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.

(1) L. Malatesta, "Progress in Inorganic Chemistry," Vol. I, F. A. Cotton, ed., 1959, p. 320.

(2) W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **22**, 305 (1961).

(3) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 78.

(4) W. Z. Heldt, *J. Org. Chem.*, in press.

(5) (a) J. A. C. Walker, "Formaldehyde," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1953, p. 337; (b) N. K. Moshichinskaya and R. L. Globus, *J. Appl. Chem. USSR*, **17**, 76, 137 (1944); (c) N. K. Moshichinskaya and Krukowskaya, *Ukr. Khim. Zh.*, **23**, 353 (1957); (d) J. M. Witzel, U.S. Patent 2,825,712 (1956); (e) C. Y. Huang and T. Tanigaki, *Chem. High Polymers* (Tokyo), **12**, 335 (1955).

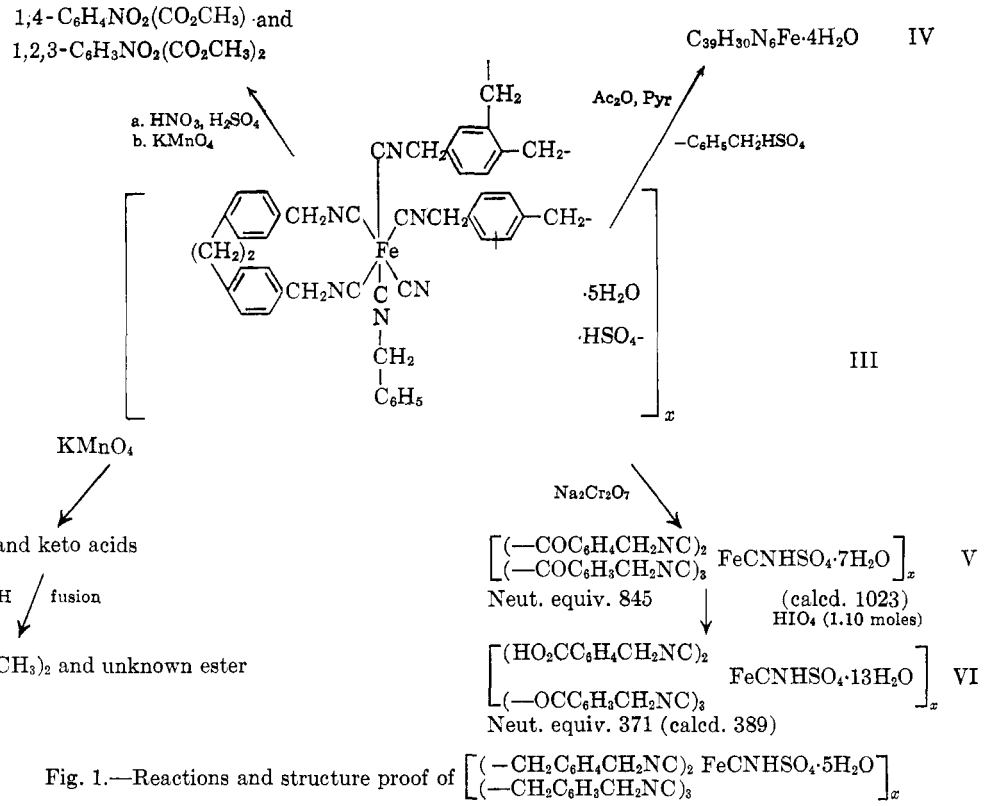


Fig. 1.—Reactions and structure proof of $\left[\begin{matrix}(-CH_2C_6H_4CH_2NC)_2\\(-CH_2C_6H_3CH_2NC)_3\end{matrix} FeCNHSO_4\cdot 5H_2O\right]_x$

Attempts to alkylate I and II with benz- or terephthalaldehyde in 96% sulfuric acid at room temperature were unsuccessful.

The structure of the reaction products was established by permanganate oxidation, sodium-potassium hydroxide fusion[6] of the keto acids formed, and subsequent esterification of all acids. The esters were then separated by vapor phase chromatography and identified by comparison with known specimens (see Table I). The predominant acid isolated was terephthalic acid along with traces of tri- or tetra-basic acids indicating *para* substitution of the aromatic rings in the complexes.

Attempts to establish the molecular weights of these reaction products were unsuccessful; most of these compositions were insoluble in all common organic solvents and contained several molecules of water which could not be removed. The water introduced an additional variable which made the interpretation of the molecular weights reported in Table I, column 12 uncertain.

The structure of one polymeric composition, $[(-CH_2C_6H_3CH_2NC)_5FeCNHSO_4\cdot 5H_2O]x$ (III), was determined in some detail (see Fig. 1). The alkylation of III with formaldehyde took place in the *para* position of the aromatic rings as evidenced from oxidation and nitration studies. The complex did not contain any hydroxyl groups; attempted acylation of III with acetic anhydride in pyridine led to the elimination of one benzyl group and the hydrogen sulfate group. No carbonyl group was introduced into IV (Fig. 1) as evidenced from the infrared spectrum, and the analysis of IV. This result indicated the presence of one unsubstituted benzyl group in III.

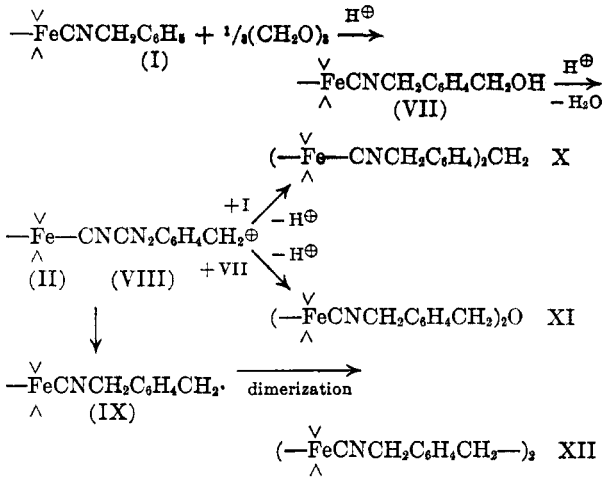
Oxidation of III with sodium bichromate yielded V, a penta ketone, which consumed 1.10 moles of periodic acid per mole of V indicating the presence of an α-diketone.[7] A tri-basic acid was isolated from this reaction mixture.

The polymeric composition III was exceedingly stable toward 50% sulfuric acid as compared with its monomer I,[2] suggesting a chelated polymer. One of the possible structures for III is indicated in Fig. 1. The low over-all yield of tri- or tetra-basic carboxylic acid isolated from the degradation of III indicates either that an extensive decarboxylation during the sodium-potassium hydroxide fusion took place, or that the complex contains two ethane bridges in one structural unit.

It is reasonable to assume that the reaction of I and II with aliphatic aldehydes proceeds similarly to the alkylation of aromatic compounds with paraformaldehyde[5]:

(6) R. C. Shiner and A. Berger, *J. Org. Chem.*, **6**, 305 (1941).

(7) E. L. Jackson, *Org. Reactions*, **II**, 341 (1944).



The most common mode of dimerization or polymerization of the carbonium ion VIII is X, which is most frequently found in the reactions of aromatic compounds with paraformaldehyde in sulfuric acid.[5] The presence of an ether linkage at 9.00 μ[8] in the infrared spectrum of the composition obtained from experiments 3 and 10, Table I, indicates that some dimerization or polymerization may take place with the formation of methylene oxy groups, *i.e.*, *via* XI.

The formation of an ethane bridge (or bridges) in III is surprising. Only reactions of phenols[9,10] and of ferrocene[11,12] have been reported to yield ethane linkages under reaction conditions yielding generally free radicals. Perhaps the carbonium ion VIII is reduced to the free radical IX which then dimerizes to XII. The presence of one ethane bridge per iron atom indicates, furthermore, a two electron transfer per iron atom. Hence the structure of III must be

$$\left[\begin{matrix}(\text{—CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NC})_2 \\ (\text{—CH}_2\text{C}_6\text{H}_3\text{CH}_2\text{NC})_2\end{matrix}\ \text{FeCNHSO}_4\cdot 5\text{H}_2\text{O}\right]_x$$

It is thus far not clear what the mechanism of this electron transfer is.

The reactivity of I, or more specifically one aromatic ring in I, toward paraformaldehyde in concentrated sulfuric acid is equivalent or greater than the reactivity of *p*-chlorophenol toward paraformaldehyde. This observation parallels the results obtained earlier[4] which indicated a powerful anchimeric assistance of the nitrogen in the transition state of the electrophilic aromatic substitutions.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p. 115.

(9) R. Hultzsch, *Z. angew. Chem.*, **60A**, 179 (1948).

(10) (a) K. Hultzsch, *Ber.*, **74**, 898, 1533, 1539 (1941); (b) E. Adler, H. von Euler, and J. V. Cedwell, *Arkiv. Kemi., Mineral. Geol.*, Ser. **A17**, No. 7 (1941).

(11) (a) K. L. Rinehart, Jr., C. J. Michejda, and P. A. Kittle, *Angew. Chem.*, **72**, 38 (1960); (b) P. J. Graham, U.S. Patent 2,709,175.

(12) (a) A. Berger, J. Kleinberg, and W. E. McEven, *Chem. Ind.*, 1245 (1960); (b) A. Berger and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961).

Experimental

Polymerization of I with Paraformaldehyde in Concentrated Sulfuric Acid.—To 200 ml. of concentrated sulfuric acid was added 23.0 g. (0.03 mole) of I, and the reaction mixture was stirred at room temperature for 2 hr. to ensure the total conversion of I into its hydrogen sulfate. To the yellow solution of the hydrogen sulfate was then added 4.5 g. (0.15 mole) of paraformaldehyde. A slurry formed immediately and the temperature rose to about 40°. The reaction mixture was stirred at room temperature for 3 hr. and was then poured into about 500 g. of ice. (The polymerization was essentially complete after about 50 sec. at 40° and no prolonged stirring was necessary.) A yellow-orange solid precipitated, and was washed several times with fresh batches of water, 96 g. A remarkable property of this yellow solid was its water absorption. The yellow material was extracted in a Soxhlet apparatus with acetone for 46 hr. and was dried at 100°/1.0 mm. in an oven, whereby most of the water was removed yielding III, 25.8 g., m.p. 280–320°.

Anal. Calcd. for III

$$\left[\begin{matrix}(\text{—CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NC})_2 \\ (\text{—CH}_2\text{C}_6\text{H}_3\text{CH}_2\text{NC})_2\end{matrix}\ \text{FeCN}\cdot\text{HSO}_4\cdot 5\text{H}_2\text{O}\right]_x$$

C, 60.23; H, 5.28; N, 9.15; Fe, 6.08; S, 3.49; H_2O, 9.8. Found: C, 60.21; H, 4.62; N, 8.73, 8.57; Fe, 5.92; S, 3.67; H_2O, 7.6.

All attempts to dissolve this material in organic solvent failed completely and no molecular weight determinations could be obtained. Infrared (KBr): 2.92 (s), 3.42 (s), 4.58 (vs), 4.72 (s), 5.85 (w), 6.25 (s), 6.69 (s), 6.99 (s), 7.45 (s), 8.20 (s), 8.60 (s), 9.05 (vs), 9.58 (w), 9.20 (w), 9.90 (w), 12.30 (w), 13.45 (w), 14.42 (s), μ.

Permanganate Oxidations of III.—Seventeen and two-tenth grams (0.02 mole) of III was added to a solution consisting of 1200 ml. of 10% sodium hydroxide and 79 g. (0.5 mole) of potassium permanganate. The reaction mixture was brought slowly, over a period of 1 hr., to reflux and was then kept at reflux for 1 hr. The reaction mixture was processed as described earlier,[4] yielding upon acidification and cooling on ice, 12.0 g. of an acidic material, m.p. >> 300°. A small amount melted at *ca.* 120° (fraction 1, last column, Table I). The aqueous solution was then evaporated to dryness on a steam bath; the solid residues were boiled three times with 150 ml. of acetone, the acetone extracts were dried with magnesium sulfate, filtered, and were evaporated to dryness, leaving 7.4 g. of a heavy oil (after drying at 25°/1.0 mm.) (fraction 2, last column, Table I).

Sodium and Potassium Hydroxide Fusions of Fraction 1 Obtained in the Previous Experiment.—To 2.0 g. of fraction 1 were added 2.5 g. each of sodium and potassium hydroxide. This reaction mixture was then heated in a silver vessel with a small flame to 220–250°, and the temperature was kept constant for 5 hr. The temperature of the reaction mixture was then lowered to about 30°, the reaction mixture was dissolved in water and the aqueous solution was concentrated on a steam bath and was acidified to yield 0.73 g. of acids, m.p. 245–300°. (No additional acids could be extracted with ether from the aqueous filtrates.)

Esterification of Acids.—Diazomethane was prepared from 20.6 g. of nitrosomethylurea in 200 ml. of ether according to the procedure of Arndt.[13]

To the acids obtained above was added 40 ml. of the ethereal diazomethane solution. After the ether had evaporated overnight, the samples were analyzed by vapor phase chromatography, and were compared with reference samples of methyl esters: ester (retention time in sec.); methyl benzoate (0.33); dimethyl phthalate (0.82); dimethyl isoterephthalate (1.0); dimethyl terephthalate (1.0); trimethyl hemimellitate (2.2); trimethyl mellitate (2.7); trimethyl mesoate (2.9).

(13) F. Arndt, *Org. Synthesis*, **II**, 165 (1955).

The column was prepared from 20% High Vac silicone grease (Dow Chemical Co.) and firebrick; the operating temperature of the column was 234° and the flow rate 50 ml./20 sec.

The ester resulting from fraction 1 had peaks at 1.0 and 3.1 sec. in the ratio 40:1. The infrared spectrum of the material identified with a retention time of 1.0 sec. was identical with that of dimethyl terephthalate, and the ester had a melting point of 137.5–143°.

Oxidation of III with Sodium Bichromate.—To the polymer prepared from 22.8 g. (0.03 mole) of I and 4.5 g. (0.15 mole) of paraformaldehyde dissolved in 60% sulfuric acid was added 63.5 g. (0.26 mole) of sodium bichromate, and the reaction mixture was stirred with a magnetic stirrer, maintaining the reaction temperature between 30–40°. The reaction mixture was then stirred for another 130 min. at room temperature, whereby all of the bichromate was reduced to chromium (III). The reaction mixture was then poured into ice (~ 500 g.), and the water-insoluble material was washed with water and was extracted with a saturated sodium carbonate solution. When the sodium carbonate solution was acidified only a trace of acids (300 mg.) was isolated, which could not be identified. The polymeric material was washed with 20% sulfuric acid and then with water, and was dried for several days at 30°/1.0 mm., yielding 22.0 g. of material.

Anal. Calcd. for V

$$\left[\begin{matrix}(\text{—COC}_6\text{H}_4\text{CH}_2\text{NC})_2 \\ (\text{—COC}_6\text{H}_3\text{CH}_2\text{NC})_3\end{matrix}\ \text{FeCN}\cdot\text{HSO}_4\cdot 7\text{H}_2\text{O}\right]_x$$

C, 54.02; H, 4.13; N, 8.22; Fe, 5.42; S, 3.11. Found: C, 53.68, 53.79; H, 4.20, 4.32; N, 8.58, 8.71; Fe, 5.51, 5.75; S, 3.12, 3.22. Infrared (KBr): 4.50 (vs), 4.70 (s), 6.00 (s). Neut. equiv. = 845, calcd. neut. equiv. = 1023 or the material was a hydrogen sulfate pentaketone.

Periodic Acid Oxidation of V.—To 4.675 g. (0.0046 mole) of the pentaketone were added 3.690 g. (0.016 mole) of periodic acid dihydrate and 100 ml. of glacial acetic acid, and the reaction mixture was stirred at room temperature. After 6 days 2.00 ml. of the solution were withdrawn and were back-titrated with 0.1016 *N* sodium thiosulfate according to a standard procedure,[14] consuming 18.60 ml. of 0.1016 *N* sodium thiosulfate. This result indicated that 5.00 mmoles of periodic acid dihydrate were consumed by the pentaketone or that 1.10 mmoles α-diketone linkages were oxidized by the periodic acid per mole of pentaketone present.

The balance of the reaction mixture was freeze-dried; the water-insoluble gray residue was washed with water and finally with acetone, yielding a white residue, 4.82 g. (after drying at 23°/1.0 mm.), m.p. >> 300°.

Anal. Calcd. for

$$\left[\begin{matrix}(\text{HO}_2\text{CC}_6\text{H}_4\text{CH}_2\text{NC})_2 \\ (\text{—COC}_6\text{H}_3\text{CH}_2\text{NC})_3\end{matrix}\ \text{FeCN}\cdot\text{HSO}_4\cdot 13\text{H}_2\text{O}\right]_x:$$

C, 47.44; H, 4.85; N, 7.17; Fe, 4.77; S, 2.74; mol. wt., 1172. Found: C, 46.97, 46.84; H, 3.84, 3.81; N, 7.30, 7.12; Fe, 5.30; 5.20; S, 1.50, 1.51; neut. equiv. = 371 (calcd. = 389).

Reaction of III with Acetic Anhydride in Pyridine.—To 2.8 g. (0.005 mole) of III were added 50 ml. of pyridine and 15 ml. of acetic anhydride, and the reaction mixture was heated for 24 hr. at 120–130°. The solution was then cooled to room temperature and poured into water; a brown solid was collected and extracted continuously with acetone in a Soxhlet apparatus. After drying, the decomposition point of the solid was 60–150°. This material failed to dissolve in all solvents tried.

Anal. Calcd. for $[C_{39}H_{30}N_6Fe\cdot 3H_2O]_x$: C, 67.64; H, 5.23; N, 12.13; Fe, 8.02. Found: C, 66.89; H, 6.15; N, 11.85; Fe, 7.94; S, 0.0.

Nitration of III.—The polymer III was prepared from 15.4 g. (0.02 mole) of I and 3.0 g. (0.10 mole) of paraformaldehyde as described above. Without isolating the polymer, 20 ml. of concentrated nitric acid was added to the reaction mixture at such a rate that the temperature remained between 32–36° (800 sec.). The reaction mixture was stirred for another 200 sec. at this temperature and was then poured into about 500 g. of ice. The yellow precipitate was filtered, was washed with water, and was extracted continuously with acetone in a Soxhlet apparatus overnight. After drying in an oven at 25°/1.0 mm., there was obtained 36 g., m.p. 195–265°. The material was insoluble in all usual organic solvents tried.

Anal. Calcd. for $[(C_{46}H_{33}O_4N_6FeS)5NO_2\cdot 7H_2O]_x$: C, 46.87; H, 4.02; N, 13.07; Fe, 4.74; S, 2.72. Found: C, 47.07, 47.17; H, 2.81, 2.98; N, 12.82, 12.84; Fe, 5.16; S, 3.55, 3.58. Infrared (KBr): 4.55 (vs), 4.72 (s), 6.22 (s), 6.52 (vs), 7.00 (s), 7.23 (s), 7.45 (vs), 7.82 (s), 12.00 (s).

Eight and eight-tenths grams of the nitrated polymer was oxidized with 79 g. (0.5 mole) of alkaline permanganate as described above, yielding 12 g. of acids (wet, m.p. 150–190°). The resulting acids were then esterified with 300 ml. of ethereal diazomethane solution, yielding 9.5 g. of esters. Fractional crystallization from methanol–water yielded two fractions: Fraction I, the more soluble, about 1 g., identified as methyl *p*-nitrobenzoate, m.p. 95–96° and Fraction II about 3.6 g., m.p. 74–75°. Fraction II did not give a melting point depression with a synthetic sample of dimethyl 2-nitroterephthalate. (Reported melting point for dimethyl 2-nitroterephthalate, 74–75°C.[15])

Reaction of I with *n*-Octanal.—To 75 ml. of concentrated sulfuric acid cooled to 10° was added 7.5 g. (0.01 mole) of I and the solution was stirred at room temperature for 1 hr. until almost all of the hydrogen bromide had escaped. Then half of the solution was added to 3.2 g. (0.025 mole) of *n*-octanal, and the reaction mixture was stirred for 10 hr. at room temperature. A brown solution formed immediately and the reaction mixture was processed as described above.

The reaction product, 6.1 g., was very soluble in chloroform, acetone, methyl ethyl ketone, and methanol. All attempts to crystallize this material failed. It was reprecipitated several times from methanol with diethyl ether and was dried as a semisolid at 25°/1.0 mm.

Anal. Calcd. for

$$\left[\begin{matrix}(\text{CH}_3(\text{CH}_2)_6\text{CHC}_6\text{H}_3\text{CH}_2\text{NC})_2 \\ (\text{C}_6\text{H}_5\text{CH}_2\text{NC})_3\end{matrix}\ \text{FeCN}\cdot\text{HSO}_4\cdot 4\text{H}_2\text{O}\right]_x:$$

C, 68.93; H, 7.31; Fe, 5.62; S, 3.22. Found: C, 68.57, 68.65; H, 7.57, 7.55; Fe, 5.48; S, 2.68.

The molecular weight of this material in nitrobenzene was 618 ± 14; inherent viscosity in methanol at 26° was 0.039; the polymer was cured in a vacuum oven at 120°/0.1 mm. for 2 hr. whereby the inherent viscosity in methanol (30.2°) increased to 0.095.

Reaction of Chloral with I in Concentrated Sulfuric Acid.—To 50 ml. of concentrated sulfuric acid was added 15.4 g. (0.02 mole) of I, and the solution was stirred at room temperature until all materials dissolved. The reaction mixture was cooled to 5°, 5.8 g. (0.04 mole) of chloral was added at once and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then poured into about 100 g. of ice. The white oil which separated was washed with water, extracted into chloroform, and the chloroform extracts were dried with magnesium sulfate and evaporated to dryness. The oil was then dried for 24 hr. at 60°/1.0 mm. in a vacuum oven, whereby most of it solidified; 9.5 g. (about one third of the material was lost in handling), m.p. 60–65°.

(14) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1954, p. 16.

(15) R. Wegschneider and H. Gehringer, *Monatsh. Chem.*, **29**, 529 (1908).

TABLE I. REACTION OF $(C_6H_5CH_2NC)_5FeCNHSO_4$(I) AND $(C_6H_5CH_2NC)_4Fe(CN)_2$(II) WITH PARAFORMALDEHYDE IN CONCENTRATED SULFURIC ACID

Exp.	Isonitrile complex G.	(Mole)	Aldehyde G.	Mole	Reaction conditions H_2SO_4, ml.	Time, min.	Temp., °C.	G. (D.p., °C.)	Found	Calcd.
1	I 23.0	(0.03)	$(CH_2O)_3$ 0.9	0.03	200	2	30	Gum		
2	I 3.85	(0.005)	$(CH_2O)_2$ 0.3	0.01	5	18	25	4.0 (195–235)	C 61.99	61.23
									N 4.65	5.05
									N 9.08	9.94
									Fe 6.55	6.62
									S 3.27	3.80
3	I 23.0	(0.03)	$(CH_2O)_3$ 1.8	0.06	200	3	25	0.45 (wet)	C 62.77	62.61
									H 4.51	4.89
									N 9.55	10.16
									Fe 6.89	6.76
									S 4.46	3.88
4	I 7.6	(0.01)	$(CH_2O)_3$ 0.6	0.02	1000	16	25	3.8 (110–225)	C 56.87	57.08
									H 4.35	4.46
									N 7.94	9.27
									Fe 6.01	6.16
									S 5.54	7.07
5	I 23.0	(0.03)	$(CH_2O)_3$ 1.8	0.06	2000	13	25	37(dry 17.1) (295–300)		
6	I 23.0	(0.03)	$(CH_2O)_3$ 4.5	0.15	200	3	25	26.4 (280–320)	C 60.21	60.02
									H 4.62	5.28
									N 8.57	9.15
									8.73	
									Fe 5.92	6.08
									S 3.67	3.49
7	I 23.0	(0.03)	$(CH_2O)_3$ 9.0	0.3	200	3	25	31.1 (≫300)		
8	I 23.0	(0.03)	$(CH_2O)_3$ 9.0	0.3	200	3	25	30.6 (≫300)		
9	II 2.8	(0.005)	$(CH_2O)_3$ 0.3	0.01	5	16	25	2.7 (125–230)	C 68.92	67.93
									H 4.76	5.07
									N 12.33	13.16
									Fe 8.78	8.75
10	II 5.6	(0.01)	$(CH_2O)_3$ 0.6	0.02	100	0.3	25	5.9 (95–200)	C 65.47	65.93
									H 4.72	5.07
									N 11.42	13.20
									Fe 8.35	8.75
11	II 5.6	(0.01)	$(CH_2O)_3$ 0.6	0.02	1000	16	25	4.0 (large loss) (155–230)	C 57.44	57.44
									H 4.67	4.82
									N 10.67	11.14
									Fe 6.99	7.40
									H_2O 2.4	
12	II 5.6	(0.01)	$(CH_2O)_3$ 1.5	0.05	100	6	25	6.8 (135–190)	C 62.46	62.29
									H 4.73	5.50
									N 10.76	11.46
									Fe 7.56	7.58
									H_2O 8.2	

[a] One or more oxygen atoms may be incorporated into the molecule in the form of ether linkages. [b] Two thirds of the total products were oxidized with permanganate. [c] Products from the permanganate oxidation obtained after KOH–NaOH

Anal. Calcd. for $[(C_6H_5CH_2NC)_4$—$CHC_6H_3CH_2NC(CCl_3)$ $FeCN\cdot HSO_4\cdot 4H_2O]_x$: C, 57.25; H, 4.80; N, 9.32; Fe, 6.19; Cl, 11.79; S, 3.55. Found: C, 57.08; H, 4.41; N, 8.76; Fe, 6.21; Cl, 8.86; S, 3.82; mol. wt. in D.M.S., 160, 165. The inherent viscosity in methanol at 30.2° was 0.148.

Competition Reactions of I and *p*-Chlorophenol for Para-

TABLE I (*Continued*)

Probable structure[a]	Inherent viscosity	Solubility, mol. wt. (cryoscopic), % H_2O found	Oxidation[b] with $KMnO_4$-products[c]
			(1) 21 g. of acid—methyl benzoate and dimethyl terephthalate (2) 9.2 g. of oil—dimethyl terephthalate and unknown ester m.p. 137.5–143°
$\left[\begin{matrix}(-CH_2C_6H_3CH_2NC)_2 & FeCN\cdot HSO_4\cdot 3H_2O \\ (C_6H_5CH_2NC)_3\end{matrix}\right]_x$		Insoluble DMF,[d] DMS[e]; H_2O = 4.0	
$\left[\begin{matrix}(-CH_2C_6H_3CH_2NC)_2 & FeCN\cdot HSO_4\cdot 2H_2O \\ (C_6H_5CH_2NC)_3\end{matrix}\right]_x$	0.029 in DMS at 25°	Soluble in DMS; mol. wt. = 240, 220	(1) 4.3 g. of acid—40% dimethyl terephthalate, unknown m.p. 225–230° (2) 11.5 g. of oil
$\left[\begin{matrix}(-CH_2C_6H_3CH_2NC)_2 & \\ HSO_3C_6H_4CH_2NC & FeCN\cdot HSO_4\cdot 2H_2O \\ (C_6H_5CH_2NC)_2 & \end{matrix}\right]_x$		Soluble in DMS; mol. wt. = 127, 134; H_2O = 3.9 (neut. equiv. = 445)	
		Insoluble in DMS,	(1) 2.8 g. acid—32% dimethyl terephthalate, unknown m.p. 250° (2) 7.5 g. oil—60% dimethyl terephthalate and unknown ester
$\left[\begin{matrix}(-CH_2C_6H_4CH_2NC)_2FeCN\cdot HSO_4\cdot 5H_2O \\ (-CH_2C_6H_3CH_2NC)_3\end{matrix}\right]_x$		Insoluble in DMS, DMF; H_2O = 7.6	(1) 12 g. acid—33% dimethyl terephthalate and unknown ester, unknown m.p. $\gg$ 300 (2) 7.4 g. oil—4% dimethyl terephthalate
		Insoluble in DMS, DMF	(1) 8.9 g. acid—4% dimethyl terephthalate, unknown m.p. $\gg$ 300 (2) No oil
		Insoluble in DMF, DMS	(1) 2.8 g. acid—82% dimethyl terephthalate, unknown m.p. 240–250° (2) 7.5 g. oil—80% dimethyl terephthalate and unknown ester
$\left[\begin{matrix}(-CH_2C_6H_3CH_2NC)_2 & Fe(CN)_2\cdot 2H_2O \\ (C_6H_5CH_2NC)_2\end{matrix}\right]_x$		Insoluble in DMF, DMS; H_2O = 2.0	
$\left[\begin{matrix}(-CH_2C_6H_3CH_2NC)_2 & Fe(CN)_2\cdot 2H_2O \\ (C_6H_5CH_2NC)_2\end{matrix}\right]_x$	0.019 in DMF at 25°	Soluble in DMS, mol. wt. = 128, 129; H_2O = 6.1	
$\left[\begin{matrix}-CH_2C_6H_3CH_2NC)_2 & \\ HSO_3C_6H_4CH_2NC & Fe(CN)_2\cdot 4H_2O \\ C_6H_5CH_2NC & \end{matrix}\right]_x$		Soluble in DMS, very soluble acetone; mol. wt. = 159, 160 (neut. equiv. = 780)	Infrared: Indicates sulfonic acid group at 8.42 μ
$[(-CH_2C_6H_3CH_2NC)_4 \quad Fe(CN)_2\cdot 6H_2O)]_x$		Insoluble in DMF, DMS	

fusion and diazomethane esterification identified by melting point, infrared and vapor phase chromatography. [d] Dimethyl formamide. [e] Dimethyl sulfoxide.

formaldehyde.—To 24 ml. of a concentrated sulfuric acid solution cooled to 10° containing 0.006 mole of I was added 768 mg. (0.006 mole) of *p*-chlorophenol and immediately thereafter 260 mg. (0.016 mole) of paraformaldehyde, and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was then poured on 50 g. of ice and the organic materials were washed several times with water. The organic mixture was then extracted with chloroform to remove unchanged I and *p*-chlorophenol formaldehyde polymers. The chloroform insoluble solid, 3.0 g., was

dissolved in acetone, the acetone solution was dried with magnesium sulfate and was evaporated to dryness; the resulting oil was dried for several days at 25°/1.0 mm., and was then analyzed.

Anal. Found: C, 39.49, 39.72; H, 4.58, 4.46; Fe, 3.49; Cl, 3.19, 2.99.

This indicates a mixture of 11% *p*-chlorophenol and 47% of the iron complex.

The experiment was repeated under the same reaction conditions but using 0.03 mole of *p*-chlorophenol. Only a solid hetero polymer formed, after drying at 25°/1.0 mm.

Anal. Found: C, 55.62, 55.26; H, 4.13, 4.17; Fe, 3.77; Cl, 12.64, 12.36; S, 4.55.

This indicates a mixture of 52% of iron complex and 45% of *p*-chlorophenol.

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Preparation of Halogenated Nitronaphthalenes, Halogenated Naphthylamines, and Their Sulfonic Acids

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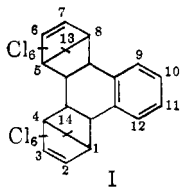
The compounds 3-bromo-2-nitronaphthalene and 3,4-dichloro-2-nitronaphthalene are prepared readily by the basic method of Danish, Silverman, and Tajima[1] for synthesis of β-substituted naphthalenes. From these compounds and their reduced analogs, sulfonic acids are derived having the unusual 3(and/or 4)-halo-2-nitronaphthalene and 3(and/or 4)-halo-2-naphthylamine relationships. Placement of the sulfonic acid functions homonuclear with or heteronuclear to the other substituents may be controlled by variations in the order and techniques of the reduction and sulfonation reactions. The reaction sequences provide an interesting new set of dyestuff intermediates for evaluation.

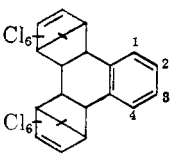
The presence of halogen atoms in dye molecules is known to lend fastness, especially chlorine fastness to the dyes. Thus, halogenated indanthrones are faster to chlorine, halogenated indigos are faster to chlorine and have better fiber affinity than their parent dyes, and chlorinated azo dyes are sometimes brighter and show improved fastness to light, bleaching, and acids.[2]

The aminosulfonic acids described here are of particular interest as dye intermediates, since they bear amino and halogeno functions in the unusual 2,3- and 2,4-relationships on naphthalene. Such configurations can be obtained only with difficulty through the standard aromatic substitution and interconversion reactions, but result directly when the method of Danish, Silverman, and Tajima[1] is applied to the preparation of the halonitronaphthalene precursors. Direct halogenation of 2-nitronaphthalene results only in compounds in which the halogens have entered positions heteronuclear to the nitro group.[3,4] Halogenation of 2-acetylaminonaphthalene[5-8] leads to other isomeric configurations, especially 1-halo-2-acetyl-aminonaphthalene.

Hyman and Danish[9] as well as Danish, Silverman, and Tajima[1] have described the preparation of 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (I), from the Diels-Alder adduction of one molecule of naphthalene and two molecules of hexachlorocyclopentadiene, and have outlined the preparation of β-substituted naphthalenes by substitution (nitration, sulfonation) of this molecule and subsequent deadduction. For simplicity this diadduct is also referred to here as DHA (Di-Hexachlorocyclopentadiene-Adduct of naphthalene and numbered as in II).



I



II

During the course of this work it was determined that the DHA may be both halogenated and nitrated in good yields on the aromatic ring and that the resulting compounds may be cracked pyrolytically to the corresponding halogenated nitronaphthalenes. These compounds may then be sulfonated and subsequently reduced, or first reduced and then sulfonated to give a variety of halogenated 2-naphthylamine sulfonic acids.

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