cenyl and phenyl groups have comparable electronegativities. (2) The C–Cl axes lie in the planes of the cyclopentadienyl rings to which the *p*-chlorophenyl groups are attached. This orientation of the C–Cl bond is expected if the cyclopentadienyl carbon atoms form the usual aromatic-type sp^2-bonds to substituents. The calculated distance between the cyclopentadienyl rings, 3.6 Å.,[22] is probably large enough to preclude distortion by steric repulsions between substituents on different rings. The vector moment of each C–Cl bond was taken as 1.56 *D*.[23]

The dipole moment for the freely rotating model was calculated using the equation for freely rotating angular groups[9,24] where α and β are the angles (α =

$$\mu = \sqrt{a^2 + b^2 + 2ab \cos \alpha \cos \beta \cos \theta}$$

β = 90°) which the moment vectors of the *p*-chlorophenyl groups make with the axes about which they rotate and θ (180°) is the angle between these axes; a and b ($a = b = 1.56$) are the electric moment vectors.

The dipole moments calculated for the various possible structures of the bis-(*p*-chlorophenyl)-ferrocene are summarized in Table II.

The experimental moment of 3.12 ± 0.03 *D* eliminates a freely rotating model (calculated μ = 2.20 *D*) and is in closest agreement with the moment expected for the 1,1′, prismatic (method I) or 1,1′-antiprismatic (method II) structure. Configurations like these with angles of only 0–36° between the two C–Cl dipole vectors would not be expected to be favored on the basis of dipole–dipole repulsions. However, the tendency for molecules to exist in "*cis*-like" configurations irrespective of such repulsions has been noted in other cases. Thus, the *cis*-configuration of disalicylide is apparently most stable and this has been attributed to resonance involving the lactone bridge.[25] An analogous preference for a *cis*-like "boat" configuration as the most stable form of 1,6-dichloro-1,5-cyclooöctadiene has been explained by operation of secondary valence forces,[26] possibly dispersion forces. Such valence forces may also account for why bis-di-(*p*-chlorophenyl)-ferrocene appears to exist in a configuration with the *p*-chlorophenyl groups quite close to one another. A similar conclusion was reached by Hampson and Weissburger[27] with regard to the orientations of the *ortho*-substituents in *o,o*′-dichlorobiphenyl.

TABLE II

DIPOLE MOMENTS CALCULATED FOR DI-(*p*-CHLOROPHENYL)-FERROCENE STRUCTURES

Structure (see I)	Dipole moment, *D*
1,1′, prismatic	3.12
1,1′, antiprismatic	2.97
1,2′, antiprismatic	1.83
1,3′, antiprismatic	0
Freely rotating cyclopentadienyl rings	2.20

Acknowledgment.—We are pleased to acknowledge several helpful suggestions by Prof. Myron Rosenblum with regard to dipole moment calculations and interpretation of the results.

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[22] The value of 3.6 Å. is obtained using a value of 1.4 Å. for the C–C ring distance and 2.0 Å. for the C–Fe distance.[3,6,7]

[23] Reference 19, p. 203.

[24] O. Fuchs, *Z. physik. Chem.*, **14B**, 339 (1931).

[25] W. Baker, W. D. Ollis and T. S. Zeally, *J. Chem. Soc.*, 201 (1951).

[26] J. D. Roberts, THIS JOURNAL, **72**, 3300 (1950).

[27] G. C. Hampson and A. Weissberger, *ibid.*, **58**, 2113 (1936).

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies in the Ferrocene Series. I. Some Reactions of Compounds Related to Monobenzoylferrocene[1]

BY NORMAN WELIKY AND EDWIN S. GOULD

RECEIVED OCTOBER 24, 1956

The ketones benzoylferrocene (I) and anisoylferrocene and several diketones have been made from ferrocene (dicyclopentadienyliron) by Friedel–Crafts acylations. Benzoylferrocene is reduced to the pinacol, 1,2-diphenyl,1,2-diferrocenylethanediol (IV), with methylmagnesium bromide in the presence of cobalt chloride; the same ketone is reduced to phenylferrocenylmethanol (II) with lithium aluminum hydride, to phenylferrocenylmethane (X) with zinc, sodium or aluminum and to still another carbinol, probably phenyldiferrocenylmethanol (IX), with sodium amalgam in benzene. The pinacol rearranges with extraordinary ease, with migration of the ferrocene moiety, and is surprisingly easily oxidized to the parent ketone by atmospheric oxygen. The secondary alcohol, phenylferrocenylmethanol, forms ethers under exceptionally mild conditions and behaves somewhat like a tertiary alcohol. These reactions suggest that a carbonium ion obtained by removal of an –OH group alpha to the ferrocene system is subject to special stabilization, possibly by dispersal of the positive charge through partial shift of *d*-electron density from the iron atom into the ring. The oxime of benzoylferrocene (VII) rearranges, through its tosylate, to the anilide of ferrocenecarboxylic acid (VIII).

The easy preparation and purification of benzoylferrocene allows the synthesis and study of a number of relatively simple compounds in which the benzene ring and the ferrocene system are attached to a common carbon atom. Chart I summarizes the transformations which we have carried out.

Acylations.—By suitable variations of reaction conditions, the Friedel–Crafts acylation of ferro-

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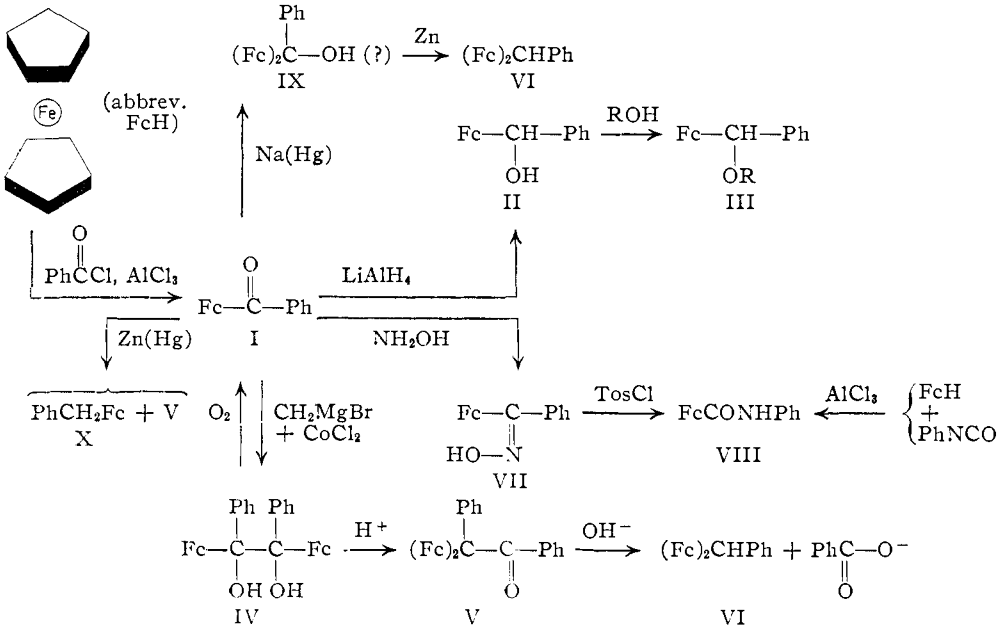
[1] Based on research carried out under Contract No. DA 30-069-ORD-1137, Project No. TB2-0001 (836), between the U. S. Army, Ordnance Department, and the Polytechnic Institute of Brooklyn.

cene may be made to yield either mono- or diketones as major products.[2] Benzoylferrocene (but no appreciable quantity of dibenzoylferrocene) is obtained from the acylation of ferrocene if equivalent quantities of ferrocene and aluminum halides are used. Since ferrocene reacts with aluminum halides (in a manner which is not yet clear), to form colored products, our most successful preparations of benzoylferrocene (I) and anisoylferrocene were carried out by slow addition of a "Perrier complex"[3] of the acid chloride and aluminum halide to ferrocene solutions.

Reductions of Benzoylferrocene.—Six different products resulting from the reduction of benzoylferrocene with various reagents have been characterized; in addition to these, several reduction products remain unidentified. Reduction with lithium aluminum hydride yields the expected secondary alcohol, phenylferrocenylmethanol (II), which is also formed in small yield from reduction with sodium. This carbinol has an unusually labile hydroxyl group since it is converted to its methyl ether (III, R = CH_3) merely on boiling with aqueous methanol. Similarly, the isopropyl ether results from the reduction of benzoylferrocene with aluminum isopropoxide in isopropyl alcohol, a situation bringing to mind the similar behavior of certain α,β-unsaturated ketones.[4]

CHART I.—TRANSFORMATIONS OF BENZOYLFERROCENE



The usual methods for bimolecular reduction of ketones to pinacols did not work when applied to benzoylferrocene. No reaction occurred when a solution of the ketone in isopropyl alcohol was irradiated in sunlight for a month,[5] whereas reduction with magnesium–magnesium iodide[6] yielded unidentified products. Among the less conventional bimolecular reduction methods attempted, the most successful was that of Kharasch and Lambert[7] using methylmagnesium bromide and cobalt(II) chloride. The pinacol IV thus obtained rearranged with remarkable ease (merely upon passing gaseous HCl over its solution in benzene) to the pinacolone V. The structure of the latter is indicated by its degradation in base to phenyldiferrocenylmethane (VI) and benzoate.

The pinacolone V is also formed as a minor product in the Clemmensen reduction of benzoylferrocene; the pinacol, which would be expected to rearrange immediately under Clemmensen conditions, is probably an intermediate here. The chief product from the Clemmensen reduction is the expected desoxo compound, phenylferrocenylmethane (X).

Reduction with sodium amalgam yields an additional alcohol which may be reduced further with zinc to VI. This evidence, together with its analysis, suggests that the alcohol is phenyldiferrocenylmethanol (IX), although it is difficult to see how such a product would arise from reduction of benzoylferrocene. This alcohol, like phenylferrocenylmethanol (II), is converted to its methyl ether merely on heating with methanol.

The exceptional ease with which carbinols II and IX are converted to their ethers and the very mild conditions under which the pinacol IV rearranges suggest that the presence of the ferrocene system in the position alpha to a hydroxyl group lowers the energy barrier to conversion of the carbinol to the corresponding carbonium ion. It does

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(2) (a) The behavior of ferrocene in the Friedel-Crafts reaction has been summarized by P. L. Pauson, *Quart. Revs.*, **9**, 409 (1955). See also: (b) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3459 (1952); (c) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **97**, 459 (1954); (d) V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955).

(3) G. Perrier, *Bull. soc. chim. France*, [3] **31**, 859 (1904).

(4) H. Lund, *Ber.*, **70**, 1520 (1937).

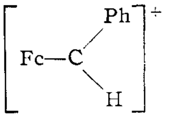
(5) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, **56**, 208 (1934).

(6) W. E. Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932).

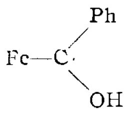
(7) M. S. Kharasch and F. L. Lambert, *ibid.*, **63**, 2315 (1941).

not seem probable that the presence of a single phenyl group and a single ferrocenyl group on a carbon atom would result in enough steric crowding to account for this effect. We suggest rather that a carbonium ion such as XI is stabilized by an unusual ability of the ferrocene system to delocalize the positive charge, possibly through a partial shift of *d*-electron density from the iron atom into the ring.

Equally remarkable is the ease with which the pinacol IV is converted back to benzoylferrocene upon exposure to air. This conversion takes place in polar solvents and in the presence of alumina or silica gel. The pinacol is most stable in the solid state (if protected from air) or in solutions of carbon disulfide or benzene. Very dilute solutions in the latter solvent show a drift in spectra; for a 0.0003 *M* solution, conversion to benzoylferrocene is over 80% complete after 4 days standing. Disproportionation, as is sometimes observed for basic solutions of pinacols,[8] evidently does not occur, for no phenylferrocenylmethanol (II) could be detected in solutions in which the pinacol had been converted to the ketone, even under conditions where the carbinol should survive. Little more can be said about this oxidation[9] on the basis of the present observations, but the possibility that it proceeds through small concentrations of the radical XII (which might be stabilized in much the same manner as carbonium ion XI) cannot, in our opinion, be excluded.



XI



XII

The Beckmann Rearrangement.—The oxime of benzoylferrocene (VII) does not react cleanly under the usual acidic Beckmann rearrangement conditions, but its *p*-toluenesulfonate rearranges in base to ferrocenecarboxanilide (VIII). Although this amide could not be hydrolyzed, either by acid or base, its identity was proved by synthesis from ferrocene and phenyl isocyanate. The structure of the amide indicates either that the phenyl group is *anti*- to the hydroxyl group of the oxime or (less likely) that the oxime is isomerized during the course of the rearrangement. Since the course of both the Beckmann[10] and pinacol[11] rearrangements are thought to be dictated largely by the configurations of the reactants, conclusions about the relative "migratory aptitudes" of the ferrocene system and the benzene ring cannot be drawn.

Experimental

Benzoylferrocene (I).—A Perrier complex[3] was prepared from 42 g. of benzoyl chloride and 42 g. of anhydrous aluminum chloride. This was dissolved in carbon disulfide and added, over a period of 0.5 hr., to a warm solution of 55 g. of ferrocene in 180 ml. of carbon disulfide. After 20 hr., the mixture was hydrolyzed, worked up in the usual manner and chromatographed on alumina. Red crystals (56 g., 67%) were obtained by crystallization from hexane; m.p. 108–109° (reported[12] 111.5–112.0°).

Anal. Calcd. for $C_{17}H_{14}OFe$: C, 70.35; H, 4.83; Fe, 19.3. Found: C, 70.38; H, 4.92; Fe, 19.0.

The infrared carbonyl band was at 1634 and phenyl absorption at 1458, 1588 and 1605 cm.$^{-1}$. Absorption of an unsubstituted ferrocene ring was at 1108 cm.$^{-1}$. Visible and ultraviolet peaks in alcohol were at 245 (ϵ 14,900), 274 (shoulder, ϵ 7,930), 362 (ϵ 1,230) and 478 mμ (ϵ 696).

Anisoylferrocene.—To 15 g. of anhydrous aluminum bromide in 70 ml. of carbon disulfide at 0° was added slowly 9.3 g. of anisoyl chloride. The resulting mixture was added slowly, with cooling, to 10 g. of ferrocene in 50 ml. of carbon disulfide. After 4 hr., the mixture was hydrolyzed and worked up in the usual manner. Chromatography on alumina yielded 4.5 g. (26%) of blood-red crystals. The product was purified further by sublimation at reduced pressure, a second chromatographic separation and, finally, crystallization from methanol–water. The yield of pure product (m.p. 82–83°) was 4.0 g. (23%).

Anal. Calcd. for $C_{18}H_{16}O_2Fe$: C, 67.50; H, 5.00. Found: C, 67.48; H, 4.97.

The infrared spectrum showed carbonyl absorption at 1612, phenyl absorption at 1515 and 1578 and absorption of unsubstituted ferrocene rings at 1110 cm.$^{-1}$.

Visible and ultraviolet absorption maxima were at 223, 284 and 477 mμ.

Anisic acid did not react with ferrocene in anhydrous hydrogen fluoride.

Benzoylferrocene oxime (VII) was prepared in pyridine[13] from 2.0 g. of benzoylferrocene. The heating period was only 2 hr. The residue was extracted with benzene and crystallization induced by adding hexane. One gram of dark red-brown crystals (48%) was obtained, m.p. 164–169° dec. A portion chromatographed on alumina and crystallized from benzene–hexane yielded orange-red needles, m.p. 158–159° (foamed), reported[12] 160° dec.

Anal. Calcd. for $C_{17}H_{15}ONFe$: C, 66.89; H, 4.91; N, 4.59. Found: C, 67.13; H, 4.82; N, 4.57.

The infrared spectrum indicated the absence of carbonyl groups. Hydroxyl absorption was at 3190, phenyl absorption at 1498, 1580 and 1600 and absorption of unsubstituted ferrocene rings at 1106 cm.$^{-1}$.

Beckmann Rearrangement of Monobenzoylferrocene Oxime.—Monobenzoylferrocene oxime (1 g.) was rearranged through its benzenesulfonyl ester by the method of Brown, Van Gulick and Schmid.[14] A benzene solution of the products was chromatographed on alumina, yielding 0.23 g. of cotton-like yellow needles, m.p. 208–210°.

Anal. Calcd. for $C_{17}H_{15}ONFe$: C, 66.89; H, 4.91; N, 4.59. Found: C, 67.81; H, 4.88; N, 4.58.[15]

The infrared amide bands were at 3280 (N–H), 1643, 1526 cm.$^{-1}$. Phenyl absorption was at 1500 and 1600 and unsubstituted ferrocene ring absorption at 1106 cm.$^{-1}$. The infrared spectrum of this amide was found to be identical to the infrared spectrum of the amide obtained from the reaction of phenyl isocyanate with ferrocene. Visible and ultraviolet maxima were at 245, 271 and 447 mμ in alcohol and chloroform.

Anilide of Ferrocenecarboxylic Acid.—To 5.0 g. of ferrocene and 2.9 g. of phenyl isocyanate in 100 ml. of carbon di-

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[8] W. Thorner and T. Zincke, *Ber.*, **10**, 1473 (1877); **11**, 65 (1878).

[9] Similar oxidations of fluorenopinacol and xanthopinacol to the corresponding ketones have been reported by C. R. Masson, V. Boekelheide and W. A. Noyes, Jr., "The Technique of Organic Chemistry," Vol. II, Arnold Weissberger, Editor, Interscience Publishers, Inc., New York, N. Y., 1956, p. 316.

[10] J. Meisenheimer, P. Zimmermann and U. v. Kummer, *Ann.*, **446**, 205 (1926).

[11] The conclusions of Curtin and co-workers, THIS JOURNAL, **73**, 3453 (1951), **74**, 5905 (1952), with regard to pinacolic deaminations and rearrangements of aryl-substituted bromohydrins probably may be applied also to the pinacol rearrangement since the three types of rearrangements are thought to proceed through similar transition states.

[12] E. Csendes, reported by M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953, p. 85.

[13] W. E. Bachmann and M. Barton, *J. Org. Chem.*, **3**, 303 (1938).

[14] R. F. Brown, H. M. Van Gulick and G. H. Schmid, THIS JOURNAL, **77**, 1094 (1955).

[15] The analyses for carbon in this compound and in a number of additional ferrocene derivatives reported here are not fully satisfactory, although there seems little doubt as to the identity of the compounds. Some difficulty is encountered in obtaining very precise combustion analyses for certain substituted ferrocenes by conventional methods.

sulfide, 3.7 g. of anhydrous aluminum chloride was added in portions, while agitating the solution. The mixture was stirred 1 hr., refluxed 1 hr., then left overnight. The carbon disulfide was decanted. The oily residue and the carbon disulfide solution were hydrolyzed and acidified separately and the carbon disulfide removed by evaporation. The solid residues were washed with water and extracted with hexane to remove unreacted ferrocene. The residues were then extracted, first with benzene, then with chloroform. A yield of 2.1 g. (25% over-all, 60% based on ferrocene not recovered) of yellow-brown needles was obtained by crystallization of the extracted material from benzene. By repeated crystallization from isopropyl alcohol, cotton-like yellow needles were obtained, m.p. 205–207°.

The infrared spectrum of this substance was identical to the spectrum of the Beckmann rearrangement product of benzoylferrocene oxime. Evaporation of the hexane left 2.8 g. (57%) of ferrocene.

1,2-Diphenyl-1,2-diferrocenyl-ethanediol.[7]—Methylmagnesium bromide was prepared by passing methyl bromide through a mixture of 0.65 g. of magnesium and 10 ml. of anhydrous ether. Under an atmosphere of nitrogen, 70 mg. of anhydrous powdered cobalt(II) chloride was added to the solution at 0°. Then 2 g. of monobenzoylferrocene in 15 ml. of benzene was added dropwise. The mixture was stirred for 1.5 hr., refluxed 2.5 hr. and stirred 0.75 hr. While a nitrogen atmosphere was maintained, 30 ml. of a saturated aqueous solution of ammonium chloride was added dropwise. The mixture was transferred to a separatory funnel, washing the reaction flask with water and a minimum of ether. The remaining solid and organic layer were extracted with portions of ammonium chloride solution till almost all the dark suspended material changed to a pale yellow solid floating at the lower interface of the organic layer. The yellow solid was washed with water, dried in the air and recrystallized from benzene under nitrogen; yield 0.76 g. (38%), m.p. 125–145° dec.

Anal. Calcd. for $C_{34}H_{30}O_2Fe_2$: C, 70.10; H, 5.15; active H, 0.34. Found: C, 69.61; H, 5.15; active H, 0.36 (lithium aluminum hydride).

The infrared spectrum showed hydroxyl absorption at 3510, phenyl absorption at 1492, 1585 and 1620 and absorption due to unsubstituted ferrocene rings at 1106 cm.$^{-1}$. Carbonyl absorption was absent.

The visible absorption spectrum in benzene showed a maximum near 445 mμ (ϵ 281). The compound does not dissolve in alcohols or paraffinic solvents.

Solutions of the compound in benzene and carbon disulfide were yellow. In chloroform, dioxane or alcohol–benzene, the solutions rapidly turned red. Chromatography on alumina converted the pinacol to red crystals whose infrared spectrum showed bands characteristic of both the pinacol and benzoylferrocene. Recrystallization yielded a product whose infrared spectrum was identical to that of benzoylferrocene. The same conversion took place very slowly in benzene solution and was studied by measuring the increase in absorption at 362 mμ, the wave length at which benzoylferrocene shows a maximum but the pinacol shows a minimum. At the end of 4 days, a dilute solution of the pinacol in benzene (0.150 g./liter) was 80% converted to benzoylferrocene.

A sample of 20 mg. of the pinacol was dissolved in 5 ml. of benzene. Hydrogen chloride gas was led over the surface for 2 min. The test-tube was stoppered and allowed to stand three days. The benzene was decanted from a green oil and chromatographed on alumina. Development of the chromatogram with hexane yielded 5 mg. of benzoylferrocene and about 4 mg. of orange crystals, m.p. 211° dec. The infrared spectrum of the latter was identical to that of phenylbenzoyldiferrocenylmethane (V).

Phenylbenzoyldiferrocenylmethane (V).—Benzoylferrocene (0.3 g.) was reduced in 1 ml. of absolute alcohol with 0.6 g. of amalgamated zinc.[16] Alcoholic hydrogen chloride (2 ml.) was added over 30 minutes. The solution was heated for 1 hr. at 100° and allowed to stand overnight. The solution was diluted with water and the precipitated solid extracted with benzene. Chromatography with benzene–hexane on alumina yielded two solids, the first an unidentified orange substance, m.p. 211° dec., the second the pinacolone V. Of the latter, 100 mg. (33%) was obtained, m.p. 195–198° dec. Infrared carbonyl absorption was at 1680, phenyl absorption at 1492, 1586 and 1600 and absorption of unsubstituted ferrocene rings at 1108 cm.$^{-1}$.

Anal. Calcd. for $C_{34}H_{28}OFe_2$: C, 72.34; H, 4.97. Found: C, 72.16; H, 5.26.

Phenyldiferrocenylmethane (VI).—A 20-mg. sample of the pinacolone V was heated at 100° for 24 hr. in 5% alcoholic potassium hydroxide. The solvent was evaporated to a low volume, extracted with water and filtered. The filtrate was extracted with ether and the ether extracts, in turn, extracted with $NaHCO_3$ solution. The bicarbonate solution was then acidified and re-extracted with ether and the ether then evaporated off. The gray-white solid which remained was sublimed to give a product, m.p. 110–115°. The X-ray powder photograph of this material was identical to that of benzoic acid. The residue from the original basic mixture was dissolved in hexane and chromatographed. In addition to a small amount of the original pinacolone, there was obtained about 10 mg. of phenyldiferrocenylmethane, m.p. 123–124° (from ethanol–water); infrared peaks were at 1106, 1492, 1586 and 1670 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{24}Fe_2$: C, 7035; H, 5.22. Found: C, 70.14; H, 5.28.

Phenylferrocenylmethane (X).—To a solution of 0.5 g. of benzoylferrocene in 5 ml. of acetic acid was added 5 g. of zinc dust. The mixture was swirled and became viscous. Three 5-ml. portions of acetic acid were added, and the mixture was allowed to stand. After 3 hr., an additional 17 ml. of acetic acid and 1 ml. of concentrated hydrochloric acid were added. After 18 hr., an additional 5 g. of zinc dust was added, then 10 ml. more of concentrated hydrochloric acid. The red color disappeared from solution. The mixture was diluted with water and filtered, whereupon the major part of the colored material was precipitated on the surface of the zinc dust. The solid was extracted with benzene and the benzene extracts chromatographed on alumina. In addition to an unidentified solid, m.p. 218° dec., and a small amount of pinacolone V, there was obtained 0.13 g. (27%) of the desired hydrocarbon, m.p. 70–74° (from low boiling petroleum ether), λ_{max} at 440 mμ, and infrared peaks at 1105, 1497, 1560, 1588, 2920 and 2980 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{16}Fe$: C, 73.91; H, 5.79; mol. wt., 276. Found: C, 74.07; H, 5.36; mol. wt., 277 (isothermal distillation).

Phenylferrocenylmethanol (II).—To a solution of 6 g. of lithium aluminum hydride in 150 ml. of anhydrous ether was added a solution of 10 g. of benzoylferrocene in 600 ml. of anhydrous ether. Stirring was continued for 2 hr. After 20 hr., the mixture was hydrolyzed and the ether decanted from the solids. On evaporation of the ether, a yield of 9.6 g. (96%) of phenylferrocenylcarbinol was obtained, m.p. 81–82° (from low boiling petroleum ether); infrared absorption peaks were at 3470 (OH), 1500, 1560 and 1106 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{16}OFe$: C, 69.86; H, 5.48; mol. wt., 291. Found: C, 69.82; H, 5.32; mol. wt., 253 (isothermal distillation).

An attempt to convert this carbinol to the corresponding bromide with PBr_3 led instead to a product believed to be **di-(phenylferrocenylmethyl) ether** (which could be made also by treatment of the carbinol with *p*-toluenesulfonyl chloride). The carbinol (0.7 g.) was dissolved in 2 ml. of dry pyridine, the solution cooled to 0°, 0.2 g. of phosphorus tribromide added dropwise and cooling continued for 1.5 hr. After two days, the solvent was evaporated off and the oil dissolved in chloroform. The white solid was removed by adding benzene, then boiling to a low volume and adding hexane. Chromatography of the filtrate yielded a very small quantity of an unidentified substance, m.p. 110–112°, and about 20 mg. of the *sym*-ether, m.p. 52–56°.

Anal. Calcd. for $C_{34}H_{30}OFe_2$: C, 72.09; H, 5.29; mol. wt., 566. Found: C, 71.72; H, 6.21; mol. wt., (Rast), 508.

The infrared spectrum showed phenyl absorption at 1492, 1588 and 1610, absorption of unsubstituted ferrocene rings at 1104 and a strong ether absorption at 1097 cm.$^{-1}$.

On boiling phenylferrocenylcarbinol in a solution of methanol and water, and crystallization from these solvents, yellow crystals were obtained, m.p. 104–108°. After rechromatographing on alumina in hexane and recrystallizing the first yellow band eluted from methanol–water, the

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[16] W. Steinkopf and A. Wolfram, *Ann.*, **430**, 115, 135 (1923).

methyl ether of phenylferrocenylmethanol (III, R = CH_3) was obtained, m.p. 111–112°.

Anal. Calcd. for $C_{18}H_{18}OFe$: C, 70.59; H, 5.88; active H, 0.0. Found: C, 70.26; H, 5.20; active H, 0.0.

The infrared spectrum showed absorption of aliphatic C–H at 2880, 2930 and 2970, phenyl absorption at 1492 and 1559, absorption of unsubstituted ferrocene rings at 1104 and very strong ether absorption at 1063 cm.$^{-1}$.

Isopropyl Ether of Phenylferrocenylmethanol (III, R = *i*-Pr–).—Benzoylferrocene (1 g.) was reduced by the method of Meerwein–Ponndorf–Verley.[17] The hydrolyzed reaction mixture was extracted with benzene, the solvent removed and the mixture extracted with Skellysolve B and chromatographed on alumina with methanol. In addition to a small amount of the methyl ether of phenylferrocenylmethanol, there was isolated 0.35 g. (33%) of yellow crystals of the isopropyl ether, m.p. 74–75°.

Anal. Calcd. for $C_{20}H_{21}OFe$: C, 72.07; H, 6.31. Found: C, 71.24; H, 6.81.

The infrared spectrum showed absorption in the aliphatic C–H region at 2880, 2930 and 2970, phenyl absorption at 1492, 1540 and 1559, absorption of unsubstituted ferrocene rings at 1104 and very strong ether absorption at 1063 cm.$^{-1}$.

Like the carbinol and the methyl ether, the isopropyl ether is soluble in concentrated hydrochloric acid.

Reduction of Monobenzoylferrocene by Sodium.—To 0.25 g. of monobenzoylferrocene in 3 ml. of benzene was added 2.5 g. of 5% sodium amalgam. The mixture was refluxed 2 hr., poured into water and filtered. The organic layer was washed, dried and chromatographed on alumina. Evaporation of solvent from the eluted yellow band, just preceding the large red band of unreacted monobenzoylferrocene, left 35 mg. of orange yellow powder, 150–170° dec. (180–185° red droplets). This substance is believed to be **phenyldiferrocenylmethanol (IX).** Infrared absorption was found at 3520 (OH), 1492 and 1600 (phenyl) and 1107 cm.$^{-1}$ (ferrocenyl).

Anal. Calcd. for $C_{27}H_{24}OFe_2$: C, 68.05; H, 5.04; active H, 0.21. Found: C, 68.44; H, 5.11; active H, 0.36.

This compound was dissolved in 95% ethanol by refluxing for 15 min. Excess zinc dust was added, then alternately, small amounts of hydrochloric acid and zinc dust till most of the color was gone from the solution. The mixture was filtered, washed, dried, extracted with benzene and the solvent evaporated. The residue was extracted with henxane and chromatographed on alumina in that solvent, yielding a yellow solid with an infrared spectrum identical to that of phenyldiferrocenylmethane (VI).

A 30-mg. sample of the hydroxy compound was refluxed with methanol for 7.5 hr. Evaporation of the methanol yielded crystals which were purified by chromatography on alumina. The resulting product 28 mg., m.p. 158° dec., is presumably the methyl ether of IX. Its infrared spectra showed peaks at 2920, 2820, 1554, 1494, 1106 and a high absorption, indicative of ethers, at 1076 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{26}OFe_2$: C, 68.55; H, 5.31. Found: C, 69.41; H, 5.59.

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[17] A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

[CONTRIBUTION FROM THE PLASTICS LABORATORY, PRINCETON UNIVERSITY]

Reductive Cleavage of Ferrocene[1]

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In contrast to the extreme resistance of ferrocene to catalytic reduction, this aromatic ring system is reduced readily by lithium in ethylamine with cleavage of the molecule to metallic iron and cyclopentadiene. The reaction of lithium with ferrocene in ethylamine is very rapid and may be stopped after several minutes with good conversion. Qualitative experiments have ascertained that other metal-amine, ammonia combinations also similarly reduce ferrocene.

No method has yet been described for a mild controlled degradation of the ferrocene ring system (bis-cyclopentadienyl iron, $Fe(C_5H_5)_2$) suitable for structure assignments for isomeric substituted ferrocenes. In this investigation a convenient degradation procedure was sought which would effect cleavage of the ferrocene molecule into its component parts and permit separate examination of each of the resulting 5-carbon rings.

The catalytic hydrogenation route to dearomatization and collapse of the ferrocene molecule appears to be unsuccessful. The resistance of ferrocene to catalytic hydrogenation over platinum has been reported by Woodward, Rosenblum and Whiting.[2] Our own attempts to hydrogenate ferrocene using the more active 5% rhodium-on-alumina in acetic acid for periods up to several weeks have given similar negative results. Under these same conditions benzene is completely hydrogenated in 5 minutes. Fischer[3] also has reported failure to hydrogenate ferrocene with Raney nickel in alcohol at 150° and 150 atmospheres.[4]

As a means of transferring an electron to the ferrocene nucleus to dearomatize the molecule, the use of alkali metals was investigated. Lithium does not attack ferrocene in refluxing ether, benzene or toluene, although attack does occur at *ca.* 200° in mineral oil with formation of metallic iron. In contrast to these slow heterogeneous reactions, however, rapid cleavage of the ferrocene molecule into metallic iron and cyclopentadiene is obtained by use of lithium in ethylamine, the amine functioning as solvent for lithium atoms. This reducing system has been investigated by Benkeser and co-workers in connection with benzenoid aromatic compounds.[5]

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[2] R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

[3] E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955).

[4] ADDED IN PROOF.—We have recently noted the interesting publication of A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 749 (1956), in which these investigators report the first successful catalytic hydrogenation of ferrocene and several of its derivatives using Raney nickel at 265–345° and 200–280 atmospheres.

[5] (a) R. A. Benkeser, R. E. Robinson, D. A. Sauve and O. H. Thomas, THIS JOURNAL, **76**, 631 (1954); **77**, 3230 (1955); (b) R. A. Benkeser, C. Arnold, R. F. Lambert and O. H. Thomas, *ibid.*, **77**, 6042 (1955).