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REACTIONS OF CO-ORDINATED LIGANDS—III

REACTIONS OF IRON ISONITRILE COMPLEXES WITH NUCLEOPHILES

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Abstract—Nucleophiles reacted with cyanopentabenzylisonitrileiron(II) bromide (X) in three different fashions: bases such as sodium hydroxide and sodium bicarbonate decomposed X to tarry polymers; potassium cyanide caused polymer formation and generated benzyl isonitrile from the complex; weak bases which form only moderately stable complexes with iron(II), e.g. methanol, ethyl mercaptan or ammonia, were benzylated.

In a previous communication we have described the synthesis of a new class of iron isonitrile complexes.(1) Relatively little work is reported on the reactions of organic ligands when co-ordinated to a metal ion; no such work was found in the literature on metal isonitrile complexes.(2) Yet considerable double bond formation has been observed between iron and the isonitrile ligand which could modify the reactivity of the organic ligand in the aliphatic, and even more so, in the aromatic series.(3) This paper describes the reactions of cyano pentabenzylisonitrileiron(II)bromide with various nucleophiles.(4)

EXPERIMENTAL

Reaction of potassium cyanide with cyanopentabenzylisonitrileiron(II) bromide (X) *in 90 per cent ethyl alcohol*

To a solution of 54 g (0·071 mole) of X in 90 per cent ethyl alcohol was added 30 g (0·45 mole) of potassium cyanide. The reaction mixture was refluxed and stirred for 72 hr. The excess solvent was then evaporated under 0·1 mm pressure and room temperature to yield as a residue a black tarry material. The distillate was Fraction *A*. Extraction of the residue with boiling chloroform (5 × 100 ml) and subsequently with boiling ethyl alcohol (3 × 100 ml) and evaporation of the extracts yielded 33·7 g of black material (*B*), which refused to crystallize, despite numerous attempts to purify it. The infra-red spectrum of *B* indicated the presence of several nitrile and/or isonitrile groups (in μ): 3·00 (*s*) 3·40 (*s*), 3·50 (*s*), 4·58 (*vs*), 4·68 (*vs*), 5·10 (*s*), 6·00 (*sh*), 6·30 (*s*), 6·18 (*s*), 6·88 (*s*), 7·22 (*m*), 7·42 (*s*), 9·03 (*s*), 14·40 (*s*). Attempts to hydrolyse this material by prolonged refluxing with 80 per cent sulphuric acid failed.

The ethanol, chloroform insoluble material, 27 g, Fraction C, gave a positive prussian blue test with ferric chloride. When 26·5 g of *C* was dissolved in 100 ml of 2 N hydrochloric acid and an excess of zinc chloride was added a white precipitate appeared which, after drying at 120°C/30 mm, consisted of 10 g of solid. Since about 70 per cent of this precipitate accounted for zinc ferrocyanide, the conversion to ferrocyanide anion must be about 40 per cent.(5)

Fraction *A* was distilled at 760 mm and then at reduced pressure through a spinning band column, yielding 6 g of N benzyl formamide, b.p. 88–90°C, 21 mm Hg, identified by comparison of its spectrum with that of an authentic sample. (Found: N, 10·98. Calc. for $C_6H_5CH_2NHCOH$: N, 10·36%).

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(1) W. Z. Heldt, *J. Inorg. Nucl. Chem*. In press.

(2) L. Malatesta, *Isocyanide Complexes of Metals*, in "*Progress in Inorganic Chemistry*", (Edited by F. A. Cotton) p. 283. Interscience, New York (1959).

(3) (a) H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc*., 799 (1945).
(b) F. A. Cotton and F. Zingales. *J. Amer. Chem. Soc*., **83**, 351 (1961).

(4) C. K. Ingold, *Structure and Mechanism of Organic Chemistry*, p. 197. Cornell University Press (1953).

(5) H. E. Williams, *Cyanogen Compounds* (2nd Ed.) p. 364, Edward Arnold, London (1948).

Exchange experiments with X *and labelled potassium cyanide*

Labelled $K^{14}CN$ was obtained from New England Nuclear Corporation. Twenty one and seven tenths milligrams (= 0·32 mmole) of $K^{14}CN$ were dissolved in 4 ml of H_2O; 1·9898 g (30·6 mmole) of inactive KCN dissolved in 4 ml of H_2O were added to the solution; the solution was stirred for several minutes and subsequently 125 ml of absolute ethanol was added, whereby $K^{14}CN$ (1·310 g) crystallized out. The $K^{14}CN$ was washed with absolute ethanol, dried and analysed by the scintillation method in methanol as described by HAYES(6). The sample contained 500 μc/g of ^{14}C. Analysis for ^{14}C in the reaction mixtures was performed according to the same method under the same conditions.

(a) To 383 mg of X (0·5 mmole) dissolved in 13 ml of 100 per cent methanol was added a solution of 33 g (0·5 mmole) of $K^{14}CN$ containing 16·5 μc in 7 ml of distilled water, and the homogenous solution was allowed to stir in a stoppered bottle for 60 hr at room temperature. The reaction mixture was then poured into 400 ml of water, the aqueous solution was extracted with chloroform, the chloroform extracts were dried with magnesium sulphate, filtered, and evaporated to dryness under reduced pressure at 28°C. The oily residue, 250 mg, was then dried at 25°C/1·1 mm overnight; analysis indicated 11·6 μc which represented an accounting for ^{14}C of 70·4 per cent in the sample isolated from the reaction mixture.

(b) Same as in (a) but the homogeneous solution was allowed to stir for 5 min instead of 60 hr before the reaction mixture was poured into water and processed. Total material isolated was 210 mg; in this case the product was crystallized after drying. Radioactive analysis gave 4·3 μc indicating an exchange of 26·1 per cent in the sample isolated from the reaction mixture.

(c) To a solution of 3·83 g (5 mmole) of X in 130 ml of methanol was added a solution of 337 mg (5·3 mmole, 20·0 μc) of $K^{14}CN$ in 70 ml of water and the homogeneous solution was stirred in a closed vessel for 60 hr at room temperature. The solution was then evaporated to dryness under reduced pressure. To the residual green oil was added 100 ml of 85 per cent sulphuric acid and the reaction mixture was heated on a steam bath for 4 hr. The reaction mixture was then cooled to room temperature and was poured onto about 400 g of ice whereby a yellow oil precipitated out. This yellow oil was dissolved in chloroform, the chloroform solution was dried with magnesium sulphate and product was crystallized from chloroform–methyl ethyl ketone. After one recrystallization from methyl ethyl ketone, 1·8 g of yellow crystals were obtained with a m.p. 156–158°C. This material did not give any melting point depression upon admixture with $(C_6H_5CH_2NC)_5FeCNHSO_4{\cdot}H_2O$(1) and their infra-red spectra were identical. Radioactive analysis indicated 8·5 × 10^{-4} μc/mg, or 7·6 per cent exchange of the cyanide group in the isonitrile complex.

Reaction of X *with* $K^{14}CN$ *in ethylene glycol dimethyl ether*

To a solution of 30·6 g (0·04 mole) of X in 250 ml of dry ethylene glycol dimethyl ether (distilled over Na) in a stainless steel vessel was added 8·463 g (0·13 mole) of potassium cyanide labelled with ^{14}C having a radioactivity of 65 μc. The reaction mixture was heated for 5 hr at 150°C under 700 atm nitrogen pressure. The reaction mixture was then cooled to room temperature and was filtered from the ethylene glycol dimethyl ether insoluble materials (*A*). The filtrates were poured onto 500 ml of ether in order to precipitate any unreacted isonitrile complexes which were ether insoluble. A light brown ether soluble mixture was obtained (Fraction I) and a dark brown ether insoluble material precipitated out which was dissolved in chloroform (*B*). Fraction *A* was then extracted with 2 × 75 ml of boiling chloroform and the chloroform extracts were combined with Fraction *B* which, after evaporation and drying at 25°C/1·0 mm, yielded 10·8 g of isonitrile complexes (Fraction II). The infra-red spectrum of Fraction II: (KBr) 2·92 (*vs*), 3·42 (*s*), 4·56 (*v*), 4·62 (*s*), 4·88 (*vs*), 6·14 (*s*), 6·68 (*s*), 6·88 (*s*), 7·42 (*s*), 8·92 (*m*), 13·60 (*s*), 14·36 (*s*), (μ). The chloroform insoluble fraction of *A*, Fraction III, was mainly an inorganic bluish-white material, 16·8 g. Fraction I was distilled first at 760 mm and subsequently under reduced pressure.

DISTILLATION

Fraction	mm Hg	Boiling point (°C)	Distilled (g)	n_D^{25}
I*a*	15	42–80	1·35	1·4640
I*b*	15	80–95 main 90–95	3·0	1·5167
Ic	1·0	115–140 main 138–140	2·7	1·5419
I*d*			4·3	
Residue				

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(6) F. N. HAYES *Int. J. Appl. Radiation and Isotopes*, **1**, 46 (1956).

The totals of Fractions I, II, and III were 38·95 g which accounted for 98 per cent of the materials used in the reaction. Fraction Ib consisted of about 80–90 per cent of benzyl isonitrile, identified by comparison with the spectra of a reference sample,⁽⁷⁾ and an unknown alcohol (ethylene glycol?) Infra-red spectrum (liquid): 2·95 (*vs*), 3·29 (*s*), 3·42 (*s*), 3·49 (*s*), 4·63 (*vs*), 5·98 (*w*), 6·22 (*w*), 6·68 (*vs*), 6·88 (*vs*), 7·08 (*w*), 7·40 (*w*), 8·32 (*s*), 9·29 (*s*), 9·82 (*vs*), 10·55 (*w*), 11·08 (*w*), 12·28 (*broad*), 12·68 (*vs*), 14·40 (*vs*), (μ). Fraction I*c* consisted of a mixture of benzyl isonitrile (about 20–30 per cent) and N-benzylformamide, identified by comparison of the reference spectra of these two compounds. Radioactive analysis gave the following results:

Fractions (g)	μc	% of total radioactivity
I*b* (3·0)	3·86	5·94
I*c* (2·7)	1·28	1·97
II (10·8)	7·63	11·73
III (16·8)	16·15	24·85
Total	28·92	44·5

The balance of radioactivity must be present in the nonanalysed pot-residue I*d*, which contained products of polymerization of benzyl isonitrile.

Reaction of X *with methanol under carbon monoxide pressure*

A solution of 54 g (0·07 mole) of X in 200 ml of methanol was pressurized with carbon monoxide to 700–850 atm and the reaction mixture was heated at 175°C for 6 hr in a stainless steel autoclave. During this period a total of 350 atm of carbon monoxide was consumed by the reaction mixture. The reaction vessel was washed well with methyl alcohol and the reaction mixture was filtered from a solid compound *A* (10·05 g). This white material was insoluble in all organic solvents such as ether, chloroform, acetonitrile, methanol, dimethylformamide and dimethylsulphoxide, but dissolved in concentrated sulphuric acid and dilute, hot sodium hydroxide. A solution of *A* in concentrated sulphuric acid evolved a gas when heated on a steambath. The infra-red spectrum in KBr showed three peaks in the nitrile, isonitrile and carbon monoxide region: 2·98 (*vs*), 3·05 (*vs*), 4·50 (*s*), 4·75 (*vs*), 4·92 (*vs*), 6·02 (*w*), 6·20 (*s*), 6·70 (*s*), (μ). The material did not melt up to 320°C. (Found: C, 29·94; H, 3·29; N, 23·91; Fe, 31·00. Calc. for $H_5Fe_2(CN)_6(CO)_3$: C, 30·28; H, 1·41; N, 23·55; Fe, 31·29. Calc. for $H_{11}Fe_2(CN)_6(CO)_3$: C, 29·78; H, 3·05; N, 23·16; Fe, 30·77%). Specific magnetic susceptibility (as solid) $\chi = 34{\cdot}1 \times 10^{-6}$ c.g.s. at 25°C.

When 512 mg of *A* were added to 5·0 ml of 1·9786 N sodium hydroxide and the solution was stirred for 1·5 hr at room temperature, then filtered from the very slight precipitates, and back titrated with 0·113 N hydrochloric acid potentiometrically, 66·5 ml of hydrochloric acid were necessary to neutralize the excess of sodium hydroxide. That means that there were 1·5 active hydrogens in the above formula weight of *A*.

On the other hand, when 277 mg of *A* were added to 3·0 ml of 1·9786 N sodium hydroxide and the mixture was heated on a hot plate to boiling, cooled to room temperature, filtered, and back titrated potentiometrically with 0·113 N hydrochloric acid, 34·5 ml of hydrochloric acid were necessary to neutralize the excess of sodium hydroxide; here the solid consumed 2·037 meq. of base or it contained about 2·65 active hydrogens. The blue residue which precipitated after acidification was filtered, washed throughly with water and was dried at 0·1 mm/25°C for several hours. (Found: C, 21·69; H, 2·23; N, 16·86; Fe, 29·26. Calc. for $Fe_7C_{24}H_{32}N_{16}O_{24}$: C, 21·84; H, 2·44; N, 16·98; Fe, 29·62%) The infra-red spectrum in KBr of this material also differed considerably from A: 2·95 (*vs*), 4·70–4·90 (*vs*, broad), 6·20 (*w*), 9·30 (*w*), 9·75 (*w*), (μ).

The filtrate of *A* was distilled through a fractionating column first at 760 mm, then at reduced pressure yielding as the main fraction 25·1 g of a colourless liquid, b.p. 104–106°C/90 mm Hg, n_D^{27} = 1·4967. Infra-red spectrum: 3·00 (*w*), 3·50 (*vs*), 5·92 (*vs*), 6·25 (*w*), 6·70 (*s*), 6·89 (*vs*), 7·25 (*vs*), 7·32 (*s*), 8·40 (*s*), 9·10 (*vs*), 9·72 (*s*), 10·40 (*s*), 10·82 (*s*), 11·07 (*s*), 13·50 (*s*), 14·35 (*vs*), (μ). The infra-red spectrum of the distillate indicated the presence of a keto or acid group. The distillate did not saponify when boiled with base and did not give a 2,4-dinitrophenylhydrazone or a semicarbazone. Finally, the distillate was purified by reduction of all contaminants with lithium aluminium hydride. To a slurry of 4·0 g (0·1 mole) of lithium aluminium hydride in 100 ml of anhydrous ether and a three neck flask (stirrer, condenser, additional funnel) was added a solution of 7·5 g of the distillate in 50 ml of ether, at such a rate the ether just refluxed. The reaction mixture was then refluxed overnight. After this

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(7) I. Ugi and R. Meyer *Ber. Dtsch. Chem. Ges.* 93, 239 (1960).

time the reaction mixture was cooled to room temperature and the excess lithium aluminium hydride was decomposed with water, and the hydroxides were dissolved by the addition of 50 ml of 20 per cent sulphuric acid. The ether layer was separated and the water layer was extracted three times with 100 ml of ether. The ether extracts were combined, dried with magnesium sulphate and distilled. Only one material was obtained in the vacuum distillation; 6·7 g, b.p. 101–103°C/80 mm, n_D^{27} = 1·4992. Infra-red spectrum of this material was nearly superimposable with that of methyl benzyl ether. The nuclear magnetic resonance spectrum of this material was identical with that of an authentic sample of benzyl methyl ether; it indicated only aromatic, methylene and methyl hydrogen in a ratio of 5:2:3.

Reaction of tetrabenzhydrylisonitrileiron(II) cyanide with anhydrous methanol

A solution of 11 g (0·0125 mole) of $((C_6H_5)_2CHNC)_4Fe(CN)_2$,(1) m.p. 242–244°C, in 70 ml of absolute methanol (Baker's analysed methanol was distilled from magnesium methoxide) was heated for 4 hr at 140°C under 780–800 atm nitrogen. The reaction mixture was then cooled to room temperature and was filtered from 2·9 g of methanol insoluble material. The methanol soluble filtrates were distilled under 16 mm pressure. Only one fraction was isolated; b.p. 148–150°C/16 mm, 4·4 g, 44 per cent conversion for $(C_6H_5)_2CHOCH_3$, n_D^{25} = 1·5650. There remained 1·8 g of pot residue which was not further identified. (Found: C, 84·27; H, 6·96. Calc. for $(C_6H_5)_2CHOCH_3$: C, 84·79; H, 7·12%). Infra-red: 3·30 (*s*), 3·40(*s*), 3·55 (*s*), 5·12(*w*), 5·30(*w*), 5·55(*w*), 6·22(*m*), 6·70(*vs*), 6·99(*vs*), 7·42 (*m*), 7·65 (*s*), 8·42 (*s*), 9·12 (*s*), 9·32 (*vs*), 9·72 (*vs*), 10·35 (*vs*), 10·85 (*w*), 10·95 (*w*), 11·55 (*w*), 12·05 (*w*), 13·25 (*vs*), 13·55 (*vs*), 14·35 (vs, broad), (μ).

Reported for $(C_6H_5)_2CHOCH_3$; b.p. 147–148/17 mm Hg.(8)

Reaction of potassium thiocyanate with X

To a solution of 15·2 g (0·02 mole) of X in 150 ml of dry (see above) ethylene glycol dimethyl ether was added 7·8 g (0·08 mole) of potassium thiocyanate (dried at 120°C/20 mm for 24 hr), and the reaction mixture was heated at 150°C for 5 hr under 700 atm nitrogen pressure. The reaction mixture was then filtered from 11·5 g of a black solid. The filtrates were distilled under 1·0 mm pressure. Only one fraction was collected, b.p. 75–155°C (main fraction, b.p. 152–155°C) 4·5 g (38 per cent conversion in reference to KSCN added). There remained 5·5 g of a black residue in the still. The infra-red spectrum of the distillate was: 3·00 (*w*), 3·30 (*w*), 3·42 (*w*), 4·62 (*w*), 4·85 (*w*), 5·95 (*w*), 6·22 (*w*), 6·68 (*s*), 6·88 (*s*), 7·25 (*s*), 7·52 (*w*), 8·20 (*s*), 9·36 (*w*), 9·75 (*w*), 14·40 (*s*), (μ).

A synthetic sample of benzyl thiocyanate was prepared from benzyl bromide and potassium thiocyanate according to the procedure of JOHNSON(9), b.p. 117–119·5/5 mm, m.p. 39–40°C (reported m.p. 41°C(10)). (Found: N, 9·58; S, 21·29. Calc. for $C_6H_5CH_2NCS$: N, 9·25; S, 21·21%). Benzyl thiocyanate showed a strong band ar 4·62 μ characteristic of the —S—C≡N absorption. The band at 4·85 μ in the reaction mixture appeared therefore to belong to benzyl isothiocyanate.(11) Judging from the intensity of the two bands at 4·62 μ and 4·85 μ, the reaction mixture consisted of approximately 3:1 ratio of benzyl isothiocyanate and benzyl thiocyanate.(12)

RESULTS AND DISCUSSION

Nucleophiles may displace the cyanide group or the isonitrile group from $(C_6H_5CH_2NC)_5FeCNBr$(X), or may react with the isonitrile group, the methylene group, or, least probably, attack the aromatic nucleus in X.

When X was heated with sodium hydroxide or sodium bicarbonate in water or dimethylformamide as the solvent (see Table 1) only polymer formation took place. Interestingly, the polymer exhibited strong infrared bands at 4·58 μ and 4·70 μ, indicating the presence of isonitrile groups. The iron was so strongly complexed it could nor be dissolved out of this polymer with 80 per cent sulphuric acid.

When X was refluxed for 16 hr with a five molar excess of triphenylphosphine, triphenylarsine or pyridine in a chloroform solution, X was recovered in 90–100 per cent.

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(8) E. BERGMANN and J. HERVEY, *Ber. Dtsch. Chem. Ges.* **62**, 915 (1929).

(9) T. B. JOHNSON and R. B. DOUGLASS, *J. Amer. Chem. Soc.* **61**, 2548 (1939).

(10) L. HENRY, *Ber. Dtsch. Chem. Ges.* **2**, 636 (1869).

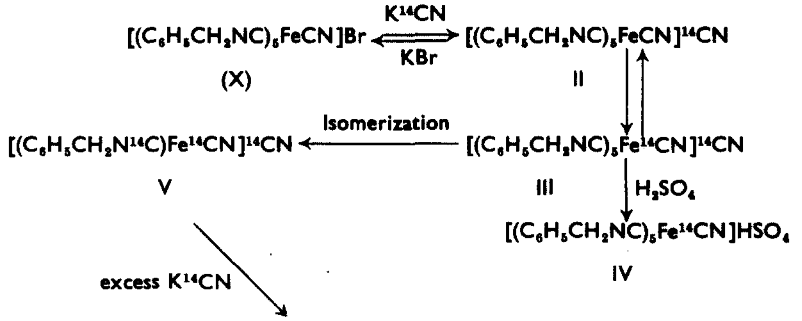
(11) (a) E. LIEBER, C. N. R. RAO and J. RAMACHANDRAN, *Spectrochim. Acta*, **13**, 296 (1959).
(b) L. S. LUSKIN, G. E. GANTERT and W. E. CRAIG, *J. Amer. Chem. Soc.* **78**, 4965 (1956).

(12) W. Z. HELDT, Unpublished results (1959).

Under similar conditions carbon monoxide is easily displaced from iron carbonyls.(13)

When X was boiled with six moles of potassium cyanide in 90 per cent ethyl alcohol, potassium ferrocyanide and *N*-benzylformamide, which is a hydrolysis product of benzyl isonitrile were identified in about 40 and 14 per cent conversions, respectively. In addition to these compounds a polymeric material formed which still contained iron and showed three strong bands in the triple bond stretching region at 4·58 μ, 4·68 μ and at 5·10 μ. Attempts to hydrolyse this polymer with 80 per cent sulphuric acid failed. Under the same reaction conditions, X underwent hydrolysis to benzyl amine with no difficulty.(1) When the KCN/X ratio was decreased from 10 to 3, the amount of benzyl isonitrile or N-benzylformamide isolated increased from 1 to 30 per cent (Table 1 and Experimental). Polymeric iron-containing products which showed two strong bands in the 4·50–4·85 region were formed when the KCN/X ratio exceeded 4; little polymer formation was observed when the KCN/X ratio remained below 3½. Potassium cyanide, therefore, when present in more than four molar excess, polymerizes the benzyl isonitrile and the concurrent iron isonitrile complexes.

FIG. 1.—Reaction of $K^{14}CN$ with $(C_6H_5CH_2NC)_5FeCNBr$.



	$C_6H_5CH_2N^{14}C$	$C_6H_5CH_2NH^{14}COH$	Benzyl Isonitrile polymer	Iron Isonitrile complexes	Inorganic cyanides and complexes
conversion	12·8%	11·0%	18·3%	10·8 g	16·8 g
radioactivity (%)	6·0	2·0	55·5(?)	11·7	24·8

The relative ease of preparation of an iron–alkyl isonitrile complex and the formation of an alkyl isonitrile in the reaction of potassium cyanide with the complex indicates a novel route for the synthesis of alkyl isonitriles. It was therefore of interest to investigate the mode of isonitrile formation from X in some detail with $K^{14}CN$ (see Fig. 1). The metathetical exchange of the bromide in X against radio cyanide (II, III), one of the first intermediates in the formation of alkyl isonitriles from X, was not instantaneous; after 5 min at room temperature only 26 per cent of bromide was exchanged against labelled cyanide, and after 60 hr only 70·5 per cent. When the products of the metathesis of X, i.e., II, III (Fig. 1) was converted into the hydrosulphate(1) IV, it was found that 7·6 per cent of the cyanide bound to iron was exchanged against radio-cyanides. Products accounting in all three experiments was only 46–65 per cent.

(13) (a) W. HIEBER and R. BREU, *Ber. Dtsch. Chem. Ges.* **90**, 1259 (1957).
(b) W. HIEBER and N. KAHLEN, *Ber. Dtsch. Chem. Ges.* **91**, 2234 (1958).

TABLE 1.—REACTIONS OF $(C_6H_5CH_2NC)_5FeCNBr$ WITH NUCLEOPHILES

Experiment no.	$(C_6H_5CH_2NC)_5FeCNBr$		Reactant		Reaction conditions				Products and identification of products
	(g)	(mole)	(g)	(mole)	Solvent (ml)	Time (hr)	Temp. (°C)	Pressure (atm)	
1	15·0	(0·02)	NaOH	0·25	H_2O 100	6	150	800 CO	Tar
2	15·0	(0·02)	$NaHCO_3$	0·2	D.M.F. 100	4·6	150	800 CO	Tar
3	14·4	(0·02)	KCN 8·58	0·13	HCN 120	5	90	closed autoclave	Tar only
4	14·6	(0·02)	KCN 10·0	0·16	CH_3OH 50 H_2O 50	5	150	closed autoclave	2·6 g N-benzylformamide (0·009 mole)
5	22·8	(0·03)	KCN 19·3	0·3	$(CH_3OCH_2)_2$ 120	6	100		0·6 g N-benzylformamide
6	15·0	(0·02)	KCN 5·2	0·08	$(CH_3OCH_2)_2$ 100	1	200	700 N_2	3·8 g of a mixture of $C_6H_5CH_2NC$ (about 35%) and $C_6H_5CH_2NHCHO$
7	15·0	(0·02)	KCN 3·9	0·06	$(CH_3OCH_2)_2$ 150	3	150	700 N_2	2·1 g of a mixture of $C_6H_5CH_2NC$ and $C_6H_5CH_2NHCHO$
8	15·0	(0·02)	CH_3OH 100 ml		none	6	175	850 N_2	FI 8·6 g solid precipitate; filtrate distilled, yielded = 3·624 g (= 36%) of $C_6H_5CH_2OCH_3$
9	30·0	(0·04)	$(CH_3)_2CHOH$ 100 ml		none	6	175	840 N_2	FI 10·65 g solid; filtrate distilled yielded = 11·91 g (42%) $C_6H_5CH_2OCH(CH_3)_2$, identified by N.M.R., I.R. analysis
10	15·0	(0·02)	CH_3CO_2H 100 ml $(CH_3CO)_2O$ 4 ml		none	2	150	850 N_2	FI 6.60 g solid; filtrate distilled yielded = 2·24 g (= 14%) of $C_6H_5CH_2OCOCH_3$; identified by I.R., N.M.R. analysis
11	15·0	(0·02)	NH_3	3·0	none	5	130	350 N_2	6·1 g of tars and 6·5 g (61% conversion) of $C_6H_5CH_2NH_2$, b.p. 103–105°C./18 mm identified as p-toluene sulphone amide. m.p. 113·4–114·0°C.
12	22·5	(0·03)	$CH_3(CH_2)_2CH_2NH_2$	1·0	none	6	175	380 N_2	17·4 g of tars, 9·8 g of benzylamine and N-(n)butyl benzylamine; identified as 9·8 g of p-toluene sulphonimides; b.p. 113·4–114·0°C. and m.p. 157·5–159·4°C, respectively
13	15·0	(0·02)	CH_3CH_2SH	1·01	none	4	130	400 N_2	2·55 g tars and 6·2 g (= 44% conversion) of benzyl ethyl thioether, b.p. 80–82°C./10 mm Hg n_D^{28} = 1·5415; analysis found C = 65·66; H = 7·86; and 1·5 g of $C_6H_5CH_2NC$; Analysis Calc. for $C_6H_5CH_2SCH_2CH_3$: C = 64·36; H = 7·56
14	15·0	(0·02)	CH_3CONH_2	1·0	none	6	175	closed vessel	Tars

The polymerizations of the liberated benzyl isonitrile and of the concurrent isonitrile complexes were diminished when the solvent was ethylene glycol dimethyl ether rather than ethyl or methyl alcohol. When X was heated with 3·25 molar excess of $K^{14}CN$ in ethylene glycol dimethyl ether in an autoclave there were formed: benzyl isonitrile, N-benzylformamide, a polymer resulting from benzyl isonitrile, iron isonitrile complexes and unreacted labelled potassium cyanide insoluble in chloroform (Fig. 1). In a simple displacement of benzyl isonitrile by $K^{14}CN$ from X all the labelled atoms should appear in the isonitrile complex and none in the displaced benzyl isonitrile. Since the benzyl isonitrile and N-benzylformamide were both labelled, an internal isomerization of III–V must have preceded the formation of isonitrile from V. Furthermore, the radioactive label was present in all of the products isolated but in each to a different extent. For example, the benzyl isonitrile was more radioactive than the N-benzylformamide which must have been formed by addition of water to benzyl isonitrile. The results indicated, therefore, the internal isomerization and the generation of benzyl isonitrile, N-benzylformamide and the polymerization of benzyl isonitrile (?) are concurrent processes in this reaction.

When the nucleophile was a weak base, and a weak complexing agent with Fe(II), then benzylation of the nucleophile was observed (see Table 1).

$$(C_6H_5CH_2NC)_5FeCNBr + H\ddot{\underset{\cdot\cdot}{X}}R \rightarrow C_6H_5CH_2XR$$

$$HXR = HOCH_3,\ HOCH(CH_3)_2,\ HO_2CCH_3,\ HNH_2,\ HNH(CH_2)_2CH_3,\ HSCH_2CH_3$$

When X was heated in methanol for 6 hr at 175°C under 700–850 atm of carbon monoxide pressure, methyl benzyl ether was isolated in 60 per cent conversion with the formation of a white methanol insoluble residue which gradually became blue:

$$(C_6H_5CH_2NC)_5FeCNBr + CH_3OH \xrightarrow[\cdots\cdots]{CO} C_6H_5CH_2OCH_3 + H_{(5-11)}Fe_2(CN)_6(CO)_3$$

This new carboxyl cyanide complex (or complex mixture?) exhibited three strong bands in the triple bond region: 4·50 μ, 4·75 μ and 4·92 μ and was paramagnetic χ (specific) $= 34{\cdot}1 \times 10^{-6}$ c.g.s. at 25°C. The complex was insoluble in the usual organic solvents (see Experimental) but dissolved in sodium hydroxide and concentrated sulphuric acid, in sulphuric acid, with the evolution of a gas. Back-titration of the alkaline solution of the complex with standard acid indicated the presence of 1·5 acidic hydrogens per mole.of complex. When heated with 2·0 N sodium hydroxide, the complex decomposed. Further work is therefore required to identify this composition definitely as a complex or as a complex mixture.

A similar displacement was observed for a tetracoordinated isonitrile complex, tetrabenzhydrylisocyanoiron(II) cyanide, which yielded benzhydryl methyl ether in 44 per cent conversion. Various highly coloured inorganic residues were obtained in these reactions which were not identified any further.

When X was reacted with potassium thiocyanate both benzyl thiocyanate and benzyl isothiocyanate were formed. Benzyl isothiocyanate was probably formed by thermal rearrangement of benzyl thiocyanate under the reaction conditions employed.[14]

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