

A New General Method for converting $\alpha\beta$ -Unsaturated Aldehydes into Saturated Imino-esters *via* α -Cyano-amines

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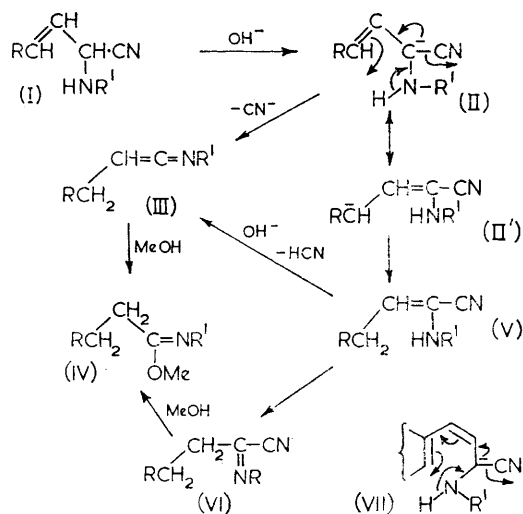
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In a recent communication¹ it was mentioned briefly that 1-anilino-1-cyano-3-phenylprop-2-ene (Ia) had been transformed into the imino-ester (IVa) by methanolic potassium hydroxide at room temperature. We report here the application of this reaction to α -cyanoamine (I) where R is aliphatic, aromatic, or heterocyclic and R¹ is phenyl or benzyl. This provides an apparently quite general route from $\alpha\beta$ -unsaturated aldehydes to imino-esters, which are easily hydrolyzed^{2,3} to esters.

The α -cyanoamines (I) were readily obtained in excellent yields from $\alpha\beta$ -unsaturated aldehydes by the procedure used for (Ia).¹ Treatment of cyanoamines (I) with hydroxide ion in methanol at room temperature afforded imino-esters (IV) in good to excellent yields[†] (see Table).

This reaction presumably proceeds through carbanion (II), which could produce the imino-esters (IV) in at least three possible ways (see Chart): by electron distribution, by a hydrogen shift,[‡] and by expulsion of cyanide ion as depicted in (II) which would give ketenimine (III), addition

to which of solvent methanol would produce iminoester (IV). Alternatively (II) could be



[†] The ultraviolet, infrared, and n.m.r. spectra and elemental analyses of the cyano-amines (I) and the amino-esters (IV) are all in accord with the structures shown.

[‡] This may or may not be intramolecular, and may be assisted by solvent participation.

TABLE
 α -Cyano-amines (I) and imino-esters (IV)

			α -Cyano-amine (I)		Imino-ester (II)	
			Yield (%)	m.p.	Yield (%)	B.P. at mm.
(a)	Ph	Ph	92	128—129 ^a	85	128—129 ^a
(b)	Ph	Ph	91	78—79	88	147—148
(c)	P-Me ₂ N-C ₆ H ₄	Ph	92	122—124	84	181—182
(d)	MeCH=CH-	Ph	98	73—74	71	86—87
(e)	C ₄ H ₄ O	Ph	98	89—90	91	121—122
(f)	Me	Ph	59 ^b	—	67	65—66

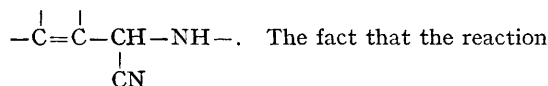
^a From ref. 1.

^b Not isolated in pure form; yield estimated from n.m.r. spectra of crude reaction mixture, which was used in the next step.

protonated to form (V) *via* canonical structure (II). Enamino-nitrile (V) either can lose a molecule of hydrogen cyanide to yield ketenimine (III) or it can tautomerise to cyanoimine (VI). Since the CN group in (VI) would be expected to behave like a pseudo-halogen, attack by solvent methanol could afford (IV) by a simple addition-elimination mechanism.

We were able to test that the enamino-nitrile (V; when R = R¹ = Ph) was an intermediate, and found that it gave the imino-ester (IVa) in 90% yield under the same conditions used for transformation of (Ia) to (IVa). Thus (V) could not be excluded as an intermediate.

The essential feature for the transformation of (I) to (IV) appears to be the structural unit,



The fact that the reaction goes when R is methyl as in (Ib) suggests strongly that the participation of aryl and heterocyclic double bonds present in (Ia, b, c and e) and of an additional double bond present in (Id) appears unlikely in this reaction [see (VII)].

The completion of the reaction§ when R¹ is benzyl as in (Ib) demonstrates that R¹ in (I) does not have to be an aryl group.

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§ This reaction was run using sodium methoxide as base in absolute methanol under nitrogen.

¹ J. S. Walia, D. H. Rao, M. Singh, and G. R. Nath, *Chem. and Ind.*, 1967, 583.

² D. H. Rao, Ph.D. Thesis, Banaras Hindu University, India, 1967.

³ J. S. Walia, D. H. Rao, and M. Singh, *Indian J. Chem.*, 1964, 2, 437.