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REACTIONS OF CO-ORDINATED LIGANDS—IV SYNTHESIS OF IRON ISONTRILE COMPLEXES BY THE

TRANSALKYLATION REACTION

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Abstract—When tetrabenzylisocyano iron (II) cyanide or cyanopentabenzylisocyano iron (II) bromide is heated with an alkyl halide (R'X) and if the benzylhalide formed is continuously removed during the reaction, products of the general formulae $(R'NC)_x(C_6H_5CH_2NC)_y$ FeCNX (x + y = 5) (X=halogen); (R'NC)₅FeBr₂ and (R'NC)₄Fe(CN)₂ are formed.

IRON isonitrile complexes are prepared by:

- (1) addition of isontriles to iron II salts such as Fe $(C10_4)_2$ (1)
- (2) addition of isonitriles to iron carbonyls,⁽²⁾ and
- (3) alkylation of ferro-cyanides with alkylhalides⁽³⁾, or alkyl sulphates^(la)

Few alkyl isonitriles were prepared having substituent groups in the alkyl chain probably because of the poor synthetic methods available for their preparation.⁽⁴⁾ No iron (II) complexes of substituted alkyl isonitriles appear to have been prepared thus far.^(Ia) This paper reports a new, relatively simple method for the preparation of a wide variety of alkyl isonitrile complexes.

EXPERIMENTAL

Reaction of $(C_6H_5CH_2NC)_5FeCNBr$ (I) with p-carbomethoxybenzyl bromide

To 15.4 g (0.02 mole) of $(C_6H_5CH_2NC)_5FeCNBr$ (I) was added 23.0 g (0.1 mole) of *p*-carbomethoxybenzyl bromide. The reaction mixture was well mixed and was then dry distilled at 4 mm, the pot-temperature of the reaction vessel being held at 95–120°C. During a period of 70 min, 8.5 g (0.05 mole) of benzyl bromide distilled over, identified by its b.p. and infra-red spectrum. The residue from the distillation, a brown oil, 28.6 g, was dissolved in chloroform and was then chromatographed on 500 g of alumina suspended in chloroform. The column was washed with 7×50 ml of chloroform, 5×50 ml of 50 per cent chloroform acetone, 3×50 ml acetone, 3×50 ml 50 per cent acetone-methanol and finally with 6×50 ml of methanol. Three distinct compounds were eluted; Fraction I, 10.5 g with chloroform; Fraction II, 9.5 g, with acetone and acetone-methanol; and Fraction III, 3.7 g, with methanol.

Fractions II and III were combined and were fractionally crystallized from methyl ethyl ketone (250 ml). The less soluble fractions (A) 2.5 g, were recrystallized once more from chloroform-carbon tetrachloride and were dried at $100^{\circ}C/1.0$ mm, melting at 234–237.5°C. Found: C, 58.86; H, 4.68; N, 8.11; Fe, 5.74; Br, 8.01. Calc. for (*p*-CH₃OCOC₆H₄CH₂NC)₅FeCNBr: C, 59.03; H, 4.37; N, 8.10; Fe, 5.38; Br, 7.70%.

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The infra-red spectrum of this material was nearly identical with that of p-(CH₃OCOC₆H₄CH₂NC)₅FeCNBr H₂O,⁽⁵⁾ m.p. 185–186·2°C, although the large discrepancies of the melting points of the monohydrate with the nonhydrated form are of interest. When samples of both compounds were mixed and dried at 100°C/1·0 mm for a prolonged time, the mixed melting point was 232–236°C, i.e., there was no melting point depression.

From the mother liquors of Fraction A there crystallized upon reduction of the volume of solvent a material, Fraction B, 1.5 g. After one recrystallization from methyl ethyl ketone this material melted at $141-142\cdot5^{\circ}$ C. Found: C, $61\cdot09$; $61\cdot29$; H, $4\cdot61$, $4\cdot44$; N, $8\cdot93$, $9\cdot01$; Fe, $6\cdot00$, $5\cdot91$; Br.9·81.

Calc. for
$$\begin{bmatrix} (p-CH_3OCOC_6H_4CH_2NC)_3\\ (C_6H_5CH_2NC)_2 \end{bmatrix}$$
 FeCNBr:

C, 61.25; H, 4.48; N, 9.12; Fe, 6.06; Br, 8.67%.

Infra-red (KBr): 3.40 (s), 4.45 (vs), 4.72 (vs), 5.78 (vs), 6.18 (s), 6.32 (w), 6.68 (w), 6.88 (s), 6.98 (vs), 7.08 (s), 7.42 (s), 7.62 (s), 7.82 (vs), 8.46 (s), 9.03 (vs), 9.82 (s), 10.38 (s), 12.00 (w), 12.55 (w), 13.35 (w), 14.35 (s), μ .

Further reduction of the mother liquors of Fraction B yielded C, $2 \cdot 0$ g. After one recrystallization from methyl ethyl ketone this material melted at 123–126°C. Found: C,58·79; H, 4·80; N, 89·5; Fe, 5·89; Br, 9·01.

Calc. for
$$\begin{bmatrix} (C_6H_5CH_2NC) \\ (p-CH_3OCOC_6H_4CH_2NC)_4 \end{bmatrix}$$
 FeCNBr \cdot H₂O:

C, 58.99; H, 4.55; N, 8.42; Fe, 5.60; Br, 8.01 %.

Except for a strong OH band at 2.92μ , the infra-red spectrum of the latter materials was practically identical with Fraction I of the following experiment.

Reaction of tetrabenzylisocyano iron (II) cyanide (II) with p-carbomethoxybenzyl bromide

To 11.5 g (0.05 mole) of *p*-carbomethoxybenzyl bromide were added 5.6 g (0.01 mole) of II, m.p. 229–230°C. The reaction mixture was well mixed and was dry-distilled under a vacuum of 5.0 mm and an oil-bath temperature of $135-162^{\circ}$ C. After 2.0 ml of benzyl bromide (b.p. 78–80°C/5.0 mm) had distilled over, the dry-distillation was discontinued. The distillation residue was dissolved in chloroform and was chromatographed on 450 g of alumina suspended in chloroform. The column was washed with 700 ml of 50 per cent acetone–chloroform, 150 ml of acetone and finally with 350 ml of 50 per cent acetone–methanol. Two fractions were eluted: Fraction I with acetone–chloroform, 2.14 g; and Fraction II with acetone–methanol, 4.9 g. Fraction I was recrystallized from methanol and methyl ethyl ketone. After several recrystallizations from these solvents the compound melted at 226–230°C (dried at 100°C/1.0 mm). Found: C, 60.85; H, 5.42; N, 8.59; Fe, 5.21; Br, 8.54.

Calc. for
$$\begin{bmatrix} p-CH_3OCOC_6H_4CH_2NC)_4\\C_6H_5CH_2NC \end{bmatrix}$$
 FeCNBr:

C, 60.07; H, 4.43; N, 8.58; Fe, 5.70; Br, 8.16%.

Infra-red (KBr): 2.92 (w), 3.40 (m), 4.56 (vs), 4.70 (s), 5.79 (vs), 6.18 (s), 6.32 (w), 6.68 (w), 6.96 (s), 7.05 (s), 7.45 (m), 7.61 (m), 7.80 (w), 8.07 (m), 8.46 (m), 9.00 (s), 9.82 (m), 10.35 (m), 11.98 (w), 14.40 (m) μ .

Reaction of II with α -bromo-p-xylene

To 11.5 g (0.02 mole) of II, m.p. 229–230°C were added 20.5 g (0.11 mole) of α -bromop-xylene. The reactants were well mixed and were dry-distilled at 8 mm, maintaining the oil-bath temperature at 125°C. After 20 min, 8 ml of a material distilled over b.p. 85–87°/8 mm. The infra-red spectrum of the distillate indicated a mixture of benzyl bromide and α -bromo-*p*-xylene, the latter being by far the major constituent in the reaction mixture. The residue was taken up in chloroform and was crystallized from chloroform-carbon tetrachloride. A white material crystallized out, m.p. $130-134^{\circ}$ C. After several more recrystallizations from methyl ethyl ketone it had a m.p. $135-136\cdot5^{\circ}$ C. Found: C, $66\cdot55$; H, $5\cdot80$; N, $11\cdot07$; Fe, $6\cdot68$; Br, $9\cdot94$.

Calc. for
$$\begin{bmatrix} (p-CH_3C_6H_4CH_2NC)_4\\ C_6H_5CH_2NC \end{bmatrix}$$
 FeCNBr:

C, 67.25; H, 5.39; N, 10.47; Fe, 6.96; Br, 9.95%.

Infra-red (KBr): 2.90 (w), 3.30 (s), 3.42 (s), 3.50 (s), 4.56 (vs), 4.71 (s), 6.10 (s), 6.25 (w), 6.45 (s), 7.08 (s), 7.25 (w), 7.42 (s), 7.60 (w), 8.05 (w), 8.35 (w), 8.45 (w), 8.95 (w), 9.62 (w), 9.81 (w), 10.40 (w), 11.93 (w), 12.45 (s), 12.62 (s), 13.33 (s) 13.79 (m), 14.40 (m) μ .

This material depressed the melting point of $(p-CH_3C_6H_4CH_2NC)_5FeCNBr \cdot H_2O^{(5)}$ upon admixture.

Partial transalkylation of I with α -bromo-p-xylene

To 22.8 g (0.03 mole) of I were added 22.5 g (0.12 mole) of α -bromo-p-xylene. The reactants were heated and stirred overnight on a steambath in a vessel closed by a calcium chloride tube and were dry-distilled at 6-9 mm pressure and an oil-bath temperature of 115–117°C. After 11 min, 3.5 ml of distillate, b.p. 82-84°C were collected. Infra-red spectrum of the distillate indicated a mixture of α -bromo-*p*-xylene and benzyl bromide. The residue was then crystallized from chloroform-carbon tetrachloride, yielding ca. 5 g of (*p*-CH₃C₆H₄CH₂NC)₅FeCNBr·H₂O, identified by mixed melting point with a reference sample and by its infra-red spectrum.⁽⁵⁾

Reaction of I with α -bromo-o-xylene

To 15.2 g (0.02 mole) of I were added 22.0 g (0.12 mole) of α -bromo-o-xylene and the reaction mixture was dry distilled under 9 mm and an oil bath temperature of 120°C. After 43 min there distilled 13 ml of a material, b.p. 84–86°C. The distillate was identified by infra-red as a mixture of α -bromo-o-xylene, benzyl bromide (about 20–35 per cent) and a nonidentified isonitrile (about 5 per cent). The residue from the distillation was then crystallized from methyl ethyl ketone. After several crystallizations a material was obtained with a melting point of 235-237°C. This material did not depress, upon admixture, the melting point of the previously prepared (o-CH₃C₆H₄CH₂NC)₄Fe(CN)₂ and the infra-red spectra of these two materials were superimposable.

Reaction of p-nitrobenzyl bromide with I

To 22.8 g (0.03 mole) of I were added 25 g (0.12 mole) of *p*-nitrobenzyl bromide. The reactants were well mixed and were distilled under 6 mm Hg and an oil bath temperature of 115–141°C. A total of 3.5 ml of distillate was collected. The distillate consisted solely of benzyl bromide, i.e. the reaction proceeded to about 20 per cent completion. The brown residue in the distillation flask was then chromatographed in the usual fashion on alumina suspended in chloroform. The column was washed with 850 ml of chloroform, 5×250 ml 50 per cent acetone-chloroform, 4×250 ml of acetone, 7×250 ml of acetone-methanol and finally with 2×250 ml of methanol. Fraction I, 12.3 g was eluted with chloroform, and was identified as starting material (i.e., 50 per cent recovery), Fraction II, 13.7 g was eluted with 50 per cent chloroform-acetone and acetone; and Fraction III, 18.7 g, with 50 per cent acetone-methanol.

Infra-red spectrum of Fraction II (CHC1₃): 3.00(s), 3.45(s), 4.58(vs), 4.72(w), 6.25(w), 6.58(s), 6.72(m), 6.92(m), 6.98(m), 7.45(s), 8.10-8.35(m), $14.45(s) \mu$. The infra-red spectrum of this material indicates definitely an isonitrile complex. All attempts to crystallize this fraction remained unsuccessful.

Fraction III was crystallized from acetone yielding 8.7 g of a solid (Fraction A). After several recrystallizations from methanol-methyl ethyl ketone, the melting point of this solid was 139–143°C. Found: C, 57.87, 57.83; H, 4.48, 4.49; N, 13.44, 13.41; Fe, 6.60; Br, 9.44.

Calc. for
$$\begin{bmatrix} (p-NO_2C_6H_4CH_2NC)_2 \\ (C_6H_5CH_2NC)_3 \end{bmatrix}$$
 FeCNBrH₂O:
C, 57.55; H, 4.12; N, 13.10; Fe, 6.53; Br, 9.35%.

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Infra-red (KBr): 3.00 (w), 3.40 (s), 4.58 (vs), 4.72 (w), 6.25 (m), 6.58 (s), 7.00 (m), 7.10 (m), 7.45 (s), 8.20-8.30 broad (s), 14.45 (s) μ .

From the mother liquors of Fraction A there crystallized 5.0 g of a yellow material which was very soluble in methyl ethyl ketone. After several recrystallizations and drying, this material melted at 85-88°C. Found: C, 46.88, 46.92; H, 3.93, 3.69; N, 12.59, 12.32; Fe, 5.14; Br. 13.50.

Calc. for
$$\begin{bmatrix} (p-NO_2C_6H_4CH_2NC)_4\\C_6H_5CH_2NC \end{bmatrix}$$
 FeBr₂·2H₂O

C, 47.18; H, 3.46; N, 12.38; Fe, 5.48; Br, 15.70%.

Infra red (KBr): 2.90 (s), 4.54 (vs), 4.72 (w), 6.22 (s), 6.58 (vs), 6.69 (w), 6.88 (w), 7.44 (vs), 9.02 (w), 9.85 (w), 11.65 (w), 12.55 (w), 13.65 (s), 14.40 $(s) \mu$.

The appearance of a cyanide band at 4.72μ , which is found to be typical of a cyanide group, makes a structural assignment of this compound uncertain.

Reaction of I with β -naphthyl bromomethane

To 15.5 g (0.02 mole) of I were added 18.00 g (0.08 mole) of β -naphthyl bromomethane, m.p. 44-45°, which was prepared according to the procedure of $SCHULZE^{(6)}$. The wellmixed reaction mixture was then dry-distilled at 115-130°C and 2.0 mm vacuum. A total of 9.9 ml, 13.1 g (0.076 mole) of benzyl bromide was collected, identified by its infra-red spectrum and boiling point. The distillation residue was dissolved in chloroform and was chromatographed as usual on 450 g of alumina. Two distinct compounds were eluted: Fraction I, 7.45 g with acetone; and Fraction II, 6.4 g, with 50 per cent acetone-methanol. Fraction I was recrystallized several times from methyl ethyl ketone, and melted after drying at 165–167°C. Found: C, 71·31; H, 4·85; N, 8·79; Fe, 5·92; Br, 7·98. Calc. for $(\beta - C_{10})$ H₇CH₂NC)₅FeCNBr H₂O: C, 72 12; H, 4 66; N, 8 26; Fe, 5 49; Br, 7 87.

$$\left| (\beta - C_{10}H_7CH_2NC)_4 \right|_{E}$$

$$\begin{array}{c|c} NC)_4 \\ C \\ \end{array} FeCNBr \cdot H_2O: \end{array}$$

Calc. for $\begin{bmatrix} (p-c_{10}\pi_7 C \pi_2) \\ C_6H_5CH_2NC \\ C, 70.96; H, 4.60; N, 8.71; Fe, 5.79; Br, 8.28\%. \end{bmatrix}$

Infra-red (KBr): 2.90 (w), 3.35 (m), 3.40 (m), 4.55 (vs), 4.72 (s), 6.20 (w), 6.30 (m), 6.62 (s), 6.60 (s), 6.89 (s), 6.99 (s), 7.28 (s), 7.50 (s), 7.85 (s), 8.95 (w), 9.85 (w), 10.42 (w), 10.55 (w), 11.25 (w), 11.70 (s), 12.25 (vs), 13.00 (w), 13.20 (s), 13.40 (vs), 14.45 (s) μ .

Fraction II was crystallized several times from methyl ethyl ketone and melted at 216-218°C after drying at 100°C/1.0 mm. Found: C, 69.58; H, 4.39; N, 9.76; Fe, 6.94.

Calc. for
$$\begin{bmatrix} \beta - C_{10}H_7CH_2NC)_2 \\ (C_6H_5CH_2NC)_3 \end{bmatrix}$$
 FeCNBr:

C, 69.43; H, 4.64; N, 9.91; Fe, 65.9%.

The infra-red spectrum (KBr) of Fraction II was almost identical with that of Fraction I; here the 2.90μ band is very weak; the isonitrile band is split slightly into two bands: 4.52μ and 4.57μ .

Reaction of I with α -bromoacetophenone

To 15.5 g (0.02 mole) of I were added 16.4 g (0.082 mole) of α -bromoacetophenone, the reaction mixture was well mixed, fused and dry-distilled at 2.8 mm and an oil-bath temperature of 135-140°C. After heating for 90 min at this temperature, 2.5 ml of distillate (b.p. 42-60°C) were collected and the reaction was discontinued. The infra-red spectrum of the distillate indicated benzyl bromide as the major constituent and acetophenone, probably an impurity in the commercial a-bromoacetophenone. The residue of the distillation was dissolved in chloroform and was chromatographed on neutral alumina suspended in chloroform. The column was then washed with 6×50 ml of chloroform, 13×50 ml of 50 per cent chloroform-acetone, 3×50 ml of acetone, 12×50 ml of 50 per cent acetone-methanol and finally with 7×50 ml of methanol. Two fractions were eluted: with chloroform, Fraction I, 25.3 g and with 50 per cent chloroform-acetone, Fraction II, 7.6 g. Fraction I was crystallized from methyl ethyl ketone, m.p. 105–120°C. After several recrystallizations from methyl ethyl ketone and drying at $25^{\circ}C/1$ mm, the material melted at 219–220°C. Found: C, 57.05; 57.35, H, 3.96, 4.06; N, 7.72, 7.70; Fe, 5.88; halogen, 17.56. Calc. for $(C_6H_5COCH_2NC)_5FeBr_2$: C, 57.41; H, 3.75; N, 7.44; Fe, 5.93; Br, 16.98%.

Infra-red (KBr): 2.95 (w), 3.40 (s), 3.50 (s), 3.75 (w), 4.52 (s), 4.60 (vs), 5.99 (s), 6.15 (w), 6.25 (s), 6.68 (vs), 6.80 (vs), 6.89 (m), 7.45 (s), 7.80 (s), 8.35 (m), 8.85 (s), 8.92 (vs), 9.05 (s), 9.15 (s), 9.60 (s), 9.85 (s), 10.60 (vs), 10.80 (s), 13.20 (vs), 13.40 (s), 13.60 (s), 13.90 (s), 14.05 (vs), 14.35 (vs), 14.60 (vs) μ .

Reaction of I with hexadecyl iodide

To 11.5 g (0.015 mole) of I were added 42 g (0.12 mole) of hexadecyl iodide (Eastman Chem. Co.) and the reaction mixture was distilled at an oil-bath temperature of $120-156^{\circ}$ C under 0.5 mm vacuum. After 98 min there distilled at 44-46°C, 3 ml of a yellowish liquid. The infra-red spectrum of the distillate indicated the presence of benzyl bromide and hexadecyl iodide.

Analysis of distillate: Br, 6.93; I, 47.18%.

The reaction residue was then boiled with chloroform, the solution was filtered hot, whereby a chloroform insoluble material, Fraction I, 0.69 g, m.p. $145-210^{\circ}$ C was isolated. This material was recrystallized from methanol-chloroform; after drying at 25° C/1.0 mm it melted at 230-231.5°C. Upon admixture of this material with (C₆H₅CH₂NC)₄Fe(CN)₂ the melting point was not depressed and the two materials showed identical infra-red spectra.

The chloroform soluble material was cooled to room temperature and was chromatographed on 750 g of neutral alumina suspended in chloroform. The column was washed with 7×50 ml of chloroform, 6×50 ml 50 per cent chloroform-acetone, 10×50 ml of acetone, 13×50 ml 50 per cent acetone-methanol and 3×50 ml of methanol. Three fractions were eluted: Fraction I, 34 g a liquid, with chloroform and 50 per cent chloroformacetone; Fraction II, 7·3 g a solid, m.p. 265-278, with acetone; and Fraction III, 6·6 g with 50 per cent methanol-acetone and methanol. Fraction I seemed to consist mainly of hexadecyl iodide and hexadecyl or benzyl isonitrile as evidenced by a strong band at 4.58μ . Fraction II was not processed any further.

Fraction III was dissolved in about 100 ml of hot methyl ethyl ketone and was filtered. The methyl ethyl ketone insoluble material, Fraction IIIA was a compound melting at 229–231.5°C, after drying in a vacuum oven. Found: C, 69.90, 69.77; H, 10.97, 10.93; N, 6.85, 6.65; Fe, 3.82; I, 8.34. Calc. for $[CH_3(CH_2)_{14}CH_2NC]_5$ FeCNI: C, 70.46; H, 11.36; N, 5.73; Fe, 3.81; I, 8.66%.

Infra-red (CHC1₃): 3.47 (vs), 3.51 (vs), 4.55 (vs), 4.72 (w), 6.31 (w), 7.46 (w), 8.12-8.30 (w), 13.75 (m), 15.25 (w) μ .

From the filtrates of compound Fraction IIIA there crystallized a yellow material, Fraction IIIB; after several recrystallizations from methyl ethyl ketone, the material melted after drying at $90.5-93.0^{\circ}$ C. Found: C, 68.94, 68.97; H, 11.26, 11.07; N, 6.10, 6.14; Fe, 4.37; I, 8.34.

Calc. for
$$\begin{bmatrix} (CH_{2}(CH_{2})_{14}CH_{2}NC)_{4} \\ C_{6}H_{5}CH_{2}NC \end{bmatrix}$$
 FeCNI:

C, 69.44; H, 10.52; N, 6.31; Fe, 4.19; I, 9.53%.

Infra-red (CHCl₃): 3.40 (vs), 4.57 (vs), 4.70 (s), 6.25 (w), 6.70 (vs), 7.27 (s), 13.60 (s), 14.40 (s) μ . Fraction IIIB gave a melting point depression with Fraction IIIA upon admixture.

Reaction of I with 3-phenoxy-l-bromopropane

To 15.0 g (0.02 mole) of I were added 37.6 g (0.12 mole) of 3-phenoxy-l-bromopropane and the reaction mixture was heated on a steam bath overnight in a reaction vessel closed by a calcium chloride drying tube. Subsequently, the reaction mixture was dry-distilled at 6-9 mm the oil-bath temperature being kept at $134-160^{\circ}$ C. After 40 min, 8 ml of liquid, b.p. 78-103°C (main fraction 78-79°C), distilled over. The infra-red spectrum of the distillate indicated a mixture of 3-phenoxy-l-bromopropane and benzyl bromide, the latter constituting about 90 per cent of the distillate. The pot-residue was dissolved in chloroform

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and was chromatographed on a column prepared from about 450 g of neutral alumina suspended in chloroform. The column was then washed with 4×50 ml of chloroform, 7×50 ml of 50 per cent chloroform-acetone, 4×50 ml of acetone, 8×50 ml of 50 per cent acetone-methanol and finally with 7×50 ml of methanol. Three different fractions were eluted: Fraction I, 11.8 g with chloroform; Fraction II, 8.5 g with 50 per cent chloroform-acetone; and Fraction III with 4.9 g with 50 per cent acetone-methanol. All attempts to crystallize Fraction I, Fraction II, and Fraction III failed. Fraction II, a yellow oil, was dried for 60 hr at $25^{\circ}C/1.0$ mm Hg and was then analysed. Found: C, 62.28; H, 6.10; N, 8.52; Fe, 6.19; Br, 8.00. Calc. for $(C_6H_5OCH_2CH_2CH_2NC)_5FeCNBr \cdot H_2O$: C, 62.13; H, 5.82; N, 8.53; Fe, 5.66; Br, 8.11%.

Infra-red (CHC1₃): 2.95 (m), 3.40 (s), 4.53 (vs), 4.73 (s), 6.28 (s), 6.72 (s), 6.84 (s), 6.98 (s), 7.25 (m), 7.50 (m), 7.80 (m), 8.10 (vs), 8.25 (vs), 8.56 (s), 9.25 (s), 9.56 (s), 10.38 (m), 10.79 (m), 11.38 (m), 14.40 (s) μ .

Reaction of I with 12-bromo-n-dodecanoic acid

To 15.0 g (0.02 mole) of I were added 33.5 g (0.12 mole) of 12-bromo-n-dodecanoic acid and the reaction mixture was dry-distilled at 1.0 mm and 140° C oil-bath temperature in the usual fashion. After 90 min, 8 ml of benzyl bromide (11.6 g or 68 per cent conversion based on exchange of all benzyl groups), b.p. 40-42°C, distilled over as the sole product (identified by the infra-red spectrum of the distillate). The residue of the reaction was then extracted with ether to remove the unreacted 12-bromo-n-dodecanoic acid. The ether insoluble material was dissolved in chloroform, was filtered several times through charcoal, and was crystallized from chloroform methyl ethyl ketone.

The material melted, after drying at 1.0 mm Hg at $61-63^{\circ}$ C. Found: C, $55\cdot16$; $55\cdot34$, $55\cdot61$; H, $8\cdot81$, $8\cdot95$, $8\cdot95$; N, $5\cdot65$, $5\cdot45$; Fe, $3\cdot68$; Br, $13\cdot73$. Calc. for (HCO₂(CH₂)₁₀CH₂NC)₅ FeBr₂·3H₂O: C, $55\cdot90$; H, $8\cdot20$; N, $5\cdot02$; Fe, $3\cdot99$; Br, $11\cdot45\%$.

Infra-red (KBr): 2.95 (s), 3.26 (sh), 3.41 (vs), 3.51 (vs), 4.50 (vs), 5.78 (vs), 6.81 (s), 6.94 (w), 7.16 (w), 7.41 (w), 7.62 (w), 7.96 (w), 8.10 (w), 8.30 (w), 8.59 (s), 9.06 (w), 9.55 (w), 11.26 (w), 12.35 (w), 13.50 (w), 13.88 (w) μ .

Simultaneous reaction of allyl bromide and p-carbomethoxybenzyl bromide with $K_4Fe(CN)_6$.

To 11.45 g (0.05 mole) of *p*-carbomethoxybenzyl bromide and 6.05 g (0.05 mole) of allyl bromide were added 15.0 g (0.015 mole) of dry K_4 Fe(CN)₆ and the reaction mixture was heated on the steam bath with stirring in a vessel closed by a calcium chloride tube for two days. The reaction mixture was then extracted with petroleum ether to remove the unreacted bromides. The petroleum ether insoluble material was extracted with boiling chloroform and the chloroform extracts were evaporated to dryness. All attempts to crystallize this material failed. Finally it was pressed on a clay-plate and was crystallized yielding about 2.0 g of a material melting at 220–230°C. After several more recrystallizations from carbon tetrachloride-chloroform the material melted at 233–237°C. The material did not depress, upon mixture, the melting point of $(CH_3O_2CC_6H_4CH_2NC)_5FeCNBr \cdot H_2O$ and the infra-red spectra of these two materials were identical.

Reaction of (C₆H₅CH₂NC)₆FeBr₂ with p-nitrobenzyl bromide

To 6.75 g (7.2 mmole) of $(C_6H_5CH_2NC)_6FeBr_2$ were added 9.33 g (43 mmole) of *p*-nitrobenzyl bromide, the reaction mixture was well mixed and was distilled under reduced pressure at 1.0 mm in the usual fashion. The reaction was stopped after about 1.5 ml of a liquid distilled over; the liquid was identified as benzyl bromide, (1.5 ml = 2.15 g = 1.3 mmole) of benzyl bromide or 18 per cent of total benzyl bromide). The residue was extracted with ether, which yielded, upon evaporation, 10.1 g of wet *p*-nitrobenzyl bromide. The ether insoluble material was then crystallized from acetone yielding 3.3 g of N-benzyl formamide and a non-identified oil. The N-benzyl formamide was identified by infra-red spectrum of an authentic sample.

RESULTS AND DISCUSSION

It was noticed earlier that the alkylations of tetrabenzylisonitrile iron (II) cyanide (II) to cyanopentabenzylisonitrile iron (II) bromide (I) and of cyanopentabenzylisonitrile iron (II) bromide to hexabenzylisontrile iron II bromide (III) with benzyl bromide are equilibrium reactions: $^{(5,7)}$

$$(C_{6}H_{5}CH_{2}NC)_{4}Fe(CN)_{2} \xleftarrow{C_{6}H_{5}CH_{2}NC} (C_{6}H_{5}CH_{2}NC)_{5}FeCNBr \xleftarrow{C_{6}H_{5}CH_{2}Br} (C_{6}H_{5}CH_{2}NC)_{6}FeBr_{2}$$

When a foreign alkyl halide was introduced into the system, these alkylation reactions could be tailored into a synthesis of new isonitrile complexes by a "trans-alkylation reaction."

$$(RNC)_{5}FeCNBr + R'Br \longleftarrow \begin{bmatrix} a. (RNC)_{4} & FeCNBr \\ R'NC & FeCNBr \\ b. (RNC)_{2} & FeCNBr \\ c. (RNC)_{2} & FeCNBr \\ (R'NC)_{3} & FeCNBr \\ d. RNC & FeCNBr \\ e. (R'NC)_{4} & FeCNBr \\ e. (R'NC)_{5} & FeCNBr \end{bmatrix} + RBr$$
(2)

The transalkylation of isonitrile complexes could be accomplished with an alkyl halide R'X, which is higher boiling then RBr, by a continuous distillation of RBr from the reaction mixture to yield b, c, d and e. The reaction is, in form, similar to the transalkylations and transesterifications found, for example, in carbon $^{(8,9)}$ and boron chemistry $^{(10,11)}$. Since the separation and crystallization of the reaction products were laborious each reaction is described in some detail in the Experimental Part and the reaction products isolated are summarized in Table 1. Considerable difficulty was encountered with the purification of these products.

A typical reaction profile is given in Fig. 1 for the transalkylation of I with *p*-nitrobenzyl bromide, and β -naphthyl bromomethane. The reactants were well mixed and were placed into a still equipped with a magnetic stirrer and two thermometers: one to measure the temperature in the distillation vessel and the other to measure the temperature of the distilling vapour. The still was connected to a graduated cylinder and was evacuated and placed into a constant temperature bath. The constant bath temperature was brought to about 120°C, at which temperature the reaction started. The temperature was maintained at about 120°C or was increased by about 15–30°C after the distillation of three moles of benzyl bromide. The progress of the reaction was followed by the rate of distillation of benzyl bromide.

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In each of the cases investigated (see Table 1) the rate of distillation of benzyl bromide decreased after about three to four moles of benzyl bromide had distilled over. Hexadecyl bromide transalkylated about twice as fast as hexadecyl chloride. No comparison was made between the relative velocity of transalkylation of hexadecyl iodide and hexadecyl bromide. The initiation period of the "transalkylation" reaction was shorter the more polar R'X suggesting perhaps a medium effect.



FIG. 1.—Rate of transalkylation of I with p-nitrobenzyl bromide (•) and with β -naphthyl bromoethane (•) as measured by the rate of distillation of benzyl bromide.

Moles R'X/ moles I*	R'X	Products isolated
4	p-NO ₂ C ₆ H ₄ CH ₂ Br	(R'NC) ₂ (RNC) ₃ FeCNBr;
		(R'NC) ₄ (RNC)FeBr ₂ ·2H ₂ O
5	p-CH ₃ CO ₂ C ₆ H ₄ CH ₂ Br	$(R'NC)_5$ FeCNBr; $(R'NC)_4$ RNCFeCNBr \cdot H ₂ O;
	•	(R'NC) ₃ (R'NC) ₃ (RNC) ₂ FeCNBr
4	C ₆ H ₅ COCH ₂ Br	(R'NC) ₅ FeBr ₂
6	o-CH ₃ C ₆ H ₄ CH ₂ Br	$(R'NC)_4Fe(CN)_2$
4	p-CH ₃ C ₆ H ₄ CH ₂ Br	(R'NC) ₅ FeCNBr·H ₂ O
4	β -naphthyl CH ₂ Br	$(\mathbf{R'NC})_5 \mathbf{FeCNBr} \cdot \mathbf{H}_2\mathbf{O};$
	,	(R'NC) ₂ (RNC) ₃ FeCNBr
8	CH ₃ (CH ₂) ₁₄ CH ₂ I	(R'NC) ₅ FeCNI; (R'NC) ₄ RNCFeCNI
6	C ₆ H ₅ O(CH ₂) ₂ CH ₂ Br	(R'NC) ₅ FeCNBr·H ₂ O
6	HCO ₂ (CH ₂) ₁₂ CH ₂ Br	$(\mathbf{R'NC})_5 \mathbf{FeBr}_2 \cdot \mathbf{3H}_2 \mathbf{O}$
Moles R'X/		

TABLE 1.—TRANSALKYLATION REACTIONS, SUMMAR	RY
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moles II*

5	<i>p</i> -CH ₃ CO ₂ C ₆ H ₄ CH ₂ Br	(R'NC)₄RNCFeCNBr		
5·5	<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ Br	(R'NC)₄(RNC)FeCNBr		
* $I = (C_6H_5CH_2NC)_5FeCNBr$; $II = (C_6H_5CH_2NC)_4Fe(CN)_2$; $R = benzyl$				

All compounds which could be isolated from the solid reaction mixtures are summarized in Table 1. The structures of the transalkylated products were determined by ultimate analysis, infra-red spectra and frequently by comparison with samples prepared by an independent route.⁽⁵⁾ Some of the samples contain water of crystallization which was absorbed from the solvent of crystallization. Iron isonitrile complexes of types II and III and probably also I are clathrate compounds⁽¹²⁾ and we have found that the water of crystallization is frequently difficult to remove. In addition to these compounds expected from equation (2), materials in which the cyano group was replaced by bromide with structures tentatively assigned as $[(p-0_2NC_2H_4CH_2NC)_4C_6H_5CH_2NC]FeBr_2 \cdot H_2O,$ $(C_6H_5COCH_2NC)_5FeBr_2$, and $(p-O_2NC_2H_4CH_2NC)_5FeBr_2\cdot 3H_2O$ were isolated as major constituents. The mode of formation of these materials is thus far not clear. In the reaction of I with o-xylyl bromide and with n-hexadecyl iodide, an isonitrile was identified among the distillation products.

The scope of the transalkylation reaction is clearly broader than the alkylation of alkali ferrocyanides with alkyl halides. The alkyl group in R'X may be activated by a carbon-carbon double bond in the α -position or may be nonactivated: it may bear a substituent such as a carboxy group. X may be chloride, bromide, or iodide.

The mechanism of the transalkylation reaction is very complex because of the multitude of products involved and the possibility of internal rearrangement within the complex.⁽¹³⁾ The first step in the reaction may be the alkylation of I to III or elimination of benzyl bromide to form either II or IV. (See Fig. 2). The alkylation of I with benzyl bromide was slower than the total transalkylation reaction with



FIG. 2.—The stereochemistry of the transalkylation reaction.

either *p*-nitrobenzyl bromide or *p*-xylyl bromide. Furthermore, no transalkylated products were obtained in the reaction of III with *p*-nitrobenzyl bromide. Therefore, the alkylation of I to III cannot be a principal step in transalkylation. Only one tetrabenzylisonitrile iron II cyanide was synthesized, m.p. $229-230^{\circ}C$: on the basis of infra-red, nuclear magnetic spectra, ⁽¹⁴⁾ and its thermal stability, it is most probably ⁽¹²⁾ H. M. POWELL and G. W. R. BARTINDALE, J. Chem. Soc. 799 (1945).

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the "trans-isomer". Transalkylation of II with *p*-carbomethoxybenzyl bromide and *p*-xylyl bromide was slower than the corresponding transalkylation of I, and different products were isolated from the two reactions. Furthermore, II was isolated in the transalkylation of hexadecyl iodide even when an excess of hexadecyl iodide was used. Hence the first step in the transalkylation of I is most probably the formation of IV. Transalkylation of I with less than stoichiometric amounts of *p*-xylyl bromide yielded the totally transalkylated product $(p-CH_3C_6H_5CH_2NC)_5FeCNBr$ · H_2O . The experiment suggests that the formation of IV may indeed be rate determining.

It was found previously⁽⁵⁾ that electron withdrawing groups in p-XC₆H₄CH₂Br impede the alkylation of K₄Fe(CN)₆ to form R₄Fe(CN)₂, R₅Fe(CN)Br and R₆FeBr₂ and electron-donating groups accelerate the alkylation of K₄Fe(CN)₆. Electron withdrawing groups, $-NO_2$, $-CO_2CH_3$, in p-XC₆H₄CH₂Br do not impede the transalkylation reaction but perhaps even accelerate it as compared to an electron donating group, X = CH₃.

The qualitative results obtained thus far seem to indicate that either (a) the electronic effects involved in the elimination reaction $(1 \rightarrow IV)$ are cancelled by the electronic requirements for the alkylation of IV or (b) the rate-determining step in the reaction is the concerted displacement of the benzyl group by the halide anion in the formation of IV: the para substituent in a-d (equation 2) should then have a relatively small influence on the rate of elimination.

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