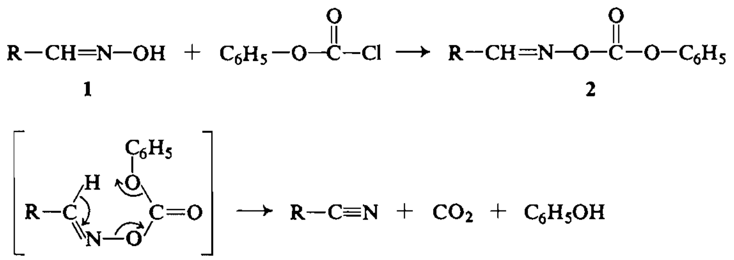
Starting oxime	Melting point of oxime carbonate (°C)	Yield of nitrile (%)
anti-p-Nitrobenzaldoxime	151 (dec)	90
syn-p-Chlorobenzaldoxime	115	90
syn-Benzaldoxime	83	85
syn-p-Methylbenzaldoxime	91	90
syn-p-Methoxybenzaldoxime	115 (dec)	85

*All decompositions were carried out at approximately 100–110°.

†Structure of carbonate is



Further work on the synthetic scope as well as the mechanistic aspects of this reaction is now underway and will be reported in due course. The reaction itself has possible synthetic use because of the relatively mild temperatures required to effect the conversion, excellent yields of the nitriles, and no use of any acidic or basic reagents.



$$\underset{\mathbf{1}}{R{-}CH{=}N{-}OH} + C_6H_5{-}O{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow \underset{\mathbf{2}}{R{-}CH{=}N{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_6H_5}$$

SCHEME 1.

All the oximes used were prepared by standard routes. The general experimental procedure is illustrated for the preparation of the carbonate of *syn*-anisaldoxime and its subsequent thermal breakdown. To a cooled (0°), stirred solution of *syn*-anisaldoxime (25.3 g, 0.17 mol) in 250 ml anhydrous ether containing 14 ml (0.18 mol) pyridine was added slowly 28.4 g (0.18 mol) of phenyl chloroformate. The resultant mixture was stirred for 10 h at room temperature and then poured on ice water (1000 ml). The ether layer was removed and the aqueous layer extracted with 800 ml methylene chloride. The combined organic extracts were washed with water, dried over sodium sulfate, and the solvent evaporated to yield the crude oxime carbonate. Recrystallization from hexane–chloroform gave 36.0 g (79%) of pure carbonate, m.p. 118° which had the following spectral data: ($CHCl_3$) 1759 (C=O stretch), 1259–1190 (ester C—O stretch), and 1024 cm^{-1} (C—O—C stretch); n.m.r. ($CDCl_3$) δ (p.p.m.) 8.44 (1H singlet, imino hydrogen $H{-}\overset{|}{C}{=}N{-}$) 7.84–6.92 (9H multiplet centered at 7.38, aromatic), 3.84 (3H singlet, phenyl CH_3—O—).

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.11. Found: C, 66.63; H, 4.76; N, 5.28.

The oxime carbonate (7.46 g, 0.028 mol) was then placed in a flask and heated until a steady stream of CO_2 evolved (110°). Then the reaction became very exothermic and external heating was discontinued. After CO_2 evolution had ceased, the resultant material was dissolved in 150 ml benzene. The benzene layer was extracted with 5% NaOH (3 × 50 ml), water (2 × 100 ml), and dried over sodium sulfate. The benzene was removed *in vacuo* yielding an oil which crystallized from hexane–chloroform. The pure nitrile (3.1 g, 85%) had a m.p. 59.0–61.0° (reported (5), 61–62°) and its spectral data (i.r. and n.m.r.) was consistent with the assigned structure.

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