The Hydroformylation Products of Acrylonitrile

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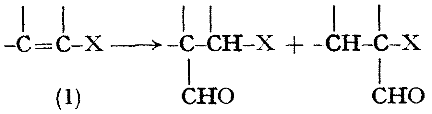
Summary The product of the catalytic hydroformylation of acrylonitrile with dicobalt octacarbonyl in methanol solution contained a new compound, α-formylpropionitrile.

THE catalytic hydroformylation of olefins of type (1) generally affords two isomers:

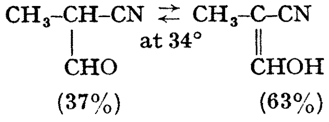


$$-\overset{|}{C}=\overset{|}{C}-X \longrightarrow -\overset{|}{\underset{\underset{CHO}{|}}{C}}-\overset{|}{C}H-X + -\overset{|}{C}H-\overset{|}{\underset{\underset{CHO}{|}}{C}}-X$$

(1)

Acrylonitrile has been claimed as a unique exception, giving only β-formylpropionitrile.[1] As a result of a re-investigation, both isomeric aldehydes have been isolated from the reaction product of catalytic hydroformylation with dicobalt octacarbonyl in methanol (see Table for the reaction products). The α-formyl isomer is a new compound; the structure was determined by spectrometric methods.

The n.m.r. and i.r. spectra of α-formylpropionitrile show that the compound exists as a tautomeric mixture:



$$\underset{(37\%)}{CH_3-\underset{\underset{CHO}{|}}{CH}-CN} \underset{\text{at } 34°}{\rightleftarrows} \underset{(63\%)}{CH_3-\underset{\underset{CHOH}{\|}}{C}-CN}$$

b.p.$_6$: 76·5—78°
n_D^{28}: 1·4607
m.p. of 2,4-dinitrophenylhydrazone: 150—151°

In methanol solution, the i.r. band at 1730 cm^{-1}, attributed to the formyl group, is observed at first, but disappears completely after 30 min. The ^{1}H n.m.r. signal of the formyl group behaves similarly to the i.r. C=O band, and the signal due to methoxy-protons (τ 6·7 doublet, *J* 10 Hz) appears and increases in intensity.

Product	Yield (%)	Product	Yield (%)
$OHC\cdot CH_2\cdot CH_2\cdot CN$	10·3	$CH_3\cdot CH_2\cdot CO_2CH_3$	0·3
$(CH_3O)_2\cdot CH\cdot CH_2\cdot CH_2\cdot CN$	70·6	$HOCH_2\cdot CH_2\cdot CH_2\cdot CN$[3]	0·5
$CH_3\cdot\underset{\underset{CHO}{|}}{CH}\cdot CN$	7·8	$CH_3\cdot CH_2\cdot CH(OCH_3)_2$	0·3
$CH_3\cdot\underset{\underset{CH\cdot(OCH_3)_2}{|}}{CH}\cdot CN$[2]	trace	$NC\cdot\overset{\overset{CH_3}{|}}{CH}\cdot CH_2\cdot CH_2\cdot CN$	1·4 1·4
$CH_3\cdot CH_2\cdot CN$[3]	3·4	$CH_3\cdot\underset{\underset{CH_2OH}{|}}{CH}\cdot CN$	0·3
$CH_3\cdot\underset{\underset{CO_2CH_3}{|}}{CH}\cdot CN$	0·9		

Initial acrylonitrile concentration: 3 M; catalyst concentration: 1·2 g/l as cobalt; initial synthesis gas ($CO : H_2 = 1 : 1$) pressure: 250 kg/cm^2; reaction temperature: 130°; solvent: methanol; Yields: based on acrylonitrile charged.

α-Formylpropionitrile polymerises spontaneously at room temperature to yield a clear glutinous material. On heating, the polymer easily depolymerises to give the monomer quantitatively. This polymer, on the basis of its i.r. and n.m.r. spectra, is considered to have a noncyclic structure. The molecular weight (osmometric, $CHCl_3$) was 244 (required value for the trimer is 249).

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[1] J. Kato, H. Wakamatsu, T. Komatsu, Y. Iwanaga, and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1961, **64**, 2142.
[2] A. Takamizawa, K. Ikawa, and M. Narisada, *J. Pharm. Soc. Japan*, 1958, **78**, 632.
[3] J. Kato, T. Ito, Y. Yabe, Y. Iwanaga, and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1962, **65**, 184.