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Hydrogen Fluoride as a Condensing Agent. V. Reactions of Dicyclopentadienyliron in Anhydrous Hydrogen Fluoride[1]

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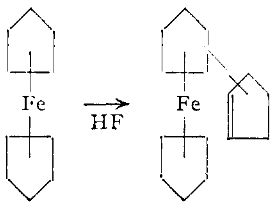
Dicyclopentadienyliron shows some reactions typical of an aromatic system while others equally typical are not observed. Acylation and condensations with aliphatic and aromatic aldehydes occur readily, but alkylations do not take place. Of special interest is the ease with which dicyclopentadienyliron reacts to give cyclopentadienyl (cyclopentenylcyclopentadienyl)-iron under the influence of hydrogen fluoride. Sulfonation of dicyclopentadienyliron forms mono- and disulfonic acids.

Dicyclopentadienyliron is reported[2] to react in many respects like a typical aromatic compound. In hydrogen fluoride, too, it shows some typical reactions attributable to the aromatic system while others well-known for aromatic systems are not observed.

Dicyclopentadienyliron, like many polynuclear compounds, dissolves in anhydrous hydrogen fluoride to form an orange colored solution. If this solution is maintained below about 20°, dicyclopentadienyliron is recovered unchanged upon dilution with water. In the presence of oxidizing agents such as air, nitrobenzene or benzoquinone, oxidation occurs. A blue solution of the cation $[Fe(C_5H_5)_2]^+$[3] showing red dichroism is formed and upon dilution with water a solution showing a similar color phenomenon is obtained. Dicyclopentadienyliron can be recovered upon reduction with ascorbic acid or by making the solution alkaline or by steam distilling the acid solution. Dicyclopentadienyliron is oxidized to $[Fe(C_5H_5)_2]^+$ when heated to 100° with sulfur dioxide in hydrogen fluoride, a condition not commonly considered oxidative. When acetic acid is used instead of hydrogen fluoride no reaction occurs and dicyclopentadienyliron is recovered unchanged. Thus, dicyclopentadienyliron in its oxidized form is stable in hydrogen fluoride up to 100°.

Quite in contrast to the preceding observations, a profound change takes place in hydrogen fluoride between 30 and 100° in the absence of oxidizing conditions. Dicyclopentadienyliron reacts to form cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron, m.p. 65° in excellent yield. The compound is formed at the expense of some dicyclopentadienyliron and iron salts are always found in the acid liquors.



Occasionally very small amounts of two compounds analyzing like a cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron for carbon, hydrogen and iron, but melting at 140 and 190° are isolated.

The cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron, m.p. 65°, readily hydrogenates to a cyclopentadienyl-(cyclopentylcyclopentadienyl)-iron, m.p. 15 to 16°. The amount of hydrogen required clearly indicates the presence of only one double bond. The two high melting isomers could not be hydrogenated.

The cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron is stable in air and can be recrystallized from alcohol without change. However, upon prolonged standing in the presence of gasolines or isoöctane it changes slowly to a less soluble product. It is surprising that a compound containing an apparently olefinic double bond should be stable in anhydrous hydrogen fluoride at 100°. Ordinarily, olefins of three or more carbon atoms dissolve in hydrogen fluoride with alkyl fluoride formation, followed frequently by polymerization at elevated temperatures.

In spite of the olefinic character of cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron, it does not condense with benzene in hydrogen fluoride. However, a compound analyzing as a cyclopentylphenyldicylopentadienyliron is obtained in a low yield when dicyclopentadienyliron is agitated in hydrogen fluoride at 30° in the presence of benzene.

Carboxycyclopentadienyl-(cyclopentadienyl)-iron changes in hydrogen fluoride to an alkali-insoluble product.

Reaction in 36% hydrofluoric acid gives quite different results from those obtained in anhydrous hydrogen fluoride. At 100° decomposition of dicyclopentadienyliron occurs. In the presence of benzene, tarry products are formed at 150°, but no reaction takes place at 100°. Although dicyclopentadienyliron is reported to be stable at temperatures as high as 450° in the vapor phase,[4] it decomposes completely to iron oxide and unidentifiable products when heated to 350° in an aqueous suspension in a closed system.

Condensations with olefins like propylene or diisobutylenes which occur so readily in the benzene series are not possible. Below 30° no reaction occurs while above 30° conversion to cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron takes place. This latter compound does not react with olefins like propylene or diisobutylenes even at 100°.

Although dicyclopentadienyliron reacts so readily to form cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron, it is nevertheless possible to obtain in hydrogen fluoride certain typical aromatic substitution reactions.

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(1) For paper IV see V. Weinmayr, THIS JOURNAL, **77**, 1762 (1955).

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, *ibid.*, **74**, 3458 (1952).

(3) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, **74**, 2125 (1952).

(4) L. Kaplan, W. L. Kester and J. J. Katz, *ibid.*, **74**, 5531 (1952).

Thus, dicyclopentadienyliron reacts in hydrogen fluoride with acetic anhydride at 30–40° to give acetylcyclopentadienyl-(cyclopentadienyl)-iron in excellent yield and purity. Condensation with benzoic anhydride or phthalic anhydride is not possible and only cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron is obtained.

Quite often reactions promoted by hydrogen fluoride are similarly promoted by sulfuric acid (such as alkylations or the Beckmann rearrangement). In an attempt to make cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron from acetic anhydride and sulfuric acid, a disulfonic acid of dicyclopentadienyliron crystallizing directly from the reaction mass was obtained in a good yield. A monosulfonic acid is formed together with some of the disulfonic acid and unreacted starting material when the amount of sulfuric acid used is reduced. No oxidation to a cation by the sulfuric acid takes place under the reaction conditions. A well-crystallized by-product which may have the composition $Fe^{++}(C_5H_5FeC_5H_4SO_{3(-)})_2 \cdot 3H_2O$[5] is always obtained in the reaction.

Dicyclopentadienyliron condenses readily with paraformaldehyde or benzaldehyde to give compounds analyzing as $(C_5H_4)_2Fe(CHR)_2(C_5H_4)_2Fe$ where R is hydrogen or phenyl. These compounds are obtained in the oxidized cationic state and are isolated by the usual methods of reduction. The formaldehyde condensation product cannot be oxidized to a diketone with chromic acid and acetic acid and only unchanged starting material and decomposition products are isolated.

Experimental

Oxidation of Dicyclopentadienyliron with Sulfur Dioxide.—Technical hydrogen fluoride (400 g.) was distilled into a steel autoclave containing dicyclopentadienyliron (66 g.). All air had been carefully replaced by nitrogen. Sulfur dioxide (46 g.) was then distilled into the vessel. A nitrogen pressure of seven atmospheres was applied and the charge temperature was raised to 100° over a period of three hours and maintained there for three hours. Upon dilution of the reaction mass a blue solution of the cation $[Fe(C_5H_5)_2]^+$ was obtained and the odor of sulfur dioxide was still noticeable. After reduction with ascorbic acid (58 g.), dicyclopentadienyliron (51 g.), free of sulfur, was recovered. Oxidation did not occur when an identical charge containing acetic acid in place of hydrogen fluoride was treated in a similar manner in a platinum lined autoclave.

Reduction of Anthraquinone.—A solution of anthraquinone (10.4 g.) and dicyclopentadienyliron (46.5 g.) in hydrogen fluoride (300 g.) was agitated in a nickel vessel for 24 hours. The precipitate obtained upon dilution with water was dried at 60° (20 mm.) for 24 hours to remove dicyclopentadienyliron by sublimation. Anthrone (11 g., m.p. 145–147°) melting at 151° after crystallization was obtained and identified by analysis and mixed melting point. Dicyclopentadienyliron (32 g.) was recovered from the blue hydrofluoric acid filtrate upon reduction with zinc dust.

Cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron.—A solution of dicyclopentadienyliron (30 g.) in hydrogen fluoride (120 g.) was heated in a nickel vessel to 100° over a period of three hours and agitated at 100° for six hours. The brown colored reaction mass was poured into ice where a tarry precipitate formed which changed slowly to a yellow solid. The supernatant dilute hydrofluoric acid was of a pale blue-green color, but upon standing at room temperature for about one-half hour the color disappeared and a small additional amount of yellow solids was obtained. The dilute hydrofluoric acid contained 30% of the iron present in the dicyclopentadienyliron charged.

The reaction product was dissolved in benzene and purified by distillation. At first dicyclopentadienyliron (1 g.) was obtained as a yellow sublimate. Then cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron (16 g.) distilled from 170 to 176° (10 mm.) and melted at 60 to 65° (distillation residue 6 g.). Upon crystallization from ethanol (15 g. in 120 cc. recovery 12 g.) it melted at 64–65°. The compound dissolved in concentrated sulfuric acid with a brown color.

Anal. Calcd. for $C_{15}H_{16}Fe$: C, 71.4; H, 6.34; Fe, 22.2; mol. wt., 252. Found: C, 71.7; H, 6.59; Fe, 22.2; mol. wt., 245.

The crystals as well as their benzene and alcoholic solutions were stable but solutions in gasoline or isoöctane deposited insoluble products after several days. The analysis of the distillation residues of several experiments varied from: C, 75.8 to 78.8; H, 6.8 to 7.4; Fe, 15.0 to 15.5.

Hydrogen fluoride containing about 2% of sulfur dioxide gave a product containing an impurity that gave off hydrogen sulfide and foamed badly during vacuum distillation. Such hydrogen fluoride could be purified readily as described in our preceding paper.[1]

From the mother liquor of the crystallization there was obtained a very small amount of a yellow product melting at 140°. It showed the same analysis as the cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron but could not be hydrogenated.

Anal. Found: C, 71.4; H, 6.34; Fe, 22.1; mol. wt., 251 (in benzene).

A second isomer with the same analysis except for the molecular weight and melting at 188 to 190° also was found in one experiment in the distillation residue from a batch of cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron.

Anal. Found: C, 71.5; H, 6.61; mol. wt., 356 in benzene, 348 in carbon tetrachloride, 525 in *o*-dichlorobenzene.

Cyclopentadienyl-(cyclopentylcyclopentadienyl)-iron.—Cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron (25 g., 0.1 mole) dissolved in thiophene-free benzene (100 cc.) was hydrogenated (0.01 g. of platinum oxide) in a Parr hydrogenation apparatus at 60 to 70°. A pressure drop indicating the utilization of 0.1 mole of hydrogen was observed. Upon distillation, cyclopentadienyl-(cyclopentylcyclopentadienyl)-iron (23 g.) was obtained as a red liquid having a freezing point of 16.3°.

Anal. Calcd. for $C_{15}H_{18}Fe$: C, 70.9; H, 7.09; Fe, 22.04. Found: C, 70.8; H, 7.02; Fe, 21.9.

Reaction of Dicyclopentadienyliron in Hydrogen Fluoride in the Presence of Benzene.—A solution of dicyclopentadienyliron (93 g.) in thiophene-free benzene (800 cc.) was agitated at 25 to 30° for 24 hours in the presence of hydrogen fluoride (500 g.) in a steel autoclave where the air had been replaced by nitrogen. The charge was diluted on ice and the benzene layer was washed acid free and evaporated in a shallow dish on the steam-bath for 24 hours to allow the unreacted dicyclopentadienyliron to sublime away. The residual oily product (34 g.) was purified in two distillations and the fraction distilling from 245 to 255° (12 mm.) (14 g.) was collected for analysis. The compound analyzed as a cyclopentylphenyldicyclopentadienyliron. It could be refluxed at atmospheric pressure at about 390° without decomposition and was soluble in concentrated sulfuric acid with a brown color which turned green after a short time.

Anal. Calcd. for $C_{21}H_{22}Fe$: C, 76.14; H, 6.67; Fe, 16.97; mol. wt., 330. Found: C, 76.7; H, 6.52; Fe, 16.82; mol. wt., 332 (in benzene).

Acetylcyclopentadienyl-(cyclopentadienyl)-iron.—A charge of dicyclopentadienyliron (84 g.), acetic anhydride (270 cc.) and hydrogen fluoride (400 g.) was agitated at 40 to 45° for 12 hours. Upon dilution in cold water (3,000 cc. or more; the reaction product was noticeably soluble in too concentrated an acid), acetylcyclopentadienyl-(cyclopentadienyl)-iron (89 g.) was obtained as an orange colored solid melting at 80–84°. Upon crystallization from isooctane (1 g. and 14 cc.) it was obtained as orange needles, m.p. 85–86°.

Anal. Calcd. for $C_{12}H_{12}FeO$: C, 36.2; H, 5.3; Fe, 24.5. Found: C, 36.4; H, 5.31; Fe, 24.3.

The product was soluble with a red color in concentrated sulfuric acid and in 36% hydrochloric acid.

Acetylcyclopentadienyl-(cyclopentadienyl)-iron was oxi-

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(5) We thank Dr. Peter L. Pauson for suggesting this formula.

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA

Compound	Solvent	1		2		3		4	
		mμ	ε	mμ	ε	mμ	ε	mμ	ε
Dicyclopentadienyliron	Isoöctane	...	....	..	..	324	61	439	101
Cyclopentadienyl-(cyclopentenylcyclopentadienyl)-iron	Isoöctane	(227)	19,400	276	8400	(325)	424	442	270
Cyclopentadienyl-(cyclopentylcyclopentadienyl)-iron	Methyl cellosolve	...	....	..	..	325	61	444	110
Carboxycyclopentadienyl-(cyclopentadienyl)-iron	Isoöctane	266	....	307	..	(355)	..	439	..
Acetylcyclopentadienyl-(cyclopentadienyl)-iron	Isoöctane	267	5,400	318	1100	(358)	148	445	289
Diammonium salt of a dicyclopentadienyldisulfonic acid	Ethanol	(240)	5,000	..	..	(320)	168	425	145
Condensation product of dicyclopentadienyliron with formaldehyde	Isoöctane	247	7,020	..	..	322	164	437	205

dized readily at room temperature with iodine in pyridine[6] to give carboxycyclopentadienyl-(cyclopentadienyl)-iron, m.p. 225–230° (needles from gasoline, 1 g. in 120 cc.) in a 50% yield.

Anal. Calcd. for $C_{11}H_{10}FeO_2$: C, 57.4; H, 4.35; Fe, 24.3. Found: C, 57.4; H, 4.51; Fe, 24.5.

Carboxycyclopentadienyl-(cyclopentadienyl)-iron (20 g.) was heated in absolute ethanol (150 g.), benzene (45 g.) and 37% hydrochloric acid (5 g.). After refluxing for 20 hours and azeotropically distilling off the water, the resulting solution was evaporated. The solid residue was dissolved in ether, the solution was washed with dilute aqueous sodium hydroxide, dried and again evaporated to dryness. The evaporation residue was crystallized from ether and 10 g. of the ethyl ester of the carboxycyclopentadienyl-(cyclopentadienyl)-iron was obtained as orange colored crystals melting at 61–62°.

Anal. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.4; H, 5.42. Found: C, 60.5; H, 5.38.

A Disulfonic Acid of Dicyclopentadienyliron.—Sulfuric acid (100%, 73 g.) was added to a slurry of dicyclopentadienyliron (93 g.) in acetic anhydride (1,000 cc.) in one hour while the temperature was allowed to rise to 46°. The dicyclopentadienyliron went into solution and a few hours later a disulfonic acid of dicyclopentadienyliron precipitated in a crystalline form. It was filtered on a sintered glass funnel and washed with acetic anhydride and petroleum ether. The coarse, yellow crystals (100 g.) absorbed moisture quickly when exposed to the air. The crystals were dissolved in water (800 cc.) and the solution was made alkaline with 28 g. of ammonia (800 cc.) and evaporated to dryness. The crude product (85 g.) was dissolved in 2,200 cc. of 95% ethanol, the solution was clarified by filtration and the pure diammonium salt of a disulfonic acid of dicyclopentadienyliron was precipitated as bright yellow crystals (50 g.) upon the addition of benzene (1,000 cc.). This compound dissolved in concentrated sulfuric acid to give a yellow color which changed to green on standing.

Anal. Calcd. for $C_{10}H_{16}FeN_2O_6S_2$: Fe, 14.74; N, 7.37; S, 16.83. Found: Fe, 15.06; N, 7.30; S, 16.8.

The acetic anhydride filtrate of the reaction mass was diluted with water and evaporated on the steam-bath to near dryness. A water-insoluble, methanol-soluble product was obtained (45 g.) as greenish-yellow crystals. It could be crystallized readily from glacial acetic acid (1 g. in 30 cc.) where it was soluble with a blue color. The product did not melt but decomposed with charring. It was soluble in concd. sulfuric acid with a blue color. The analysis was in fair agreement with the following empirical formula: Calcd. for $C_{20}H_{24}Fe_3O_9S_2$: C, 37.5; H, 3.75; Fe, 26.25; S, 10.00. Found: C, 36.1; H, 4.3; Fe, 26.6; S, 9.9.

A Monosulfonic Acid of Dicyclopentadienyliron.—Sulfuric acid (100%, 4.9 g.) was added at 25–33° to a slurry of dicyclopentadienyliron (37 g.) in acetic anhydride (200 cc.). The reaction mass was agitated overnight. The undissolved solids were filtered and identified by mixed melting points as unreacted dicyclopentadienyliron (15.8 g.). The acetic anhydride filtrate was poured into water (1,000 cc.) and heated to 80°. An additional amount of dicyclopentadienyliron (10 g.) thus was separated. The dilute acetic acid solution was evaporated on a steam-bath. The residue was slurried in an excess of aqueous ammonia, clarified by filtration and evaporated to dryness. The residue (12 g.) was dissolved in absolute methanol. The solution was clarified by filtration and again evaporated. An ammonium salt of a monosulfonic acid of dicyclopentadienyliron (11 g.), was obtained.

Anal. Calcd. for $C_{10}H_{13}FeO_3NS$: C, 42.4; H, 4.59; Fe, 19.78; N, 4.95; S, 11.32. Found: C, 41.3; H, 4.1; Fe, 17.36; N, 5.3; S, 10.7.

Condensation of Dicyclopentadienyliron with Formaldehyde.—A solution of dicyclopentadienyliron (20 g.) and paraformaldehyde (4.8 g.) in hydrogen fluoride (400 g.) was heated in a nickel vessel to 100° over a period of three hours and agitated at 100° for three hours. The blue hydrogen fluoride solution was poured on ice and an insoluble brown solid (2.3 g.) was filtered off. The dilute hydrogen fluoride solution showed the red-blue dichroism typical for the cationic form of dicyclopentadienyliron. This solution was agitated with zinc dust (100 g.) until it became colorless (one hour). The solid which precipitated was filtered with the zinc dust and extracted with hot benzene (500 cc.). The product obtained upon evaporation of the yellow benzene filtrate (10.6 g.) melted at 191°. Crystallization from high-boiling petroleum ether (1 g. in 5 cc.) did not change the melting point.

Anal. Calcd. for $C_{22}H_{20}Fe_2$: C, 66.62; H, 5.05; Fe, 28.37; mol. wt., 396. Found: C, 66.3; H, 5.56; Fe, 28.17; mol. wt., 402.

The compound dissolved in concentrated sulfuric acid with a green color. It could be distilled in an open test-tube without decomposition and without leaving a residue. A similar condensation using concentrated sulfuric acid instead of hydrogen fluoride gave only tarry products.

Condensation of Benzaldehyde with Dicyclopentadienyliron.—A solution of dicyclopentadienyliron (5 g.) and benzaldehyde (4.3 g.) in hydrogen fluoride (100 g.) was heated to 100° for three hours. A yellow crystalline compound (4.7 g., m.p. 220°) was isolated from the clarified blue dilution mass (4.8 g. of brown material was insoluble) by reduction with zinc dust. Upon crystallization from high-boiling petroleum ether, yellow crystals melting from 260–265° were obtained.

Anal. Calcd. for $C_{34}H_{28}Fe_2$: C, 74.4; H, 5.11; Fe, 20.43. Found: C. 74.53; H, 5.86; Fe, 19.86.

The data in Table I 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.

Acknowledgment.—The writer is indebted to Dr. C. J. Pedersen who collected and interpreted the ultraviolet and visible spectra, and to Dr. F. S. Arimoto who had prepared the ethyl ester of the carboxycyclopentadienyl-(cyclopentadienyl)-iron.

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(6) L. Carroll King, THIS JOURNAL, **66**, 894 (1944).