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The Condensation of Dicyclopentadienyliron with Aromatic Diazonium Salts

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Dicyclopentadienyliron in its cationic form $[Fe(C_5H_5)_2]^+$ reacts with aromatic diazonium salts to give aryl substituted derivatives of dicyclopentadienyliron.

Derivatives of dicyclopentadienyliron have been made in the past from dicyclopentadienyliron in its organic solvent soluble form. No reactions other than salt formation are reported for the oxidized, cationic form $[Fe(C_5H_5)_2]^+$ of dicyclopentadienyliron. It was of interest to find that dicyclopentadienyliron in its oxidized, cationic form $[Fe(C_5H_5)_2]^+$ reacts readily with aromatic diazonium salts in a dilute acid medium to give a variety of substituted dicyclopentadienylirons.

The reaction is carried out by oxidizing dicyclopentadienyliron[1] with concentrated sulfuric acid to form $[Fe(C_5H_5)_2]^+$ and mixing this dilute sulfuric acid solution with diazonium salts of aromatic amines at about room temperature. Reaction occurs with nitrogen evolution and dicyclopentadienylirons substituted with one or more aryl groups are obtained (see Table I). A variety of aryl substituted dicyclopentadienylirons can be made in which the phenyl groups are substituted with functional groups capable of further reactions.

Usually the coupling between diazonium salts and an aromatic compound to form asymmetrical biaryls takes place in a water-immiscible aromatic medium on the weakly acid or preferably alkaline side and often at elevated temperatures.[2] In contrast to this, the coupling of dicyclopentadienyliron occurs on the strongly acidic side, in water solutions and at low temperatures. Elevated temperatures produce only the usual phenolic decomposition products of the diazonium salts.

Monoaryl and polyaryl substituted dicyclopentadienylirons usually are obtained simultaneously. The polyaryl substituted compounds are obtained directly as precipitates which are insoluble in the dilute sulfuric acid. Even after several crystallizations they melt over a range of several degrees which indicates that probably mixtures of isomers rather than pure compounds are isolated. The monoaryl dicyclopentadienylirons usually are formed in smaller amounts and are always present in the cationic, dilute acid-soluble form. Addition of reducing agents precipitates them readily.

The question of whether or not the polyaryl substituted dicyclopentadienylirons carry the aryl groups on one ring of dicyclopentadienyliron or whether they were distributed over both rings could not be decided. The dipole moment of the dicyclopentadienyliron substituted with two *p*-chlorophenyl groups is high. Thus, the possibility remains open that the substituents are on one cyclopentadienyl ring or on adjacent sides of both rings. The absence of a dipole moment would indicate that substitution is on both rings on opposing sides.[3]

The fact that dicyclopentadienyliron substituted with as many as eight phenyl groups can exist was demonstrated when a bis-(tetraphenylcyclopentadienyl)-iron was prepared from tetraphenylcyclopentadiene and ferrous chloride with sodamide in liquid ammonia. Pauson reports[4] that he was unable to prepare a bis-(tetraphenylcyclopentadienyl)-iron.

It is interesting to note that the cyclopentadienyl-(phenylcyclopentadienyl)-iron obtained from dicyclopentadienyliron and diazotized aniline is identical with the one obtained when cyclopentadienylsodium is treated in liquid ammonia with *p*-dibromobenzene and ferrous chloride. Obviously, a substitution of one bromine by a hydrogen had taken place in the latter reaction which led *via* condensation with an unsubstituted cyclopentadienylsodium to the formation of cyclopentadienyl-(phenylcyclopentadienyl)-iron. Similarly unsymmetrical condensations are reported in Pauson's paper.

Experimental

***p*-Chloroaniline and Dicyclopentadienyliron.**—Dicyclopentadienyliron (100 g.) was added to 96% sulfuric acid (500 g.) while allowing the temperature to rise to 50°. Sulfur dioxide was evolved and the blue solution of $[Fe(C_5H_5)_2]^+$ resulted. This solution was kept at room temperature overnight, then poured into ice and water. *p*-Chloroaniline (64 g.) was diazotized in 20% sulfuric acid (500 cc.) at 0–5°. The diazonium salt solution was poured into the above solution of $[Fe(C_5H_5)_2]^+$ at room temperature and agitation was continued until the unreacted diazonium compound could not be detected by coupling with β-naphthol. A considerable amount of foaming occurred because of the formation of a fine precipitate and the constant evolution of nitrogen.

A light brown precipitate was obtained upon filtration (65 g.). The crude product was extracted with benzene (1,000 cc.) and the solid obtained on evaporation was crystallized from high boiling petroleum ether. The di-(*p*-chlorophenyl)-dicyclopentadienyliron thus obtained melted at 192° and dissolved in sulfuric acid with a brown color.

Anal. Calcd. for $C_{22}H_{16}Cl_2Fe$: C, 64.8; H, 3.93; Cl, 17.44; Fe, 13.75. Found: C, 64.8; H, 4.06; Cl, 17.5; Fe, 14.1.

The dilute sulfuric acid filtrate of the reaction mass was deep blue. Upon the addition of a reducing agent (ascorbic acid) a mixture of unreacted dicyclopentadienyliron and cyclopentadienyl-(*p*-chlorophenylcyclopentadienyl)-iron was obtained which could not be separated by crystallization. However, the dicyclopentadienyliron could be removed by sublimation on the steam-bath and the pure cyclopentadienyl-(*p*-chlorophenylcyclopentadienyl)-iron was obtained as yellow crystals melting at 122° after crystallization from 90% acetic acid. It dissolved in 96% sulfuric acid with a green color showing yellow fluorescence.

Anal. Calcd. for $C_{16}H_{13}ClFe$: C, 64.9; H, 4.39; Cl, 11.9. Found: C, 64.4; H, 4.5; Cl, 12.0.

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(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951); G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

(2) R. Hirsch, *Ber.*, **23**, 3705 (1890); M. Gomberg and W. E. Bachmann, THIS JOURNAL, **46**, 2339 (1924); M. Meerwein, E. Boeckner and K. von Emster, *J. prakt. Chem.*, **152**, 237 (1939).

(3) We thank Prof. J. D. Roberts for having carried out the dipole moment measurements.

(4) P. L. Pauson, THIS JOURNAL, **76**, 2187 (1954).

TABLE I

Dicyclopentadienyliron reacted with diazotized:	Reaction products	Yield, %	M.p., °C.	Color in 96% H_2SO_4	Analyses, % Formula	Calcd.	Found
Aniline	Cyclopentadienyl-(phenylcyclopentadienyl)-iron	17	110–111[a]	Green	$C_{16}H_{14}Fe$	C, 73.2 H, 5.34 Fe, 21.35	C, 73.2 H, 5.49 Fe, 21.4
	Diphenyldicyclopentadienyliron	20	140–144[b]	Brown	$C_{22}H_{18}Fe$	C, 78.1 H, 5.32 Fe, 16.55	C, 78.0 H, 5.44 Fe, 16.0
p-Aminodiphenyl	Tri-(*p*-diphenyl)-dicyclopentadienyliron	50	135–140[c]	Brown	$C_{46}H_{34}Fe$	C, 86.0 H, 5.29	C, 85.8 H, 5.36
p-Nitroaniline	Cyclopentadienyl-(*p*-nitrophenylcyclopentadienyl)-iron	10	163[d]	Yellow	$C_{16}H_{13}FeNO_2$	C, 62.5 H, 4.23 Fe, 18.25 N, 4.56	C, 63.1 H, 4.33 Fe, 17.77 N, 4.33
	Di-(*p*-nitrophenyl)-dicyclopentadienyliron	60	>300[e]	Brown	$C_{22}H_{10}FeN_2O_2$	Fe, 13.13 N, 6.57	Fe, 12.89 N, 6.72
o-Aminobenzoic acid	Di-(*o*-carboxyphenyl)-dicyclopentadienyliron	15	195[f]	Green changing to red	$C_{24}H_{18}FeO_4$	C, 67.6 H, 4.23 Fe, 13.14	C, 67.3 H, 4.12 Fe, 14.0
	Mixture of tri- and tetra-(*o*-carboxyphenyl)-dicyclopentadienyliron	35	134–140[g]	Brown			C, 68.4 H, 4.09 Fe, 9.36
1-Amino-8-naphthoic acid	(8-Carboxy-1-naphthyl cyclopentadienyl)-(cyclopentadienyl)-iron	6	220[h]	Green changing to red	$C_{21}H_{10}FeO_2$	C, 70.8 H, 4.5 Fe, 15.73	C, 70.4 H, 4.43 Fe, 15.6
	Tri-(8-carboxy-1-naphthyl)-dicyclopentadienyliron[a]	30	Above 300 dec.[i]	Brown changing to olive	$C_{43}H_{28}FeO_6$	C, 72.9 H, 3.9 Fe, 7.91	C, 73.1 H, 4.3 Fe, 7.5
p-Aminophenol	Cyclopentadienyl-(*p*-hydroxyphenylcyclopentadienyl)-iron[l]	60	165[k]	Yellow, green fluorescence	$C_{16}H_{14}FeO$	C, 69.05 H, 5.04 Fe, 20.15	C, 69.3 H, 5.23 Fe, 20.0

[a] Yellow crystals, from 80% acetic acid (9 g. in 300 cc.). [b] Yellow-brown crystals, from glacial acetic acid (3 g. in 50 cc.). [c] Brown crystals, from butyl alcohol (30 g. in 700 cc.). [d] Dark purple crystals, from high boiling gasoline (8 g. in 100 cc.). [e] Dark purple crystals, from pyridine (20 g. in 100 cc.), upon standing for several days. [f] Pale yellow crystals, from glacial acetic acid (18 g. in 50 cc.). [g] Yellow-brown solid, from dilute ammonia with hydrochloric acid. [h] Orange crystals, from glacial acetic acid (7 g. in 100 cc.), m.p. not sharp. [i] Brown solid, from dilute ammonia and acetic acid. [k] Yellow crystals, from high boiling gasoline (3 g. from 250 cc.). [l] A poly-(*p*-hydroxyphenyl)-dicyclopentadienyliron also was obtained but could not be separated from a sulfur-containing impurity.

TABLE II

ULTRAVIOLET AND VISIBLE SPECTRA

Compound	Solvent	1 mμ	1 ε	2 mμ	2 ε	3 mμ	3 ε	4 mμ	4 ε
Dicyclopentadienyliron	Methanol	242	2,090	..	....	325	76	441	102
Cyclopentadienyl-(*p*-chlorophenylcyclopentadienyl)-iron	Ethanol	243	17,100	281	13,200	(320)	1540	449	422
Di-(*p*-chlorophenyl)-dicyclopentadienyliron	Ethanol	245	26,900	285	16,100	(346)	2620	454	810
Cyclopentadienyl-(phenylcyclopentadienyl)-iron	Ethanol	237	16,100	277	9,900	(320)	1160	447	322
Diphenyldicyclopentadienyliron	Ethanol	243	18,700	282	14,400	(323)	1840	450	754
Tri-(*p*-diphenyl)-dicyclopentadienyliron	Ethanol	273	35,000	..	....	(363)	5840	..	..
Cyclopentadienyl-(*p*-nitrophenylcyclopentadienyl)-iron	Ethanol	(266)	6,150	325	12,500	(406)	1440	503	2460
Cyclopentadienyl-(*p*-hydroxyphenylcyclopentadienyl)-iron	Ethanol	242	15,900	280	12,800	(345)	294	446	294

The condensations shown in Table I were carried out essentially identical with the one above. When alkali-soluble products were formed, they were separated by extraction with sodium hydroxide or ammonia and isolated by precipitation with acids. The yields are based on dicyclopentadienyliron.

Bis-(tetraphenylcyclopentadienyl)-iron.—Sodamide was prepared from sodium (2.3 g.) in liquid ammonia (100 g.) containing ferric nitrate (0.2 g.). 1,2,3,4-Tetraphenylcyclopentadiene, m.p. 178° (18.5 g.),[5] was added, followed about an hour later by ferrous chloride (15 g) which had been prepared by heating anhydrous ferric chloride in chlorobenzene.[6] Xylene (100 cc.) was added, the ammonia was allowed to distil off and the charge was agitated at room temperature overnight. A precipitate was formed which was filtered and extracted with hot xylene. After the evaporation of the xylene, bis-(tetraphenylcyclopentadienyl)-iron (8.8 g.) was obtained as a red solid, m.p. 305°. Upon crystallization from chlorobenzene (50 cc.) it formed deep red crystals, m.p. 322°.

Anal. Calcd. for $C_{58}H_{42}Fe$: C, 87.6; H, 5.29; Fe, 7.05. Found: C, 87.3; H, 5.35; Fe, 7.06.

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(5) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1936).

(6) P. Kovacic and N. O. Brace, THIS JOURNAL, **76**, 5491 (1954).

p-Dibromobenzene and Cyclopentadienylsodium.—Cyclopentadienylsodium was prepared from cyclopentadiene (33 g.) by the method used in the preceding experiment. p-Dibromobenzene (59 g.) and xylene (300 cc.) were added at the boiling point of the liquid ammonia. The ammonia was allowed to distil off overnight. The next day liquid ammonia (500 g.) and sodium (11.5 g.) again were added. One hour later ferrous chloride (45 g.) was added. After standing at room temperature for several days the xylene solution was distilled. Dicyclopentadienyliron (10 g.) was obtained first. The fraction distilling from 230–240° (33 mm.) (15 g.) was crystallized from alcohol and cyclopentadienyl-(phenylcyclopentadienyl)-iron identical with that obtained from dicyclopentadienyliron and diazotized aniline was obtained.

Anal. Calcd. for $C_{16}H_{14}Fe$: C, 73.2; H, 5.34; Fe, 21.35; mol. wt., 262. Found: C, 73.5; H, 5.32; Fe, 21.3; mol. wt., 250.

The data in Table II give the absorption maxima in mμ and the corresponding extinction coefficients. The maxima in parentheses are either shoulders or buried peaks. The others are clear maxima. Blank spaces indicate either that the spectra did not cover these regions or that no definite conclusions could be drawn from the curves.

The spectra were obtained with a Cary recording spectrophotometer model 11.

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The Reaction of Cyanogen and Related Nitriles with 1,3-Dienes. VIII. Catalyst Evaluations[1]

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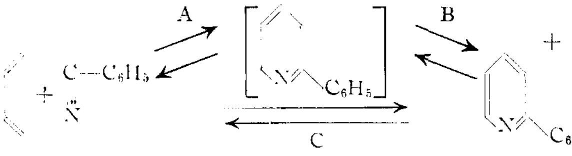
The activity of Al_2O_3 in the nitriles–dienes cyclization–dehydrogenation reaction at 400° is investigated. The thermal stabilities of benzonitrile and related nitriles and heptane over Al_2O_3 at 400° also have been examined to gain information on the mechanism of the reaction on this surface. The activity of the alumina in promoting the rate of the nitriles–dienes cyclization is best understood as another example of the general acid catalysis of diene addition reactions.

The synthesis of phenylpyridine by the reaction of benzonitrile with butadiene at 400° is an example of a more general reaction for the formation of pyridinic products from nitriles and dienes. In a previous communication[3] the thermodynamic aspects of the two step process, and the over-all reaction



have been considered, and the results for fifteen different catalysts described. In the temperature range of 400°, the free energy changes for the cyclization (A) and dehydrogenation (B) steps are +23 and −27 kcal./mole, respectively. The over-all process (C) is thermodynamically favored because of the very large negative ΔF for the second step. Accordingly, catalysts which promote the high temperature Diels–Alder cyclization step (A) are of direct interest for the catalytic synthesis of pyridines from nitriles and dienes. In present work, the catalyst tests[3] are extended to an investigation of the activity of Al_2O_3 in the nitriles–dienes cyclization–dehydrogenation reaction at 400°. The benzonitrile–butadiene reaction, with 2-phenylpyridine as product, again was selected as the test reaction because of the high thermal stability of this nitrile. The thermal stabilities of related nitriles and heptane over Al_2O_3 also have been examined to gain information on the mechanism of the reaction on this surface.

Experimental

The benzonitrile (Eastman Organic Chemicals practical grade) was dried over P_2O_5 and distilled at 50 mm. pressure before use. The butadiene (Matheson Co. Inc.) was a C.P. grade of a purity not less than 99%. It was passed through drierite and distilled once before use.

Catalysts.—All catalysts were prepared in 1/8 inch pellet form by Harshaw Chemical Co. for this work. The following were the specifications in the five catalysts used in this investigation:

Code	Type	Composition
A-1	Al_2O_3	99% Al_2O_3, 0.5% Na_2O, 0.03% SiO_2, 0.03% Fe_2O_3
A-2	Al_2O_3	93% Al_2O_3 . . . 6.0% SiO_2, 0.5% CaO
A-3	Al_2O_3	100% Al_2O_3
C-1	Cr_2O_3–Al_2O_3	4% Cr_2O_3, 96% Al_2O_3 (type A-1)
C-2	Cr_2O_3–Al_2O_3	4% Cr_2O_3, 96% Al_2O_3 (type A-3)

Each catalyst was preheated as described in the previous work.[3] In addition the pure alumina catalysts were heated at 500° and about 10^{-4} mm. pressure for 24 hr. and flushed with nitrogen before each experiment.

Apparatus and Procedure.—The apparatus and procedure for the catalyst activity tests have been described elsewhere[3] in detail. The relative surface areas were determined by a modified form of the B.E.T. apparatus as described by Barr and Anhorn.[4] The catalyst samples were degassed at 350°, before the surface areas were measured, for 12 hours using a mercury diffusion pump.

Phenylpyridine Reaction.—The experimental conditions for the benzonitrile–butadiene cyclization–dehydrogenation tests and the yields are summarized in Table I. Each run was 2 hours long and the temperature is a weighted average observed for the catalyst during this period. The reaction mixture, an equimolar mixture of butadiene, benzonitrile and nitrogen, was metered at controlled rates to give approximately a 4-second reaction time in each case (Table I). The total material balance shows, within experimental error, a satisfactory account for the total input as crude

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(1) Abstracted in part from the thesis submitted by W. J. G. McCulloch in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), Rensselaer Polytechnic Institute, Troy, N. Y.

(2) Research Corporation Fellow in Chemistry, 1951–1953.

(3) G. J. Janz, W. J. G. McCulloch and E. F. Timpane, *Ind. Eng. Chem.*, **45**, 1343 (1953).

(4) W. E. Barr and V. J. Anhorn, "Scientific Glass Blowing," Instruments Publ. Co., Pittsburgh, Pa., 1949, p. 273.