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:

$$\begin{array}{c|c} | & | & | & | & | \\ -C = C - X & \longrightarrow & -C - CH - X & + & -CH - C - X \\ | & & | & | \\ (1) & CHO & CHO \end{array}$$

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:

CH_3 - CH - $CN \rightleftharpoons CH_3$ - C - CN		b.p. ₆ : 76·5—78°
at 34		n_D^{28} : 1.4607
ĊHO	ĊНОН	m.p. of 2,4-dinitrophenyl-
(37%)	(63%)	hydrazone: 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 ¹H 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.

	Yield		Yield
Product	(%)	Product	(%)
OHC·CH ₂ ·CH ₂ ·CN	10.3	CH3.CH2.CO2CH3	0.3
(CH ₃ O) ₂ ·ČH·ČH ₂ ·CH ₂ ·CN	70.6	HOCH2·CH2·CH2·CN3	0.5
ĊH ₃ ·CH·CN	7.8	$CH_3 \cdot CH_2 \cdot CH(OCH_3)_2$	0.3
СНО			
CH3 ·CH ·CN	trace	CH _a	1.4
$CH \cdot (OCH_3)_2^2$		NC·CH·CH ₂ ·CH ₂ ·CN	1.4
CH ₃ ·CH ₂ ·CN ³	$3 \cdot 4$	CH ₃ ·CH·CN	0.3
		сн ₂ он	
CH ₃ ·CH·CN	0.9		
CO ₂ CH ₃			

Initial acrylonitrile concentration: 3 M; catalyst concentration: 12 g/l as cobalt; initial synthesis gas (CO: $H_2 = 1:1$) pressure: 250 kg/cm²; 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, CHCl₃) was 244 (required value for the trimer is 249).

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