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# Derivatives of Dicyclopentadienyliron[1]

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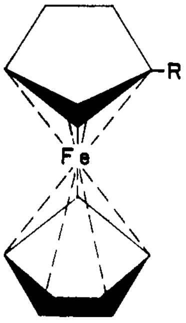
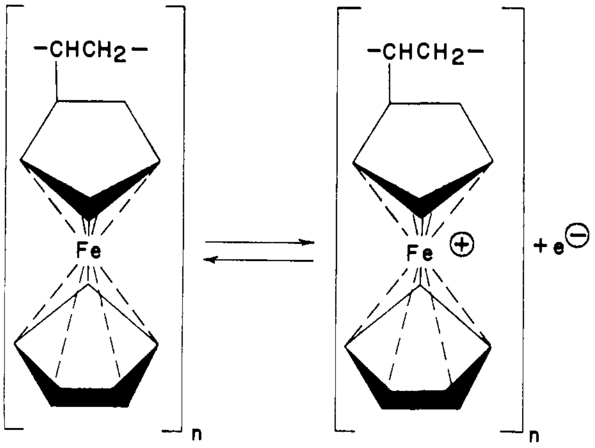
The syntheses and properties of the amino, vinyl and related derivatives of dicyclopentadienyliron are described.

Several substituted dicyclopentadienylirons have been reported, among which are the mono-[2] and the diacetyl[3] derivatives, the mono-[2] and dicarboxylic[3] acids and the mono- and polyphenyldicyclopentadienylirons.[4] We wish now to record several new monosubstituted dicyclopentadienylirons.

Aminocyclopentadienyl-(cyclopentadienyl)-iron (VII) was prepared from carboxycyclopentadienyl-(cyclopentadienyl)-iron (II)[5] *via* the Curtius rearrangement. The acid chloride III was readily prepared and converted to the acid azide V. This lost nitrogen smoothly on warming in benzyl alcohol, with the formation of the benzylurethan VI. The amino compound VII was obtained by hydrolysis or hydrogenolysis of the urethan.



| | |
|---|---|
| I | $-COCH_3$ |
| II | $-COOH$ |
| III | $-COCl$ |
| IV | $-CONH_2$ |
| V | $-CON_3$ |
| VI | $-NHCOOCH_2C_6H_5$ |
| VII | $-NH_2$ |
| VIII | $-NHCOCH_3$ |
| IX | $-C(CH_3)=NOH$ |
| X | $-C(CH_3)HOH$ |
| XI | $-C(CH_3)HOCOCH_3$ |
| XII | $-CH=CH_2$ |
| XIII | $-CH_2CH_3$ |



More direct routes to VII were attempted without success. Reaction of the amide IV with potassium hypobromite resulted in black, intractable materials, and a small amount of the acid II. Attempted Beckmann rearrangements of the oxime IX and of the acetyl compound gave no identifiable product.

Aminocyclopentadienyl-(cyclopentadienyl)-iron is a tan solid, m.p. 155°. It is soluble in dilute hydrochloric acid, and is precipitated from such solutions on addition of alkali.

Cyclopentadienyl-(vinylcyclopentadienyl)-iron (XII) was obtained in a straightforward manner. Acetylcyclopentadienyl-(cyclopentadienyl)-iron (I) was reduced with lithium aluminum hydride to the methylcarbinol X. Pyrolysis of the carbinol or its acetate XI gave the desired vinyl derivative, a low-melting, red solid with a strong camphor-like odor.

The vinyl derivative proved to be polymerizable; several homo- and copolymerizations are summarized in Table I. The polymers were all soluble in benzene and insoluble in methanol. Clear, brittle films could be cast from solutions of the solid polymers.

TABLE I

POLYMERIZATIONS EMPLOYING CYCLOPENTADIENYL-(VINYLCYCLOPENTADIENYL)-IRON

| Catalyst | Comonomer | Product |
|---|---|---|
| 85% $H_3PO_4$ | None | Viscous oil |
| Persulfate | None | Oil |
| Azodi- | None | Solid, m.p. 280–285° |
| isobutyro- | Me methacrylate | Solid, m.p. 190–210° |
| nitrile | Styrene | Solid, m.p. 158–165° |
| Persulfate | Chloroprene | Elastomer |

The solid homopolymer exhibited the reversible oxidation–reduction properties characteristic of dicyclopentadienyliron. On oxidation with aqueous ceric sulfate, polycyclopentadienyl-(vinylcyclopentadienyl)-iron dissolved to give a deep blue solution. This, on treatment with aqueous ascorbic acid deposited the yellow, reduced polymer.

Polymers and copolymers of the vinyl derivative were readily cross-linked with formaldehyde. This no doubt involves condensation of the carbonyl compound with the aromatic-like five-membered rings, as has been demonstrated[6] with the parent compound, dicyclopentadienyliron. Such cross-linked polymers also exhibited the reversible oxidation–reduction reaction. In the oxidized valence state the polymers were blue, insoluble solids.

Cyclopentadienyl-(ethylcyclopentadienyl)-iron (XIII) was obtained readily by Clemmensen reduction of the acetyl derivative I.

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[1] Presented in part by Madison Hunt at the 126th Meeting of the American Chemical Society, New York, N. Y., September 12–17, 1954.

[2] V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955), U. S. Patent 2,683,157.

[3] R. B. Woodward, M. Rosenblum and M. C. Whiting, *ibid.*, **74**, 3458 (1952); M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

[4] P. L. Pauson, *ibid.*, **76**, 2187 (1954).

[5] Roman numerals in parentheses refer to the numbered structural formulas, and not to the valence state of iron. Unless otherwise indicated, iron is in the ferrous state.

[6] Reference 2; also V. Weinmayr, U. S. Patent 2,694,721.

## Experimental

Acetyl- and carboxycyclopentadienyl-(cyclopentadienyl)-iron were prepared as reported by Weinmayr.[2]

**The oxime IX** of the acetyl derivative had m.p. 169–170° after recrystallization from ether.

*Anal.* Calcd. for $C_{12}H_{13}FeNO$: C, 59.4; H, 5.36; Fe, 23.0; N, 5.76. Found: C, 59.9, 59.6; H, 5.64, 5.29; Fe, 23.6; N, 5.4, 5.5.

**The amide IV** of carboxycyclopentadienyl-(cyclopentadienyl)-iron was obtained by reaction of the acid chloride III (see below) with concentrated ammonium hydroxide. After recrystallization from a chloroform–ether mixture, it had m.p. 168–170°.

*Anal.* Calcd. for $C_{11}H_{11}FeNO$: C, 57.7; H, 4.62; N, 6.13. Found: C, 57.2; H, 4.84; N, 6.1, 5.9.

**Aminocyclopentadienyl-(cyclopentadienyl)-iron (VII).**—Carboxycyclopentadienyl-(cyclopentadienyl)-iron (13.7 g.) was stirred with 13.7 g. of phosphorus pentachloride in 150 ml. of dry benzene for two hours at room temperature. The reaction mixture was filtered and the filtrate concentrated *in vacuo* at 100° to remove the benzene and phosphorus oxychloride. The residue was dissolved in 100 ml. of acetone, the solution cooled to 0–5° and treated all at once with 4.0 g. of sodium azide dissolved in a few ml. of water. After one-half hour at room temperature, the reaction mixture was poured into 1 liter of cold water. The precipitate was separated by filtration and sucked free of excess water on the filter. It was then extracted with three 100-ml. portions of cold ether. The extracts were combined, treated with Darco, dried over magnesium sulfate and concentrated to give the acid azide V, 4.0 g. (26%), m.p. 74–75°. (A second crop was obtained by concentrating the mother liquors and adding petroleum ether, 2.35 g., m.p. 68–73°).

*Anal.* Calcd. for $C_{11}H_9FeN_3O$: C, 51.8; H, 3.56; N, 16.5. Found: C, 51.5, 52.4, 51.5; H, 3.36, 3.49, 3.91; N, 16.5, 16.7, 16.8, 17.0.

The infrared spectrum showed the characteristic azide absorption at 4.45 and 5.88 $\mu$.

A solution of 0.85 g. of the acid azide V in 15 ml. of benzyl alcohol was heated slowly in an oil-bath to 200°. Gas evolution was observed at 100–140°. The benzyl alcohol was removed by distillation *in vacuo*, and the residual oil crystallized on stirring with a mixture of ether and petroleum ether: 0.90 g. (80%), m.p. 100–105°. After two recrystallizations from ether–petroleum ether, the benzylurethan VI had m.p. 112–113°.

*Anal.* Calcd. for $C_{18}H_{17}FeNO_2$: C, 64.5; H, 5.11; N, 4.18. Found: C, 63.7, 63.9; H, 5.18, 5.32; N, 4.6, 4.9.

The infrared spectrum showed absorption at 3.0, 5.9 and 6.45 $\mu$.

The urethan VI was hydrolyzed as follows. Eight-tenths of a gram was boiled under nitrogen for six hours with 25 ml. of 10% (w./v.) potassium hydroxide. The cooled reaction mixture was extracted with three 50-ml. portions of ether and the combined extracts washed twice with 10-ml. portions of cold 6 *N* hydrochloric acid. Most of the colored material was acid-soluble. The acid extracts were rendered strongly alkaline with 25% (w./v.) potassium hydroxide and then extracted with three 50-ml. portions of ether. The combined extracts, after being dried over magnesium sulfate, were concentrated to a yellow, crystalline solid, m.p. 140–143°. After two recrystallizations from ether–petroleum ether, the aminocyclopentadienyl-(cyclopentadienyl)-iron had m.p. 149–151°. The melting point seems to be sensitive to small amounts of impurities; values as high as 155° have been obtained in subsequent preparations.

*Anal.* Calcd. for $C_{10}H_{11}FeN$: C, 59.7; H, 5.52; N, 6.97. Found: C, 59.5, 59.6; H, 5.19, 5.09; N, 6.9, 7.2.

In methanol solution aminocyclopentadienyl-(cyclopentadienyl)-iron exhibits strong end absorption below 2500 Å., and maxima at 2830 Å. ($\epsilon$ 4,540) and 4110 A. ($\epsilon$ 3,140). The infrared spectrum in Nujol mull showed absorption at 2.9–3.15, 6.16 and 6.65 $\mu$.

On acetylation with acetic anhydride and pyridine, the amino derivative gave an acetyl derivative, m.p. 170.5–172° after recrystallization from chloroform–ether.

The amine VII was also obtained by hydrogenolysis of the urethan VI. A methanol solution of 4.7 g. of VI was hydrogenated at 70 atmospheres and 75° for four hours. Raney nickel catalyst was employed. After removal of the catalyst the methanol solution was concentrated to dryness *in vacuo*. The residue, 2.7 g. (96%), had m.p. 135–142°. After recrystallization from ether–petroleum ether, the amino derivative had m.p. 151–155°. This was not depressed when the product was mixed with a sample of the amino derivative obtained by alkaline hydrolysis of the urethan.

Several attempts to hydrogenate the urethan with a platinum catalyst, with or without added hydrochloric acid, were unsuccessful; urethan was recovered and no hydrogen absorbed. This result was very likely due to inactivation of the catalyst by impurities. The urethan was recovered unchanged from reactions with phenyl- and methylmagnesium halides. No identifiable compound could be obtained from an attempted acid hydrolysis of the urethan. Lithium aluminum hydride reacted readily with the urethan; the product, however, was not crystalline.

**Cyclopentadienyl-($\alpha$-hydroxyethylcyclopentadienyl)-iron (X).**—A 4-neck 1-liter flask equipped with a reflux condenser, nitrogen inlet, stirrer and dropping funnel was charged with 22.8 g. of I and 500 ml. of anhydrous ether. The solution was stirred and treated dropwise with a solution of 1.9 g. of lithium aluminum hydride in ether and heated under reflux for two hours. The excess lithium aluminum hydride was destroyed with ethyl acetate and the resulting reaction mixture was treated with a solution of 26.8 g. of ammonium chloride dissolved in water. After being stirred 0.5 hour at 0°, the reaction mixture was filtered and the organic layer separated. After having been washed twice with water the ether solution was concentrated to dryness and the residue was allowed to crystallize. The crude carbinol weighed 20.5 g. (89%) and had m.p. 69–72°; mixed m.p. with I was 52–55°. A portion was recrystallized from a mixture of ether and petroleum ether to obtain orange rods, m.p. 73–75°.

*Anal.* Calcd. for $C_{12}H_{14}FeO$: C, 62.64; H, 6.13. Found: C, 63.07, 63.05; H, 6.13, 6.09.

The infrared spectrum in Nujol mull showed absorption in the hydroxyl region and none in the carboxyl region.

One gram of the carbinol was dissolved in 5 ml. of pyridine and 2 ml. of acetic anhydride at 0° and allowed to stand overnight at room temperature. The solution was concentrated *in vacuo* to dryness and the residue allowed to crystallize. The product was suspended in a little petroleum ether and filtered to obtain the crude acetate, m.p. 63–65°. This was further purified by sublimation at 60° and 0.2 mm. to obtain pure acetate XI, m.p. 67–68°.

*Anal.* Calcd. for $C_{14}H_{16}FeO_2$: C, 61.79; H, 5.93. Found: C, 60.9, 62.3, 61.0; H, 5.76, 5.87, 6.04.

The infrared spectrum showed strong absorption at 5.78 $\mu$. There was no absorption in the hydroxyl region.

**Cyclopentadienyl-(vinylcyclopentadienyl)-iron (XII). A. By Pyrolysis of the Carbinol X.**—A 10-g. sample of cyclopentadienyl-($\alpha$-hydroxyethylcyclopentadienyl)-iron (X) was distilled at reduced pressure into a tube measuring 2.8 × 20 cm. and packed with alumina. The tube was heated to 200°. The distillation, carried out at 36 mm., required about 0.5 hour. After having been cooled, the tube packing was extracted with several portions of ether and the ether extracts concentrated and distilled under reduced pressure. The product had b.p. 80–85° (0.2 mm.) and m.p. 48–49°. It was very soluble in ether, petroleum ether and methanol and possessed a camphor-like odor. The yield was 1.93 g. (21%).

*Anal.* Calcd. for $C_{12}H_{12}Fe$: C, 67.96; H, 5.71; Fe, 26.33. Found: C, 67.8, 67.6; H, 5.67, 5.56; Fe, 26.8, 26.3.

The infrared spectrum showed strong absorption at 6.12 $\mu$. In methanol solution the compound showed strong absorption below 2500 Å. and maxima at 2730 Å. ($\epsilon$ 7,640) and at 4420 Å. ($\epsilon$ 1,130).

**B. By Pyrolysis of the Carbinol Acetate (XI).**—A 10-g. sample of the carbinol was converted to the acetate by the procedure described and the crude product distilled under reduced pressure into a tube measuring 2.8 × 20 cm. packed with Pyrex wool. The tube was heated to 175° and the distillation was carried out at 3 to 5 mm. The pyrolysis required about 0.5 hour. The product was washed from the packing with petroleum ether and the resulting solution concentrated *in vacuo* to give the crude vinyl derivative, m.p. 45–49°. The crude product was further purified by sublimation at 45–50° and 0.4 mm. to give material of m.p. 48–49°. The yield was 5.2 g. (56%).

**C. Polymerization. Acid.**—The vinyl compound (0.4 g.) was heated with one drop of 85% phosphoric acid at 80° for two hours. The product was a viscous oil insoluble in methanol but readily soluble in benzene.

**Azodiisobutyronitrile.**—The vinyl derivative (0.5 g.) was heated with 5 mg. of azodiisobutyronitrile at 80° for one hour. A further portion of 5 mg. of the catalyst was then added and the heating was continued for a total of two hours. The cooled product was a very viscous sirup. It was stirred with 2 cc. of methanol and filtered to give 0.25 g., m.p. 280–285°. The polymer was a tan powder insoluble in ether and methanol and soluble in chloroform and benzene. Clear brittle films were cast from benzene solution.

The yield of methanol-insoluble polymer was increased when larger amounts of catalyst and longer heating periods were employed.

**Persulfate.**—An emulsion consisting of 1 g. of XII, 1 ml. of water and 20 mg. of potassium persulfate was heated with stirring at 80° for six hours. The viscous polyvinyl derivative obtained was insoluble in methanol. When precipitated from benzene solution into methanol the product was an oil.

**Cross-linking with Formaldehyde.**—A 5-g. sample of solid polyvinyl derivative was heated six hours at 60° in 100 g. of hydrogen fluoride with 0.5 g. of paraformaldehyde. The reaction mixture was poured into water containing excess ascorbic acid. The resulting precipitate was filtered and washed with water until neutral. The cross-linked polymer thus obtained weighed 4.2 g. and was insoluble in boiling benzene.

**Oxidation of the Polyvinyl Derivative.**—A suspension of 1 g. of solid vinyl polymer in a solution of 2.5 g. of ceric sulfate in 50 ml. of water was stirred for two hours at room temperature. The dark blue solution obtained was filtered and the filtrate treated with excess ascorbic acid to give 1.0 g. of reduced polymer.

**Copolymerization of the Vinyl Derivative. Methyl Methacrylate.**—A solution of 2.0 g. of methyl methacrylate and 1.06 g. of XII (20 mole %) was heated at 80° for three hours with 30 mg. of azodiisobutyronitrile. The resulting polymer was dissolved in benzene (10 ml.) and added with stirring to 100 ml. of cold methanol. The copolymer weighed 2.0 g. and had m.p. 190–210°.

*Anal.* Calcd.: Fe, 9.12. Found: Fe, 10.3, 10.5.

The analysis indicates that 23.5 mole % of XII copolymerized. Films cast from benzene–chloroform solution were brittle.

**Styrene.**—A solution of 4 g. of the vinyl derivative (20 mole %) in 7.86 g. of styrene was heated at 80° two hours with 0.12 g. of azodiisobutyronitrile. The resulting viscous liquid was dissolved in benzene and the solution poured into methanol to obtain a yellow solid, 8.0 g., m.p. 158–165°.

*Anal.* Calcd.: Fe, 8.89. Found: Fe, 4.3, 4.2.

Films cast from benzene or chloroform were brittle.

**Chloroprene.**—A solution of 4.0 g. of Nancy Wood rosin, 5.0 g. of XII and 100 g. of chloroprene was emulsified under nitrogen with 100 ml. of water containing 1 g. of sodium hydroxide. The emulsion was transferred to a 500-ml. flask and stirred at 40° in a nitrogen atmosphere. One-half gram of potassium persulfate was added; polymerization began almost immediately. The temperature was maintained with the aid of an ice-bath at 39–41° until the reaction was complete (about one hour). The mixture was allowed to stir at room temperature for 20 minutes. The latex was coagulated by pouring into brine. The resulting orange-yellow, tough elastomer was washed on a washing mill and dried on a smooth mill at 100°. The mill dried product was dark brown, very tough and had an odor resembling, but fainter than, XII. The sample of mill-dried product showed the following analysis:

*Anal.* Calcd.: Fe, 1.21. Found: Fe, 1.15, 1.11.

**Cyclopentadienyl-(ethylcyclopentadienyl)-iron (XIII).**—Twenty grams of zinc was amalgamated by stirring ten minutes with 2 g. of mercuric chloride, 1 ml. of concentrated hydrochloric acid and 20 ml. of water. The aqueous phase was decanted and a mixture of 10 g. of the acetyl derivative I, 15 ml. of water and 20 ml. of concentrated hydrochloric acid was added. The reaction mixture was stirred under reflux for 18 hours. Five-ml. portions of acid were added at six hours and again at 12 hours after the start of the reaction. The product was separated with the aid of 100 ml. of ether. The ether solution was dried over magnesium sulfate and distilled through a short Vigreux section. Most of the material which distilled had b.p. 74–76° (0.2 mm.); the yield was 2.3 g. (25%).

*Anal.* Calcd. for $C_{12}H_{14}Fe$: C, 67.3; H, 6.59. Found: C, 67.3, 67.5; H, 6.67, 6.57.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

# Polysubstituted Cyclohexanes. The Synthesis of 9-Hydroxy-2-azabicyclo[3.3.1]nonane

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The preparation of *trans–cis-* and *cis–cis*-ethyl 3-amino-2-hydroxycyclohexaneacetate (XVa and XVb) from 2-carbethoxycyclohexanone, is reported. The synthesis of an isomer of 9-hydroxy-2-azabicyclo[3.3.1]nonane (XIX) is described. The stereochemistry of the amino alcohols XVa, XVb and XIX is discussed and a comparison is made between the behavior of isomeric vicinally trisubstituted cyclohexanes (type i) and simpler (1,2) and (1,3) disubstituted homologs (types ii, iii and iv).

Of significance in the chemistry of cyclohexane derivatives is the possibility of group interactions in polysubstituted systems, in particular as these interactions are affected by the relative configuration of the groups. Although conformational analysis has been applied mostly to polycyclic compounds,[2,3] it has proved to be of value also in an interpretation of the chemistry of simple and more flexible cyclohexanes.[4]

The present study is concerned with the behavior of stereoisomeric amino alcohol esters and acids of type i, in which the possibility exists for the formation of lactones (derivatives of 2-oxabicyclo[4.3.0]-nonane, v) or lactams (derivatives of 2-azabicyclo-

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[1] From part of the Ph.D. Thesis of John W. Sargent.

[2] (a) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954); (b) O. Hassel, *Quart. Revs.*, **7**, 221 (1953).

[3] (a) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953); (b) W. S. Johnson, *Experientia*, **8**, 315 (1951).

[4] (a) D. Y. Curtin, *Record Chem. Progress*, **15**, 111 (1954); (b) J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton, *J. Chem. Soc.*, 4102 (1954); (c) G. E. McCasland, THIS JOURNAL, **73**, 2295 (1951); (d) C. C. Price and G. Berti, *ibid.*, **76**, 1211 (1954); (e) D. Y. Curtin and S. Schmuckler, *ibid.*, **77**, 1105 (1955).