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A SYNTHESIS OF *CIS*-α,β-UNSATURATED NITRILES BY KINETICALLY CONTROLLED DECARBOXYLATION

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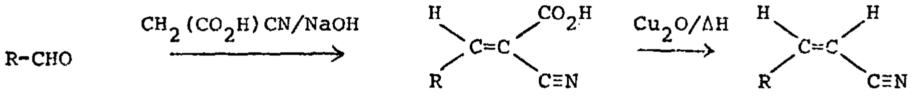
The Doebner condensation of aldehydes with cyanoacetic acid gives a *cis/trans* mixture of α,β-unsaturated nitriles containing a high proportion of the *trans* isomer[1]. The purification of the minor *cis* isomer has been accomplished by inefficient and laborious fractional distillation or crystallisation[2,3]. However, Knoevenagel reaction gives the intermediate α-cyano-acrylic acids in high yield[1,3]. It has been suggested[4] that in these compounds the carboxylic acid group lies exclusively *trans* to the larger β-substituent thus the nitrile group is necessarily *cis* orientated. Thus kinetically controlled decarboxylation should yield exclusively the *cis*-α,β-unsaturated nitrile.



We have found that Cu, Cu_2O or Cu_2O/bipyridyl or 1,10 phenanthroline mixture catalysed decarboxylations gives variable yield of the *cis* nitrile in solution (e.g. benzene, 1,2-dichlorobenzene) but extensive isomerisation to the *trans* isomer occurs under the experimental conditions, as assayed by g.l.c. The kinetically formed *cis* isomer[5] is isomerised possibly *via* a vinyl copper intermediate[6] or more likely by an addition-elimination process[4]. However, thermal decarboxylation *in vacuo* (0.2 mm Hg) using cuprous oxide as catalyst was performed removing the *cis* isomer *as it was formed*. We have found that Cu_2O is superior to copper powder for this purpose. This procedure effects a simple, reproducible technique for obtaining an isomeric mixture containing 70-90% of the *cis* isomer. The optimum catalyst ratio was not established. One experiment using silver^{I} oxide as catalyst gave 90% *cis* isomer. The results are summarised in the table.

Typical Procedure; Preparation of *cis-cinnamonitrile*

α-cyano-β-phenyl acrylic acid[8] (25 g) was intimately mixed with cuprous oxide (1.0 g) in a round bottom flask clamped horizontally leading to a cooled receiver *in vacuo* (0.2 mm Hg). The solid was heated slowly with a

Bunsen flame to effect a reasonable rate of decarboxylation (≈20 min). The product (8.5 g) was estimated by N.M.R. integration as being 13% *trans* isomer ($CDCl_3$:δ=5.6, 5.9 doublet; J=17 Hz) and 87% *cis* isomer (δ=5.28, 5.47, J=12.6 Hz). Pure *cis* cinnamonitrile was readily obtained on distillation through a spinning band column as a colourless liquid b.p. 106°C (10 mm Hg).

TABLE: DECARBOXYLATION RESULTS OF α-CYANO-β- ARYL ACRYLIC ACIDS

α-cyano-β-aryl carboxylic acid R=	Yield of α,β-unsaturated nitrile mixture	% *cis* isomer (% *trans* in brackets)	b.p.° or m.p.°C of pure *cis* isomer
phenyl	46	87 (13)	b.p.105-106 (10 mm Hg)
"	Lit[2], 50	37 (63)	
o-chlorophenyl	80	78 (22)	b.p. 90-92 (1.2 mm Hg)
"	Lit[6], 45	22 (78)	
3,4-dichlorophenyl	49	70 (30)	m.p. 60-60.5
p-chlorophenyl	72	73 (27)	m.p. 66.5-67.5
"	Lit[7], -	38.5 (61.5)	
2-thiophenyl	53	80 (20)	b.p.126 (10 mm Hg)
"	Ag_2O catalyst, 71	90 (10)	
p-bromophenyl	63	85 (15)	m.p. 69-69.5
2,6-dichlorophenyl	79	82 (18)	m.p. 25-26
m-trifluoromethyl phenyl	75	70 (30)	b.p.110-112 (10 mm Hg)
p-tert.butyl phenyl	50	87 (13)	b.p.160 (0.1 mm Hg)

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