Preparation of *N*-Phenyl-*N*-(α-cyanobenzyl)hydroxylamines

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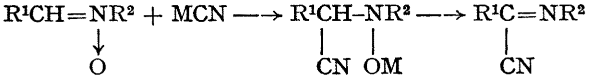
Summary The first preparation of *N*-phenyl-*N*-(α-cyanobenzyl)hydroxylamines is described.

α-CYANOHYDROXYLAMINE (I), a 1,3-adduct of hydrogen cyanide with cyclic[1] and aliphatic[2] nitrones, is thought to be an intermediate in the reaction of hydrogen cyanide with aromatic nitrones[3] and in other reactions,[4] although no evidence for its existence has been reported. The only product actually obtained in these reactions was a cyanoimine (II). We report here the first isolation of an *N*-phenyl-*N*-(α-cyanobenzyl)hydroxylamine.



$$\mathrm{R^1CH{=}}\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{N}}\mathrm{R^2} + \mathrm{MCN} \longrightarrow \mathrm{R^1}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{CH}}{-}\underset{\substack{|\\ \mathrm{OM}}}{\mathrm{N}}\mathrm{R^2} \longrightarrow \mathrm{R^1}\underset{\substack{|\\ \mathrm{CN}}}{\mathrm{C}}{=}\mathrm{NR^2}$$

(I) (II)

M=H, Na, or K

The studies on the reactivities of various nitrones with hydrogen cyanide were performed with dry alcohol as solvent, in an ice box. A pale yellow crystalline solid formed after one week, on treating α,*N*-diphenyl nitrone with liquid hydrogen cyanide. The solid was chromatographed on a silica gel column with benzene as eluant and the second eluate fraction gave a white crystalline solid. Recrystallisation of the solid from n-hexane gave white needles, the m.p. of which could not be determined since they were converted into cyanoimine (II) on heating.

Evidence that the material has structure (Ia) was obtained from: (i) elemental analysis, (ii) i.r. (KBr) ν_{max} 3270 (OH), 2245 cm^{-1} (CN), (iii) n.m.r. [$(CD_3)_2SO$] τ 3·77 (s, 1H, C*H*CN), 2·3—3·0 (m, 10H, Ar*H*), 0·77 (s, 1H, O*H*), and (iv) on dehydration, the material gave α-cyanobenzylideneaniline (II). When aqueous alcohol was used as the reaction medium, more (II) than (I) was produced.

Compounds (Ia—i) were obtained by this procedure.

p-X·C_6H_4·CH(CN)·N(OH)·C_6H_4·Y-p
(I)

	X	Y		X	Y
(a)	H	H	(f)	CN	H
(b)	Cl	H	(g)	H	Cl
(c)	OMe	H	(h)	H	Me
(d)	Me	H	(i)	H	OMe
(e)	NMe_2	H			

Even in alcoholic solution the hydroxylamine is gradually converted into the corresponding cyanoimine (II) at room temperature; the conversion is accelerated by the addition of bases and by raising the temperature. In dilute aqueous caustic alkali solution the dehydration occurs instantaneously even at 0°.

Preliminary studies suggested that an electron-donating substituent on the α-phenyl ring reduces the rate of dehydration, while an electron-withdrawing substituent aids the reaction. In the reaction of α-*p*-nitrophenyl-*N*-phenyl nitrone with liquid hydrogen cyanide, no hydroxylamine was obtained.

(*Received, December* 15*th*, 1970; *Com.* 2164.)

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