Reactions of Coordinated Ligands. V. Electrophilic Substitutions of Cyanopentabenzylisonitrileiron(II) Hydrogen Sulfate and Dicyanotetrabenzylisonitrileiron(II)[1]

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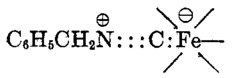
Nitration, sulfonation, alkylation, and bromination of cyanopentabenzylisonitrileiron(II) hydrogen sulfate (I) and dicyanotetracyanobenzylisonitrileiron(II) yielded almost exclusively products in which the electrophilic group entered the *para* position. Competition experiments indicated that the nitration of one of the benzene rings in I is *ca.* 350 times faster than the nitration of benzene. The main resonance structure of the isonitrile group complexed to divalent iron appears to be the immonium form,



$$C_6H_5CH_2\overset{\oplus}{N}:::C:\overset{\ominus}{Fe}—$$

and hence the aromatic rings should be strongly deactivated in electrophilic aromatic substitutions. Since the opposite is true, an anchimeric assistance of the nitrogen in the transition state of aromatic electrophilic substitutions is invoked. This anchimeric assistance is rendered ineffective when a strong Lewis acid is complexed with the lone electron pair on the nitrogen.

Iron isonitrile complexes[2] and especially cyanopentabenzylisonitrileiron(II) hydrogen sulfate (I) and dicyanotetrabenzylisonitrileiron(II) (II) are extremely stable toward concentrated acids.[3] These systems seem to offer, therefore, the opportunity to study the reactions and reactivities of the coordinated aromatic ligands toward electrophilic agents.

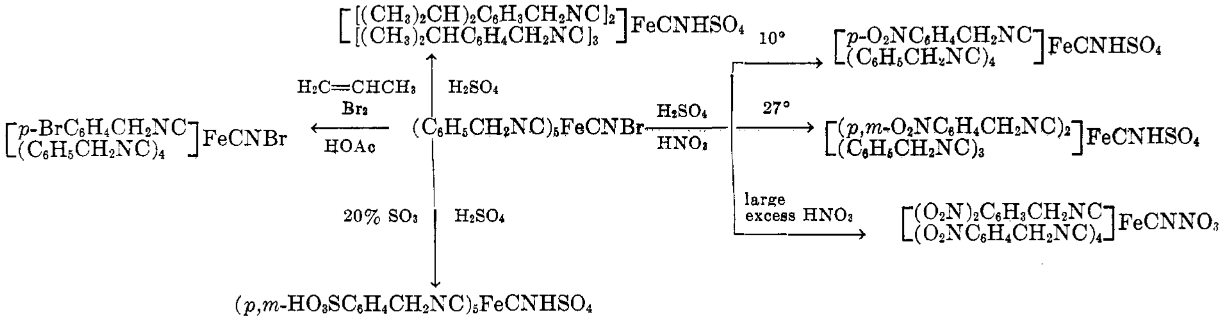


Fig. 1.—Electrophilic aromatic substitutions in $(C_6H_5CH_2NC)_5FeCNHSO_4$.

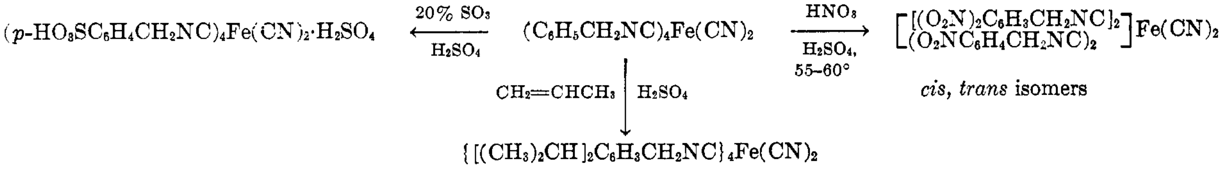


Fig. 2.—Electrophilic aromatic substitutions in $(C_6H_5CH_2NC)_4Fe(CN)_2$.

The nitration, sulfonation, bromination, and alkylation of I and II are described and summarized in Fig. 1 and 2. The position of substitution in the aromatic ring was established by permanganate oxidation of the reaction products, subsequent esterification with diazomethane, and by comparison of the esters with the known compounds. Substitution occurred predominantly in the *para* position. Only trace quantities of the *meta* isomers (<5%) were detected and then only if more than one electron-withdrawing group were introduced into the complex. Nitration of II with a large excess of 70% nitric acid in sulfuric acid yielded two different hexanitrated products, m.p. 143–144 and 117–118° apparently *cis, trans* isomers.

Two resonance forms may be written for the isonitrile group[4]:

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[1] Presented in part at the 6th International Conference on Coordination Chemistry 1961, Detroit, Michigan.

[2] (a) L. Malatesta, "Progress in Inorganic Chemistry," F. A. Cotton, ed., Vol. 1, Interscience Publishers, Inc., New York, N. Y. 1959, 283. (b) E. G. J. Hartley, *J. Chem. Soc.* (London), **99**, 1549 (1911).

[3] W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **22**, 305 (1961).

[4] I. Ugi and R. Meyr, *Ber.*, **93**, 239 (1960).

TABLE I

DETERMINATION OF RELATIVE REACTIVITY OF $(C_6H_5CH_2NC)_5FeCNHSO_4$ (I) FOR THE NITRONIUM ION IN THE PRESENCE OF BENZENE AND TOLUENE

Complex, g. (mmole)	Aromatic, mg. (mmole)	HNO_3, (mmole)	Temp., °C.	Nitrated aromatics, mmole NO_2	Nitrated complex, mmoles NO_2	Nitrated complex isolated
1.90 (2.5)	Benzene 975 (12.5)	5.6	10	0.03	2.1	$\left[\begin{matrix}(O_2NC_6H_5CH_2NC\\(C_6H_5CH_2NC)_4\end{matrix}\right]FeCNHSO_4 \cdot H_2O$
1.90 (2.5)	Toluene 1150 (12.5)	5.6	10	0.075	2.5	
1.90 (2.5)	Benzene 975 (12.5)	7.6	27	0.06	3.8	$\left[\begin{matrix}(O_2NC_6H_4CH_2NC)_2\\(C_6H_5CH_2NC)_3\end{matrix}\right]FeCNHSO_4 \cdot 3H_2O$
1.90 (2.5)	Toluene 1150 (12.5)	7.6	27	0.12	3.8	

$$\underset{A}{R:\ddot{N}::C:} \longleftrightarrow \underset{B}{R:\overset{\oplus}{N}:::\overset{\ominus}{C}:}$$

In a complex the isonitrile may act both as an acceptor and as a donor ligand:

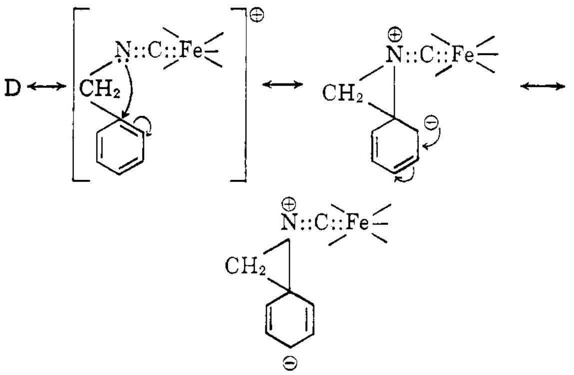
$$\underset{C}{R:\ddot{N}::C::Me} \longleftrightarrow \underset{D}{R:\overset{\oplus}{N}:::C:\overset{\ominus}{Me}}$$

Cotton has shown[5] that as the valency of the metal atoms increases from zero to two, structure B, in which a negative charge is developed on the carbon, is favored in preference to A. Hence D is the predominant structure in the complex. Still, considerable double bond formation between the iron and carbon bond takes place as indicated by the shortening of the iron-carbon bond.[6]

The immonium form B should be strongly *meta* directing and should deactivate the benzene ring toward electrophilic substitutions.[7] Goss, Ingold, and Wilson have found that trimethylbenzylammonium chloride when nitrated yields 88% of the *meta* isomer and only 12% of the *ortho* and *para* isomers.[8] Unfortunately, attempted nitration of benzyl isonitrile under similar conditions yielded only substituted hydrolysis products of benzyl isonitrile. Nitration, sulfonation, propylation, and bromination of both I, II, and cyanopentabenzylisonitrileiron(II) bromide (III) yielded predominantly the *para* isomers. Although overall product accounting in the degradative steps was only 50–80%, the *para* position in the isonitrile complexes is the preferred site of electrophilic substitutions contrarywise to trimethylbenzylammonium chloride.

When 5 moles of benzene and 1 mole of I competed in concentrated sulfuric acid for the nitronium ion, it was found that the nitration of the first ring of I proceeded *ca.* 350 times faster than the nitration of benzene (Table I).[9,10] Similarly the nitration of the first ring in I was *ca.* 180 times faster than the nitration of toluene.

Hence, a powerful anchimeric, rate-accelerating effect[11] must operate in the transition states of the electrophilic substitutions of I which exceeds the electron withdrawing effect of the immonium form D in the monopositive cation I:



Closely analogous transition states in the solvolysis of β-chloroethylamines indicate that the anchimeric effect in these systems may accelerate the reaction rate by a factor of 10^3–10^4, as compared to the aliphatic halide in which the nitrogen is replaced by a carbon atom.[12]

This anchimeric assistance of the nitrogen on the rate of electrophilic substitution in the aromatic ring of I is rendered ineffective by the addition to the reaction mixture of a strong Lewis acid, such as aluminum trichloride. Apparently the stronger Lewis acid adds to the slightly basic nitrogen of the isonitrile group, thereby inhibiting the anchimeric assistance.[13] All attempts to acylate I, II, or III with acetyl and benzoyl chloride and aluminum chloride as the catalyst in an excess of benzoyl

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[5] (a) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961). (b) Ref. 2a, p. 289.

[6] E. G. J. Hartley and H. M. Powell, *J. Chem. Soc.*, 101 (1933).

[7] Hammett's σ value for the $(CH_3)_3\overset{\oplus}{N}$-group for the *para* position is +0.859 compared to $\sigma = +0.778$ for the $—NO_2$ group for the *para* position [H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953)]. Hence the nitration of an ammonium compound should be slower than the nitration of benzene by a factor of 10^2–10^3 (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, 1953).

[8] F. R. Goss, C. K. Ingold, and I. S. Wilson, *J. Chem. Soc.*, 2440 (1929); F. R. Goss, W. Hankard and C. K. Ingold, *ibid.*, 250 (1927); C. K. Ingold and I. S. Wilson, *ibid.*, 810 (1927).

[9] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

[10] The rate is faster than the preliminary results reported earlier, W. Z. Heldt in "Proceedings of the 6th International Conference on Coordination Chemistry," S. Kirschner, ed., The Macmillan Company, New York, 1961, p. 321.

[11] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

[12] (a) P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947); *ibid.*, **71**, 1415 (1949). (b) B. Cohen, E. R. Van Artsdalen, and J. Harris, *ibid.*, **70**, 281 (1948); *ibid.*, **94**, 1875 (1952).

[13] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Academic Press, Inc., 1959, p. 63.

chloride or nitrobenzene as the solvent were unsuccessful, even under stringent conditions.[14]

Experimental

Nitration of I with Nitric Acid–Sulfuric Acid.—To 80 ml. of concentrated sulfuric acid cooled to 10° was added 15.0 g. (0.019 mole) of III. The mixture was stirred at room temperature for 3 hours, and dry nitrogen was bubbled into the solution to assure total removal of hydrogen bromide. Then 20 ml. of 70% nitric acid was added to the reaction mixture, whereupon the temperature increased to 45°. After all the nitric acid was added, the temperature was maintained at 40–45° for another 25–30 min., and then the reaction mixture was poured into 250 g. of ice. A heavy yellow oil, 13.0 g., separated. Attempts to crystallize this material failed. The compound was purified by fractional precipitation from methanol–water. It was finally dried at 25°/0.1 mm. for 48 hr. and was analyzed.

Anal. Calcd. for $\left[\begin{matrix}(O_2N)_2C_6H_3CH_2NC\\(O_2NC_6H_4CH_2NC)_4\end{matrix}\right]FeCNNO_3\cdot 6H_2O$: C, 44.45; H, 3.73; N, 16.44; Fe, 5.04. Found: C, 44.87; H, 3.29, 3.33; N, 16.84, 16.73; Fe, 5.33; S, 0.23. (KBr): 4.53 (vs), 4.70 (s), 6.20 (s), 6.54 (vs), 7.40 (s), 12.50 (s).

Permanganate Oxidation of the Nitrated Products.—To 8.0 g. ($\cong$ 0.01 mole) of the yellow oil was added 120.0 ml. of 10% sodium hydroxide containing 16 g. (0.1 mole) of potassium permanganate. The reaction mixture was then heated at 90° ± 5° for 3 hr. Subsequently, the excess permanganate was decomposed with methanol, the manganese dioxide formed was filtered off, and the residue on the filter was washed with 250 ml. of hot water. The aqueous filtrates were acidified and were continuously extracted with ether in a liquid-liquid extractor for 24 hr. The ethereal solutions were dried with magnesium sulfate and were evaporated to dryness yielding 5.8 g. of acids. This acid mixture was esterified with diazomethane (200 ml.) prepared from 50 g. (0.2 mole) of *N*,*N'*-dinitrosodimethyltetraphthalamide in 500 ml. of ether and 150 ml. of 50% potassium hydroxide.

After the solution was evaporated to dryness, the residue was dissolved in chloroform and analyzed for methyl benzoate and methyl nitrobenzoates by an infrared spectroscopic procedure. Methyl benzoate could be determined quantitatively by its band at 9.73 μ, methyl *o*-nitrobenzoate at 14.32 μ, methyl *m*-nitrobenzoate at 11.18 μ, and methyl *p*-nitrobenzoate at 9.84 μ.

The infrared determination indicated that only methyl *p*-nitrobenzoate and a nonidentified methyl dinitrobenzoate were present in this reaction mixture. This result was confirmed by chromatography of the ester mixture on alumina. Only methyl *p*-nitrobenzoate, m.p. 95–96°,[15] 80% conversion, and a nonidentified methyl dinitrobenzoate, m.p. 69–70°, in about 20% conversion, were identified.

Nitration of II with Concentrated Nitric Acid–Sulfuric Acid.—To 3.047 g. (0.0053 mole) of II was added a mixture of 50 ml. of concentrated sulfuric acid and 25 ml. of concentrated nitric acid warmed to 60°. The reaction mixture was stirred for 30 min. at 55–60°, and was then poured on 200 g. of ice, whereupon a yellow solid precipitated. This solid was washed three times with 100 ml. of water and was then extracted with 250 ml. of boiling methyl ethyl ketone. There remained 2.450 g. (Fraction I) of a material, m.p. 143–144°, which was insoluble in 250 ml. of boiling methyl ethyl ketone. The sample was dried for analysis at 40°/1.0 mm.

Anal. Calcd. for $\left[\begin{matrix}[(O_2N)_2C_6H_3CH_2NC]_2\\(O_2NC_6H_4CH_2NC)_2\end{matrix}\right]Fe(CN)_2\cdot H_2O$: C, 47.23; H, 2.80; N, 19.44; Fe, 6.46. Found: C, 46.72, 46.97; H, 2.99, 2.91; N, 18.77, 19.02; Fe, 6.15. IR ($CHCl_3$): 4.58 (vs), 4.74 (s), 6.21 (s), 6.52 (s), 7.40 (s).

The methyl ethyl ketone extracts (Fraction II) were reduced to about 100 ml. by slowly evaporating the solvent. There crystallized a yellow material, which was dried at 40°/1.0 mm. 0.720 g., m.p. 117–118°.

Anal. Calcd. for $\left[\begin{matrix}[(O_2N)_2C_6H_3CH_2NC]_2\\(O_2NC_6H_4NC)_2\end{matrix}\right]Fe(CN)_2\cdot H_2O$: C, 47.23; H, 2.80; N, 19.44; Fe, 6.46. Found: C, 47.19, 47.32; H, 3.00, 3.25; N, 18.92, 18.92; Fe, 6.22. The infrared spectrum of this material was practically identical with that of Fraction I.

Determination of Relative Reactivity of I for Nitronium Ion in the Presence of Toluene or Benzene.—To 25 ml. of 0.1 *M* solution of I in concentrated sulfuric acid cooled to 10° was added 1.150 g. (12.5 mmoles) of toluene or 0.975 g. (12.5 mmoles) of benzene. To this solution was then immediately added 5 ml. of a 1.1 *M* solution of nitric acid in concentrated sulfuric acid cooled to 10°, and the reaction mixture was stirred at 10 ± 2° for 2 hr. The reaction mixture was then poured into ice; the solution was extracted three times with 100 ml. of ether; the ethereal extracts were combined, dried with magnesium sulfate and filtered; and the ether was distilled. The residue was analyzed for nitro groups at 6.52 μ by an infrared spectroscopic method using acetonitrile as solvent.

From the aqueous solution there separated an oil which was processed and analyzed for nitro groups by the above method. The experiments are summarized in Table I. All attempts to crystallize the oil failed. Chromatography on alumina and subsequent elution of the column with acetone yielded only one main fraction; after drying at 25°/0.1 mm. for 48 hr.

Anal. Calcd. for $\left[\begin{matrix}O_2NC_6H\ CH_2NC\\(C_6H_5CH_2NC)_4\end{matrix}\right]FeCNHSO_4\cdot H_2O$: C, 59.42; H, 4.61; N, 11.83; Fe, 6.74; S, 3.87. Found: C, 59.30; H, 4.50; N, 11.45; Fe, 6.33; S, 3.97.

When the nitration mixture was stirred for 110 min. at room temperature, instead of at 10° under otherwise identical conditions, a dinitrated product was isolated, by the above procedure.

Anal. Calcd. for $\left[\begin{matrix}(O_2NC_6H_4CH_2NC)_2\\(C_6H_5CH_2NC)_3\end{matrix}\right]FeCNHSO_43H_2O$: C, 54.22; H, 4.44; N, 12.34; Fe, 6.15; S, 3.53. Found: C, 53.28, 53.42; H, 3.67, 3.60; N, 12.71, 12.84; Fe, 5.77; S, 3.26. All attempts to crystallize the material failed.

Permanganate oxidation of both the mono- and dinitrated products as described above yielded 60–72% of acids. Esterification of these acids with diazomethane yielded methyl benzoate, methyl *p*-nitrobenzoate, and in case of the dinitrated compound, methyl *m*-nitrobenzoate in about 5% conversion as determined by the infrared spectroscopic method and subsequent chromatographies on alumina.

Sulfonation of I with 20% Sulfur Trioxide.—To 100 ml. of 20% sulfur trioxide cooled to 0° was added 15.2 g. (0.02 mole) of I in such a manner that the reaction temperature did not exceed 25°. The reaction mixture was then stirred at 25° for 1 hr., poured onto 130 g. of chipped ice, and then extracted continuously with ether until all the water and sulfuric acid were removed (about 6 weeks). The solid residue, 8.6 g., had a melting point of 87–110°, neut. equiv.: Found 1180, Calcd. 1206.

Anal. Calcd. for $(HSO_3C_6H_4CH_2NC)_5FeCNHSO_4\cdot 3H_2O$: C, 40.39; H, 3.47; N, 6.89; Fe, 4.58; S, 15.78. Found: C, 40.22, 40.40; H, 4.34, 4.33; N, 6.91, 7.11; Fe, 4.46; S, 15.27. Infrared (KBr): 4.52 (vs), 4.72 (w), 7.10 (s), 8.12 (vs), 8.65 (vs), 8.95 (vs), 9.70 (vs), 9.92 (vs).

Attempts to esterify this acid with diazomethane failed. The acid was neutralized with 1.0 *N* potassium hydroxide in absolute methanol to pH = 7.0. The resultant white precipitate was then extracted in a Soxhlet with methanol; the methanol soluble material was filtered off and was dried at 70°/0.1 mm.

Anal. Calcd. for $[(KO_3SC_6H_4CH_2NC)_5FeCN]_2SO_4\cdot 2H_2O$. C, 36.54; H, 2.92; N, 6.24; Fe, 4.14; S, 13.09. Found:

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[14] H. C. Brown and F. R. Jensen, *J. Am. Chem. Soc.*, **80**, 2291 (1958).

[15] J. Wilbrend and F. Beilstein, *Ann.*, **128**, 263 (1863).

C, 36.68, 36.86; H, 3.11, 3.07; N, 5.21, 5.48; Fe, 4.47; S, 13.03.

Permanganate Oxidation of $(HO_3SC_6H_4CH_2NC)_5Fe\text{-}CNHSO_4 \cdot 3H_2O$.—To 3.45 g. (2.8 mmoles) of the pentasulfonic acid in 100 ml. of distilled water was added 4.74 g. (30 mmoles) of potassium permanganate. The reaction mixture was stirred at room temperature for 96 hr., resulting in decoloration of all permanganate. An additional 4.74 g. of potassium permanganate was added and the reaction mixture was boiled for 1 hr. under reflux. The excess potassium permanganate was reduced with methanol, and the manganese dioxide was filtered off and was extracted with 100 ml. of a 1% sodium hydroxide solution. The aqueous filtrates and the sodium hydroxide extracts were then evaporated to dryness on a steam bath. The solids were acidified with dilute sulfuric acid and were extracted with methanol. Fractional precipitation with ether yielded 1.7 g. (60%) of sulfobenzoic acids, m.p. 245–260°. (Reported for *p*-sulfobenzoic acid, m.p. 259–260°,[16b] for *m*-sulfobenzoic acid, m.p. 141°.[16b] The infrared spectrum of this acid mixture indicated that it consisted chiefly (>90%) of the *para* isomer with the *meta* isomer as an impurity.

Sulfonation of II with 20% Sulfur Trioxide.—To 100 ml. of 20% sulfur trioxide cooled to 0° was added 11.5 g. (0.02 mole of II in such a manner that the temperature did not exceed 25°. The reaction mixture was then stirred at room temperature for 30 min. and was poured onto 60 g. of ice. This dilute sulfuric acid solution was extracted continuously with ether, until a semisolid appeared in the liquid-liquid extractor. This solid was redissolved in absolute methanol and the methanol was allowed to evaporate to near dryness, whereby a crystalline material separated out (Fraction I). The solid was recrystallized from methanol and was dried at 35°/1.0 mm., m.p. 152-154°.

Anal. Calcd. for $(HO_3SC_6H_4CH_2NC)_4Fe(CN)_2 \cdot H_2SO_4$: C, 41.04; H, 3.04; N, 8.45; Fe, 5.61; S, 16.12. Found: C, 40.74; H, 4.03; N, 8.57; Fe, 5.54; S, 14.70. Infrared (KBr): 4.60 (vs), 4.76 (s), 7.10 (w), 8.40 (vs), 8.90 (s), 9.63 (s), 9.89 (s).

The filtrate of Fraction I was diluted with methanol and neutralized to pH 3.5 with 1.0 *N* potassium hydroxide in methanol. A precipitate formed which was extracted in a Soxhlet with methanol for 5 days. The methanol soluble material, 7.15 g., was dried at 70°/1.0 mm. and analyzed.

Anal. Calcd. for $(KO_3SC_6H_4CH_2NC)_4Fe(CN)_2 \cdot 2H_2O$: C, 37.56; H, 2.78; N, 7.73; Fe, 5.14; S, 11.80. Found: C, 36.95, 36.96; H, 3.14, 3.24; N, 8.60, 8.54; Fe, 5.28; S, 11.60.

Permanganate oxidation of 8.3 g. (0.01 mole) of the tetrasulfonic acid as described above yielded about 5.0 g. of solids, m.p. 250–260° after drying at 30°/1.0 mm. (Reported melting point for $p\text{-}HSO_3C_6H_4CO_2H$ is 259–260°.[16] This acid was esterified with diazomethane in the usual fashion to give an ester, m.p. 97–99.5° (Reported melting point for $p\text{-}HO_3SC_6H_4CO_2CH_3$ is 99–100°, for $p\text{-}CH_3O_3SC_6H_4CO_2H$, 195–196°).[17]

Alkylation of I with Propylene in Concentrated Sulfuric Acid.—To 200 ml. of concentrated sulfuric acid was added 15.5 g. (0.02 mole) of III while the temperature was kept at 10°. Propylene was bubbled with stirring into this solution at a rate of 1000 cc./min. After 3 hr., addition of propylene was discontinued, and the reaction mixture was poured onto ice (200 g.). The water insoluble organic oil was washed with water, taken up into about 200 ml. of chloroform, and the chloroform was dried with magnesium sulfate. The dried chloroform solution was then chromatographed on 700 g. of neutral alumina. The column was washed four times with 100 ml. of chloroform, four times 100 ml. of 50% chloroform–acetone, four times 100 ml. of acetone, four times 100 ml. 50% acetone–methanol, and four times with 100 ml. of methanol. Two fractions were eluted: Fraction I, 15.2 g., with acetone; and Fraction II, 8.6 g., with 50% acetone–methanol, methanol. All attempts to crystallize either Fraction I or Fraction II failed.

Fraction I, a slightly yellow oil, was dried at 25°/1.0 mm. and was analyzed.

Anal. Calcd. for

$$\left[\begin{matrix}[(CH_3)_2CHC_6H_4CH_2NC]_3 \\ \{[(CH_3)_2CH]_2C_6H_3CH_2NC\}_2\end{matrix}\right]FeCNHSO_4:$$

C, 70.30; H, 7.41; N, 7.93; Fe, 5.27; N, 7.99; Fe, 5.14. Infrared ($CHCl_3$): 3.00 (w), 3.40 (s), 4.10 (w), 4.58 (w), 4.71 (s), 61.21 (s), 6.68 (s), 6.82 (s), 6.95 (s), 7.05 (w), 7.12 (w), 7.22 (w), 7.32 (s), 7.45 (s), 8.10–8.30 broad, 9.10 (w), 9.30 (w), 9.50 (w), 10.88 (w), 11.19 (w).

The NMR spectrum of this compound in deuterochloroform (with tetramethylsilane as an internal reference) showed a doublet centered at $\delta = 1.2$ ($J = 6$ c.p.s.) and a septuplet centered at $\delta = 3.0$ characteristic of the isopropyl group.[18] The position of substitution was not determined.

Alkylation of II with Propylene in Concentrated Sulfuric Acid.—To 11.2 g. (0.02 mole) of II was added 200 ml. of cold (0°) concentrated sulfuric acid and the alkylation procedure outlined for I was followed. After 3 hours the reaction mixture was poured onto 500 g. of ice, whereupon a solid precipitated. The solid was washed with water and was dried at 25°/1.0 mm., yielding 22.5 g., m.p. 118–166°. The solid was then taken up in chloroform, the chloroform solution was dried with magnesium sulfate, and was then chromatographed on 500 g. of neutral alumina suspended in chloroform. The chromatographic column was developed four times with 50 ml. of chloroform, ten times with 50 ml. of acetone, with 300 ml. of 50% acetone–methanol, and finally with 400 ml. of methanol. The chloroform eluents yielded Fraction I, 2.72 g.; the acetone eluents, Fraction II, 4.65 g.; and the methanol eluents, Fraction III, 12.4 g. Fraction II was recrystallized several times from methyl ethyl ketone and chloroform and was dried at 25°/1.0 mm., m.p. 247–248°.

Anal. Calcd. for $\{[(CH_3)_2CH]_2C_6H_3CH_2NC\}_4Fe(CN)_2 \cdot H_2O$: C, 74.81; H, 8.44; N, 9.03; Fe, 6.0. Found: C, 75.15, 75.24; H, 9.02, 9.12; N, 8.41, 8.59; Fe, 5.95. Infrared($CHCl_3$): 2.76 (s), 2.92 (w), 3.31 (vs), 3.38 (s), 4.18 (s), 4.59 (vs), 4.78 (s), 6.22 (w), 6.58 (s), 6.78 (vs), 7.03 (s), 7.50 (w), 8.22 (vs), 9.58 (s), 10.78 (s), 11.78 (s), 11.80 (s).

The NMR spectrum of this compound showed the septuplet characteristic of the isopropyl group (see above).

Oxidation of $\{[(CH_3)_2CH]_2C_6H_3CH_2NC\}_4Fe(CN)_2 \cdot H_2O$ with Potassium Permanganate.—To 1.320 g. (1.46 mmoles) of $\{[(CH_3)_2CH]_2C_6H_3CH_2NC\}_4Fe(CN)_2 \cdot H_2O$ was added a solution of 6.8 g. (44 mmoles) of potassium permanganate dissolved in 150 ml. of 10% sodium hydroxide, and the reaction mixture was refluxed over 6 hr. After the reaction mixture was processed in the usual way (the acids were continuously extracted with ether in a liquid-liquid extractor), 500 mg. of acids were isolated, m.p. 215–217° (reported m.p. for trimellitic acid, 216°)[19]

Bromination of III in Acetic Acid.—To 11.5 g. (0.015 mole) of III was added 100 ml. of glacial acetic acid, 12.5 g. (0.078 mole) of bromine and 500 mg. of iron powder, after which the reaction mixture was refluxed for 16 hr. The reaction mixture was cooled to room temperature and poured into 200 ml. of a saturated sodium bisulfite solution, whereupon a solid material precipitated. This solid was washed with 100 ml. of cold 20% sulfuric acid, and the 20% sulfuric acid insoluble material (blue) was dissolved in chloroform. The chloroform solution was washed with aqueous sodium bicarbonate and then water, and was finally dried with

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(16) (a) D. Dimroth and W. von Schaedel, *Ber.*, **40**, 2413 (1907). (b) H. J. Taverne, *Rec. trav. chim.*, **27**, 53 (1906).

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magnesium sulfate and chromatographed on 500 g. of neutral alumina suspended in chloroform. The column was developed with chloroform, acetone, 50% acetone–methanol, and finally with methanol. The methanol fractions yielded upon evaporation 8.0 g. of a yellow oil which failed to crystallize from all the common solvents tried. It was, therefore, dried for several days at 25°/1.0 mm., and was analyzed.

Anal. Calcd. for $\begin{bmatrix}(BrC_6H_4CH_2NC)\\(C_6H_5CH_2NC)_4\end{bmatrix}FeCNBr\cdot H_2O$: C, 58.31; H, 4.30; N, 9.95; Br, 18.93; Fe, 6.61. Found: C, 58.23, 58.08; H, 4.96, 4.98; N, 9.84, 9.32, Br, 18.59, 18.32; Fe, 6.61.

Permanganate oxidation of this complex as described above and subsequent esterification yielded only methyl *p*-bromobenzoate identified by comparison with an authentic sample by vapor phase chromatography.

II, 23.0 g. (0.03 mole), was brominated as described in the previous experiments but was refluxed only for 2 hr., and the reaction mixture was processed in a similar fashion. Without separating the possible isomeric products, the total reaction products were oxidized with 47.4 g. of potassium permanganate in 800 ml. of 10% sodium hydroxide, and the acids were isolated by continuous extraction with ether. Esterification and separation of the esters by vapor phase chromatography on Cellite indicated that only methyl *p*-bromobenzoate and methyl *o*-bromobenzoate (trace) were present.

Attempted Acylation of III.—To a solution of 7.5 g. (0.009 mole) of III in 100 ml. of freshly distilled benzoyl chloride was added 13.2 g. (0.1 mole) of freshly sublimed aluminum chloride. The reaction mixture was then stirred for 19 hr. at 26° and was poured onto ice. The yellow oil was dissolved in chloroform, the chloroform solution was washed with 4 *N* sodium hydroxide, then with water, and was dried with magnesium sulfate. The chloroform solution was chromatographed on neutral alumina.[3] Only one compound was eluted from the column, m.p. 106–108°.[3]

Anal. Calcd. for $(C_6H_5CH_2NC)_5FeCNCl\cdot 2H_2O$: C, 66.62; H, 5.32; N, 11.37; Fe, 7.55; Cl, 4.80. Found: C, 66.30, 66.25; H, 5.39, 5.30; N, 11.27; Fe, 7.64; Cl, 4.97. No material which contained a keto group was detected.

When the acylation was performed in nitrobenzene as the solvent at temperatures between 25–100°, employing aluminium chloride–III ratios of 1:30, no benzoylated products of III could be detected by means of chromatographies on alumina.

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Reactions of Coordinated Ligands. VI. Reaction of Cyanopentabenzylisonitrileiron(II) Hydrogen Sulfate and Dicyanotetrabenzylisonitrileiron(II) with Aliphatic Aldehydes

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Reactions of cyanopentabenzylisonitrileiron(II) bromide and dicyanotetrabenzylisonitrileiron(II) with aliphatic aldehydes in 96% sulfuric acid yielded the expected substituted benzyl alcohols as first reaction products which subsequently reacted with the elimination of water to yield oligo and polymeric materials. One particular resinous product investigated in some detail suggested that the intermediate benzyl carbonium ion may be reduced to free radicals which dimerize with the formation of dibenzyl compositions.

Tetra- and penta-coordinated aliphatic isonitrile complexes are very stable toward dilute and concentrated Lewis acids.[1,2] This stability toward Lewis acids can be utilized to demonstrate differences in reactivity toward electrophilic agents in the coördinated, as compared to the noncoordinated, ligand.

In a previous communication we have reported that the reaction of cyanopentabenzylisonitrileiron (II) bromide (I) and dicyanotetrabenzylisonitrileiron(II) (II) with acyl halides under the usual Friedel-Crafts condition[3] using aluminum chloride as catalyst, was unsuccessful.[4] We wish now to report a simple alkylation procedure for I and II, using aliphatic aldehydes as alkylating agents and sulfuric acid as the Lewis acid catalyst.[5]

Results and Discussion

When I was dissolved in cold 96% sulfuric acid, the reaction mixture stirred at room temperature to ensure complete conversion of I to its hydrogen sulfate[2] and then paraformaldehyde added, a rapid reaction took place with a considerable evolution of heat. Depending upon the experimental conditions employed, yellow to orange-colored monomeric or polymeric materials were formed (see Table I). No reaction of I and II with paraformaldehyde took place at room temperature when the sulfuric acid concentration was less than 75%.

Compounds I and II reacted also with *n*-octanal and chloral to yield compositions similar to those obtained with I and II and paraformaldehyde.

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