in 300 ml of anhydrous ether was added 23.1 g (0.155 mol) of a mixture of the esters **2** and **3** (1:9) in 100 ml of anhydrous ether. During the 1-hr addition, the mixture was cooled with an ice bath. After refluxing for 3 hr, excess hydride was destroyed by the addition of wet ether (100 ml) and then water (200 ml). The mixture was then stirred for 1 hr. A 5% sodium sulfate solution (400 ml) was added, and the aqueous phase was separated from the organic layer. The aqueous phase was extracted with two 300-ml portions of ether. Removal of the solvent on a rotary evaporator and vacuum distillation of the residue gave 16.3 g (90.0%) of a mixture of alcohols **14** and **15**, bp 90–94° (0.4 mm). On redistillation, a cut with bp 88° (0.35 mm) was taken for analysis: ir (neat) ν_{OH} 3350 (broad, strong), $\nu_{C=C}$ 1670 cm^{-1}; nmr (CD$_3$COCD$_3$) δ 5.3–5.7 (m, C=CH), 4.07 (d,

J = 7 Hz, C=CHCH$_2$OH), 3.2–4.2 (m, CH$_2$CH$_2$OH and OH), 1.2–2.5 (m, ring CH$_2$), 0.95 ppm (d, J_{PCH} = 3.0 Hz, PCH$_3$). Addition of D$_2$O simplified the 3.2–4.2 multiplet to a triplet (J = 7 Hz) for CH$_2$CH$_2$OH; from the area of this and the C=CH-CH$_2$OH signal, the composition of the mixture was 12% **14**–88% **15**.

Anal. Calcd for C$_8$H$_{15}$OP: C, 60.74; H, 9.56; P, 19.58. Found: C, 60.74; H, 9.65; P, 19.33.

Registry No.—**1**, 16327-48-3; **2**, 28399-79-3; **3**, 28399-80-6; **6**, 1552-92-7; **8**, 28399-82-8; **12**, 28399-83-9; **12** methiodide, 28399-85-1; **13**, 28399-84-0; **14**, 28405-55-2; **15**, 16469-47-9.

# Ferrocene Studies. XIX.[1a] Synthesis of 1,2-Terferrocene[1b,c]

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An unequivocal route of synthesis of 1,2-terferrocene (**2**) has been developed. Cyclocondensation of ferrocil (**9**) and acetone was accomplished in 79% yield to give 3,4-diferrocenyl-4-hydroxy-2-cyclopenten-1-one (**10**), which was reduced to 3,4-diferrocenyl-2-cyclopenten-1-one (**11**) by the action of titanium(III) chloride in 95% yield. The cyclopentenone was converted to the corresponding diferrocenylcyclopentenol (**12**). The latter compound proved to be rather sensitive to most reaction conditions, but its dehydration was eventually effected in acceptable yield. The resulting diene was shown to be a single substance, 1,2-diferrocenyl-1,3-cyclopentadiene (**4**). It was converted to its aromatic anion by treatment with *n*-butyllithium, and the former allowed to react with iron(II) chloride in the presence of cyclopentadienyl anion. While ferrocene itself was the major product of the reaction, 1,2-terferrocene also resulted in small yield. The title compound, which is an orange crystalline substance, was characterized by the usual set of spectral data.

Despite an increasing interest in systems containing directly bonded ferrocene nuclei,[2] only one of the three constitutionally isomeric possibilities for assembly of three ferrocene nuclei (**1**, **2**, and **3**) has heretofore been

1   **2**   **3**
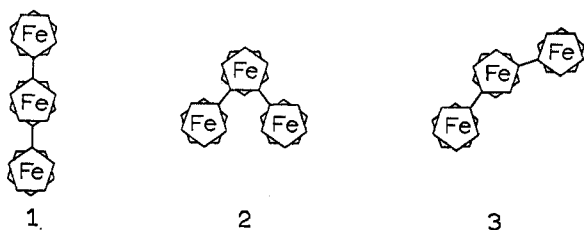
synthesized. 1,1'-Terferrocene (**1**) was obtained *via* construction of the central ferrocene nucleus[3] and *via* direct coupling[4] of ferrocene nuclei, but no unequivocal synthesis of either of the two remaining isomeric terferrocenes (**2** and **3**) has been previously reported. Synthesis of 1,2-terferrocene (**2**), however, has been accomplished in this laboratory, and we now report on that work.

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(1) (a) Previous paper: S. I. Goldberg, W. D. Bailey, and M. L. McGregor, *J. Org. Chem.*, **36**, 761 (1971); (b) Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, No. 309; (c) taken in part from the doctoral dissertation submitted by J. G. B. to the Graduate School of the University of South Carolina, July 1967, in partial fulfillment of the requirements for the Ph.D. Degree; (d) Fellow of the National Science Foundation, 1963–1964, and holder of the C. Jules Seideman Memorial Fellowship, 1965–1966, established by Columbia Organic Chemicals Co., Inc.

(2) See D. E. Bublitz and K. L. Rinehart, Jr., *Org. React.*, **17**, 1 (1969), and M. D. Rausch, *Chem. Commun.*, 502 (1970), for accounts of, and references to, much of the work in this area.

(3) K. L. Rinehart, Jr., D. G. Ries, and P. A. Kittle, 149th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, Abstracts, P-23.

(4) A. N. Nesmeyanov, V. N. Drozd, V. A. Sazonova, V. I. Romanenko, A. K. Prokofev, and L. A. Nikonova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 667 (1963).

Our synthesis scheme pivoted on an unequivocal preparation of 1,2-diferrocenylcyclopentadiene (**4**).[5] In this way structural ambiguity as regards disposition of the two ferrocenyl groups on the central ferrocene nucleus would be avoided. Formation of the central ferrocene nucleus, *via* complexing of **4** and cyclopentadiene (both as anions) about the central iron atom, was projected as the final step. This plan proved to be successful, although the final ferrocene-forming step occurred in disappointingly low yield.
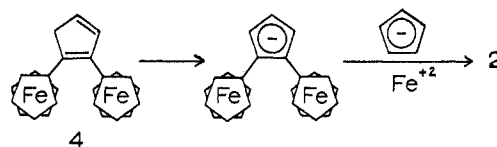

Our initial approach toward development of a synthesis of **4** lay in attempts to effect intramolecular pinacol formation of the dione **5**, followed by didehydration of the pinacol (**6**). We were, however, unsuccessful in all attempts to achieve this goal. While the majority of these experiments led only to recovery of the starting dione, electrolytic reduction, a technique that worked well with benzophenone to give benzopinacol,[6] appeared promising in that the red color characteristic of **5** was discharged. However, the product of electrolytic reduction (yellow) underwent decomposition (dark brown) during every attempt to isolate it.

Weliky and Gould[7] found that benzoylferrocene was converted to its pinacol with methylmagnesium bro-

(5) Obviously, any combination of the three possible double bond isomers was acceptable. In actual fact, however, only **4** was obtained.

(6) S. Swann, S. W. Briggs, V. C. Neklutin, and A. T. Jerome, *Trans. Electrochem. Soc.*, **80**, 163 (1941).

(7) N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957).

5

| MeMgBr
| CoCl₂

7   +   8
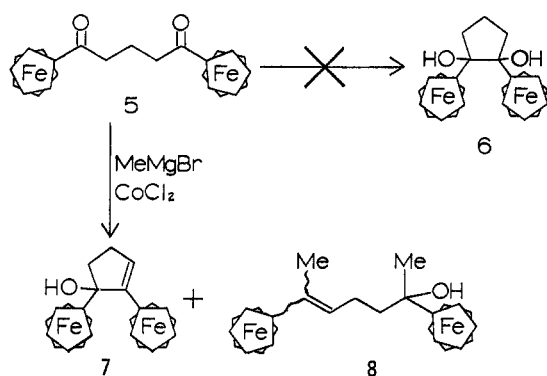
mide in the presence of cobaltous chloride when other methods failed. In the present case, this method gave a product whose spectral properties were consistent with a mixture of **7** and **8**. Additional efforts to develop the pinacol route were made, but the reaction was abandoned in favor of an alternative synthesis of **4**.

The successful synthesis of **4** was finally achieved through development of the first step of the sequence, cyclic aldol condensation of acetone and ferrocil (**9**).


9   10
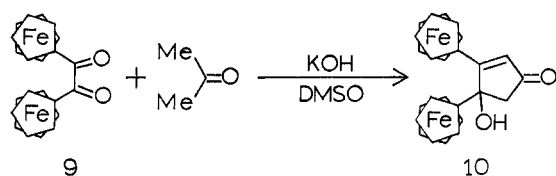
Ferrocil (**9**) was dissolved in a mixture of thoroughly deoxygenated ethanol and dimethyl sulfoxide, followed by addition of potassium hydroxide. The resulting solution was maintained near 60° while acetone was slowly added. The reaction, which was monitored by means of thin layer chromatography, was complete in 5.5 hr. It gave 3,4-diferrocenyl-4-hydroxy-2-cyclopenten-1-one (**10**) in dark red crystalline form in 79% yield after purification.

Each of the two oxygen functions in **10** represented a potential means for introduction of the desired second double bond. We first explored the feasibility of reduction of the carbonyl function by means of the Wolff–Kishner process, to be followed by dehydration of the resulting tertiary alcohol to **4** or its equivalent. However, each attempt to effect Wolff–Kishner reduction of **10** resulted only in extensive decomposition. We then turned to the second option, removal of the hydroxyl group in **10** followed by use of the remaining carbonyl function for introduction of the second double bond.

Pauson and Csendes[8] effected removal of the tertiary hydroxyl groups in 1,1'-bis(diphenylhydroxymethyl)-ferrocene to 1,1'-bis(diphenylmethyl)ferrocene by treatment of the former with titanium(III) chloride. In the present work, the action of titanium(III) chloride on **10** in a mixture of glacial acetic and hydrochloric acids provided a smooth and highly efficient (95% yield) means of replacement of the hydroxyl group with hydrogen. The product (**11**) was obtained as a high melting, deep red, crystalline material which was easily decomposed during alumina chromatography, but which was purified by recrystallization from methyl-

(8) P. Pauson and E. Csendes, as cited in M. Rosenblum's doctoral dissertation, Harvard University, 1953.

ene dichloride. Reduction of **11** with sodium borohydride gave the corresponding alcohol (**12**) which proved to be a very difficult substance to handle owing to its ease of decomposition. The highly sensitive nature of **12** also made it difficult to effect its dehydration without extensive decomposition. Dehydration of **12** was, however, finally accomplished by allowing a dilute solution of the unsaturated alcohol in methylene chloride to percolate through a narrow layer of neutral alumina which was sandwiched between layers of silicic acid. This process provided **4** in 46% yield over the two steps from **11**.

10 ⟶   11   ⟶   12 ⟶ **4**

4a   4b
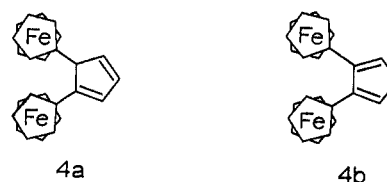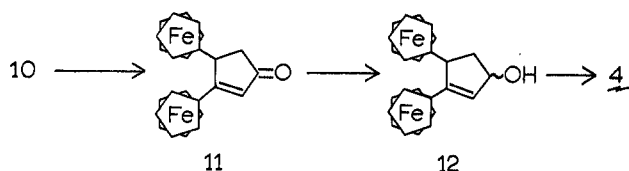
Although there are three constitutional double bond isomers possible for 1,2-diferrocenylcyclopentadiene (**4**, **4a**, and **4b**), the material obtained from dehydration of **12** gave a nuclear magnetic resonance spectrum consistent only with **4**. Thus, display of two different vinyl protons (δ 6.17 and 6.55) and two allylic protons (δ 3.33) argued strongly against the presence of detectable amounts of either one or both of the other isomers (**4a** and **4b**). Structure **4a** possesses three vinyl protons and one allylic proton, while the two vinyl protons in **4b** would not be expected to exhibit different chemical shifts.

n-Butyllithium was used to convert **4** to its aromatic anion, and the latter was allowed to react with iron(III) chloride and cyclopentadienyl anion. As expected this process gave mostly ferrocene. It also gave the desired 1,2-terferrocene (**2**) in low yield (10% crude and 2.2% purified material), but the third possibility, 1,1',2,2'-tetraferrocenylferrocene, was not detected.

1,2-Terferrocene is an orange crystalline compound with mp 191–193°. It is characterized by a rather simple infrared spectrum and a nuclear magnetic resonance spectrum with a single set of complex signals centered at δ 4.05. The presence of a complex set of conformational equilibria is suggested by the rather significant change in appearance of these signals in the spectrum determined at a slightly higher temperature.

Experimental Section

General.—Temperature readings are uncorrected. Ultraviolet spectra were measured in ethanol–methylene chloride [19:1 (v/v)] solutions with either a Cary Model 14 or a Perkin-Elmer Model 202 spectrophotometer. Infrared spectra were recorded (individually cited sampling) on a Perkin-Elmer Model 337 spectrophotometer. Proton magnetic resonance (pmr) spectra were determined at 60 MHz with a Varian A-60 instrument near 36° in solutions (individually cited) containing 2–3% tetra-

methylsilane (TMS). Chemical shifts were recorded under the δ convention in parts per million relative to TMS (0 ppm). An AEI Model MS-9 mass spectrometer was used[9] to obtain the mass spectral data.

Column elution chromatography was carried out on either alumina (Merck, acid-washed or Woelm, nonalkaline) or silicic acid (Bio-Rad, Sil A). Eluting solvents are cited below. Thin layer chromatography (tlc) was carried out on silicic acid (Merck, silica gel G) which was coated (0.25 mm) onto glass and activated at 120° during 12–15 hr. A solvent system of hexane, xylene, and ethyl acetate (2:1:1 by volumes) was used. Combustion analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1,3-Diferrocenoylpropane (5).—A solution containing glutaryl chloride (17.2 g, 0.102 mol) and anhydrous aluminum chloride (34.0 g, 0.255 mol) in methylene chloride (100 ml) was added dropwise to a stirred solution of ferrocene (45.5 g, 0.245 mol) in methylene chloride (250 ml) which was kept near 0° and under a blanket of dry nitrogen. The initial light amber colored solution slowly became deep violet as the addition progressed. When the addition was complete the reaction mixture was allowed to warm to room temperature. The stirring was continued (nitrogen blanket) while the reaction mixture was protected from light during 10–12 hr, after which time evolution of hydrogen chloride had ceased. The reaction mixture was cooled by an external ice bath, and its was hydrolyzed by dropwise addition of an aqueous solution of ammonium chloride [150 ml, 15% (w/w)]. Before the hydrolysate was allowed to warm to room temperature, ascorbic acid (5 g) was added to reduce the ferricinium species (light blue) present. After the hydrolysate was extracted with methylene chloride (seven 100-ml portions), the extracts were combined and washed with several portions of aqueous sodium hydroxide solution, followed by several portions of water, and finally with several portions of saturated aqueous sodium chloride solution. All aqueous extracts were combined and acidified (external indicator) with hydrochloric acid to give γ-ferrocenoylbutyric acid, 2.6 g (8.5% yield), mp 132–136° (lit.[10] mp 136–137°).

The organic residue left from the series of aqueous extracts was dried (CaCl₂) and evaporated to a dark red material which was chromatographed on alumina (Merck, acid-washed). Initial elution with hexane caused development of a fast-moving yellow band which gave ferrocene, 12.6 g (27.3% recovery). Not until a mixture of benzene and ether [7:3 (v/v)] was used did further development of the column take place. A red-colored band was eluted to provide 1,3-diferrocenoylpropane (5): 15.6 g (35.7% yield); mp 132–133° (recrystallized from cyclohexane); ir (CH₂Cl₂) 3085, 3040, 1100, 998 (ferrocenyl), 2970–2880 (aliphatic CH), and 1665 cm⁻¹ (conjugated ketone); pmr (CCl₄) δ 4.85 (4 H, t, J = 2 Hz, α-ferrocenyl protons), 4.50 (4 H, t, J = 2 Hz, β-ferrocenyl protons), 4.20 (10 H, s, protons of unsubstituted ferrocenyl rings), 2.85 (4 H, apparent t, J = 6 Hz, COCH₂), and 2.10 (2 H, m, COCCH₂CCO).

Anal. Calcd for C₂₅H₂₄Fe₂O₂: C, 64.14; H, 5.17; Fe, 23.56. Found: C, 64.56; H, 5.25; Fe, 23.58.

Reaction of 1,3-Diferrocenoylpropane (5) with Methylmagnesium Bromide and Cobalt(II) Chloride.—While a fair number of methods, under various conditions, were investigated for their ability to effect an intramolecular condensation of 5, only the treatment of 5 with methylmagnesium bromide and cobalt(II) chloride showed promise. An account of the other attempts is given in an earlier section of this paper.

Gaseous methyl bromide was led into a mixture (nitrogen blanket) of magnesium turnings (1.27 g, 52.3 mg-atoms), tetrahydrofuran (100 ml), and ether (100 ml) at a rate sufficient to maintain a gentle reflux. After all of the magnesium metal was consumed (about 30 min), the mixture was cooled to 0° and finely powdered anhydrous cobalt(II) chloride (0.324 g, 2.49 mmol) was added. The solution immediately evolved a gas and became dark red. After a solution of 1,3-diferrocenoylpropane (5) (2.12 g, 4.52 mmol) in tetrahydrofuran (100 ml) was added dropwise, the whole mixture was stirred during 30 min at 0° before it was allowed to warm to room temperature where it was maintained and stirred for an additional 12-hr period. Hydrolysis was effected by addition of 100 ml of ice water. The hydroly-

zate was exhaustively extracted with ether, and the combined ethereal extracts, after several washings with water, were dried and evaporated to a dark brown oil. The residue was chromatographed on alumina (Merck, acid-washed). Elution with hexane provided an orange oil (0.218 g); a black tar (1.22 g) was obtained from a dark-colored band eluted with hexane–ethyl acetate [1:1 (v/v)]; the starting material (0.436 g, 20.2% recovery) was eluted with hexane–ethyl acetate [1:2 (v/v)].

Purification of the orange oil by molecular distillation [100° (0.7 mm), air bath] gave a condensate (orange oil) that was submitted to mass spectral analysis.[9] Spectra, determined at 14 and 70 eV, and at various temperatues, showed the material to be a mixture consisting of two components, m/e 452 (M⁺) and 482 (M⁺). This information together with the ir data (give below) indicated the probable presence of 2,3-diferrocenyl-3-hydroxy-1-cyclopentene (7) and 2,6-diferrocenyl-6-hydroxy-2-heptene (8): ir (CH₂Cl₂) 3640 (OH nonbonded), 3100, 3050, 1100, 998 (ferrocenyl), 3000, 1650, 850–790 (conjugated, trisubstituted double bond), 2960, 2860, 1460, 1390 (CH₃), 2925, 2855, and 1470 cm⁻¹ (CH₂). Further investigation of the mixture was not pursued.

Desoxyferrocoin.—A mixture of ferrocenylacetic acid[11] (5.34 g, 21.9 mmol) in 25 ml of freshly distilled phosphorus trichloride was kept at 40° (stirring) for 3.5 hr. After the resulting solution (light brown) was decanted, it was evaporated to leave a residue of crude ferroceneacetyl chloride. This material was taken up in 100 ml of methylene dichloride and added dropwise to a cold (0°), stirred solution of freshly sublimed ferrocene (5.18 g, 27.8 mmol) in 200 ml of methylene dichloride. After that addition was complete, a second solution, consisting of boron trifluoride etherate (6.0 g, 35 mmol) in 100 ml of methylene dichloride, was also added dropwise to the cold reaction mixture. The reaction mixture, which had changed to deep violet, was stirred for 0.5 hr at 0° before an additional quantity of boron trifluoride etherate (5.7 g, 34 mmol in 75 ml of methylene dichloride) was added, and the whole mixture was allowed to come to room temperature and stirred overnight.

Addition of 100 ml of 10% aqueous sodium acetate solution was followed by successive washings of the organic phase of the hydrolysate with water (six 200-ml portions) and saturated sodium chloride solution (100-ml portions). After the organic solution was dried (CaCl₂), it was evaporated to a residue which was chromatographed on alumina (Merck, acid-washed). Hexane developed and eluted a band from which ferrocene (4.06 g, 78.3% recovery) was obtained. A mixture of hexane, methylene chloride, and ethyl acetate [1:1:1 (v/v/v)] was used to elute a red band which provided desoxyferrocoin: 2.24 g (24.8% yield based on ferrocenylacetic acid); mp 160–163° (lit.[12] mp 159–161°); ir (CH₂Cl₂) 3100, 3050, 1100, 998 (ferrocenyl), and 1600 cm⁻¹ (conjugated ketone).

Ferrocil (9).—A solution of desoxyferrocoin (6.27 g, 15.2 mmol) in 225 ml of methylene dichloride, containing freshly prepared[13] activated maganese dioxide (13.0 g), was stirred at room temperature during 6 hr before it was filtered and the filtrate evaporated to dryness. Examination of the residue by thin layer chromatography (tlc) revealed a large amount of unchanged desoxyferrocoin (R_f 0.62). Consequently, the residue was retreated with activated maganese dioxide (12 g) in methylene dichloride overnight. The product of the second treatment was chromatographed on alumina (Merck, acid-washed). Only one large, diffuse, red band was developed (benzene). This was slowly collected in many fractions which were analyzed by tlc to determine those fractions that contained the desired product, ferrocil (9): 5.03 g (77.6% yield); mp 191–194° (lit.[14] mp 193.5–195.5°); ir (CH₂Cl₂) 3100, 3050, 1100, 995 (ferrocenyl), and 1650 (broad, conjugated diketone); nmr (CDCl₃) δ 4.95 (4 H, t, J = 3 Hz, α-Fc H), 4.65 (4 H, t, J = 3 Hz, β-Fc H), and 4.25 (10 H, s, unsubtd Fc H).

3,4-Diferrocenyl-4-hydroxy-2-cyclopenten-1-one (10).—A mixture of anhydrous ethanol (200 ml) and pure dry dimethyl sulfoxide (300 ml) maintained at 60° was thoroughly deoxygenated by bubbling purified nitrogen through it for 1 hr. The system was kept under a nitrogen blanket and protected from light while

(9) We are indebted to Dr. Henry M. Fales of the National Heart Institute, Bethesda, Md., for the mass spectral data cited herein.

(10) K. L. Rinehart, Jr., D. J. Curby, and P. E. Sokol, *J. Amer. Chem. Soc.*, **79**, 3420 (1957).

(11) D. Lednicer, J. K. Lindsay, and C. R. Hauser, *J. Org. Chem.*, **23**, 653 (1958).

(12) K. L. Rinehart, Jr., C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, **81**, 3162 (1959).

(13) J. A. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Herms, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(14) K. L. Rinehart, Jr., A. F. Ellis, C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, **82**, 4112 (1960).
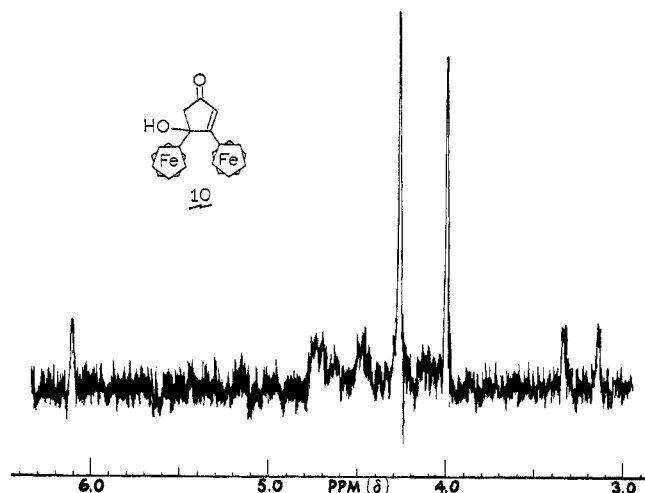
Figure 1.—Nmr spectrum of 3,4-diferrocenyl-4-hydroxyl-2-cyclopenten-1-one.

potassium hydroxide (5.0 g, 89 mmol) and ferrocil (9) (4.64 g, 10.9 mmol) were introduced. After the reaction mixture was stirred for several minutes, and while it was kept between 55 and 60°, anhydrous acetone (30 ml, 24 g, 0.50 mol) was added at a rate of 5–6 ml/hr. The course of the reaction was monitored by tlc over the period of the addition: complete disappearance of the ferrocil spot (R_f 0.62) with formation of the product spot (R_f 0.23) after 5.5 hr.

The reaction mixture was diluted with 1 l. of ice–water, and the resulting suspension was exhaustively extracted with methylene dichloride. The basic aqueous residue was acidified with phosphoric acid and extracted with three 100-ml portions of methylene dichloride. The combined organic extracts were washed with water before they were dried ($CaCl_2$) and evaporated to a dark red oil. This material proved to be too sensitive to alumina to allow chromatography without extensive decomposition. It was, however, purified by initial crystallization and recrystallization from cold ether–hexane [1:5 (v/v)] solutions to give 3,4-diferrocenyl-4-hydroxy-2-cyclopenten-1-one (10): 3.99 g (78.9% yield); mp 210–213° dec; ir (CH_2Cl_2) 3560 (hydroxyl), 3100, 3040, 1100, 998 (ferrocenyl), 1690, and 1590 (cyclopentenone); nmr ($CDCl_3$) δ 6.12 (1 H, apparent s, vinyl proton), 4.8–4.0 (8–9 H, complex, α- and β-Fc H and OH), 4.26 (5 H, s, unsubstd Fc H), 4.0 (5 H, s, unsubstd Fc H), 3.34 (1 H, apparent d, J = 1–2 Hz), and 3.14 (1 H, apparent d, J = 1–2 Hz) (see Figure 1); uv [EtOH–H_2O–CH_2Cl_2, 19:1:1 (v/v/v)] 220 nm (ε 19,900), 255 (13,000), and 312 (8400); mass spectrum[9] m/e (intensity relative to M⁺) 468 (M⁺ + 2, 6.2), 467 (M⁺ + 1, 33), 466 (M⁺, 100), 465 (M⁺ − 1, 5.0), 464 (M⁺ − 2, 14) [calcd[15] for $C_{25}H_{22}Fe_2O_2$: 468 (M⁺ + 2, 6.1), 467 (M⁺ + 1, 32.3), 466 (M⁺, 100), 465 (M⁺ − 1, 3.6), and 464 (M⁺ − 2, 12.7)]; other prominent high mass peaks 448 (48), 420 (15), 384 (17), 328 (58), and 300 (42).

Anal. Calcd for $C_{25}H_{22}Fe_2O_2$: C, 64.40; H, 4.76. Found: C, 64.85; H, 4.78.

3,4-Diferrocenyl-2-cyclopenten-1-one (11).—A mixture of glacial acetic acid (40 ml), water (8 ml), and 12 *N* hydrochloric acid (2 ml) was heated to a temperature just below boiling and thoroughly deoxygenated by allowing a stream of purified nitrogen to bubble through. After the mixture was allowed to cool to room temperature, it was stirred while anhydrous titanium-(III) chloride (Stauffer Chemical Co.) (1.0 g, 6.5 mmol) was added. The resulting blue solution was added dropwise to a solution of 3,4-diferrocenyl-4-hydroxy-2-cyclopenten-1-one (10) (1.01 g, 2.17 mmol) in 100 ml of deoxygenated glacial acetic acid, while the latter solution was stirred and kept at 50°. After the addition was complete, the reaction mixture was stirred at 50° during an additional 3.5-hr period. The reaction mixture was then hydrolyzed by addition of 700 ml of ice–water and exhaustively extracted with methylene dichloride. The combined extracts were washed successively with water, dilute sodium bicarbonate solution, water, and saturated aqueous sodium chloride solution before they were dried and evaporated to a red powder,

(15) Computer program by Albert Shirley, Senior Research Project, University of South Carolina, 1968.
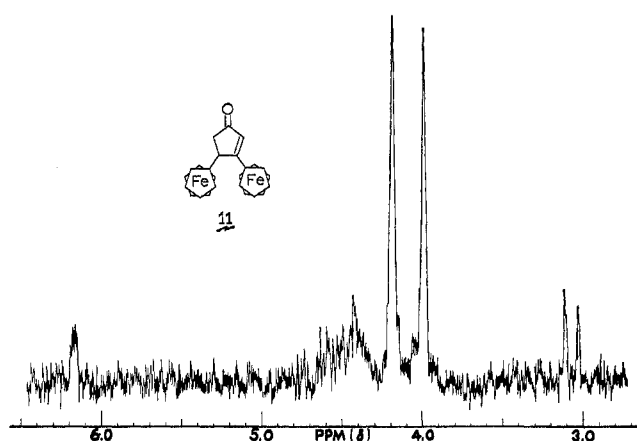

Figure 2.—Nmr spectrum of 3,4-diferrocenyl-2-cyclopenten-1-one.

3,4-diferrocenyl-2-cyclopenten-1-one (11), 0.93 g (95% yield). Thin layer chromatographic analysis showed this material (R_f 0.38) to be contaminated by only a trace of starting material (R_f 0.22). A portion of the product was recrystallized from cold (−30°) methylene chloride to give deep red crystals: mp 226–227° dec; ir (CH_2Cl_2) 3100, 3050, 1100, 998 (ferrocenyl), 1685, and 1590 cm⁻¹ (cyclopentenone); nmr ($CDCl_3$) δ 6.18 (1 H, apparent t, J = 1–2 Hz, vinyl proton), 4.8–4.3 (9 H, complex, methine proton, α- and β-Fc H), 4.20 (5 H, s, unsubstd Fc H), 4.00 (5 H, s, unsubstd Fc H), 3.12 (1 H, apparent d, J = 1–2 Hz), and 3.05 (1 H, apparent d, J = 1–2 Hz) (see Figure 2); uv [EtOH–H_2O–CH_2Cl_2, 19:1:1 (v/v/v)] 214 nm (ε 24,000), 256 (9000), and 311 (11,000).

Anal. Calcd for $C_{25}H_{22}Fe_2O$: C, 66.71; H, 4.93. Found: C, 66.42; H, 5.13.

1,2-Diferrocenyl-1,3-cyclopentadiene (4).—A solution of 3,4-diferrocenyl-2-cyclopenten-1-one (11) (87.3 mg, 1.94 mmol) in tetrahydrofuran (25 ml) was added slowly to a stirred solution of sodium borohydride (4.0 g, 96 mmol) in anhydrous ethanol (30 ml), while the system was maintained near 55° by external heating. After 5 hr the initial deep red mixture had changed to light yellow. It was cooled before 50 ml of 5% (v/v) aqueous ammonium chloride solution was added. Exhaustive extraction of the hydrolyzate with ether, followed by evaporation of the combined and dried ($CaCl_2$) extracts under nitrogen, gave an orange oil whose infrared spectrum showed the presence of the desired diferrocenylcyclopentenol: ir (CH_2Cl_2) 3590, 3445 (hydroxyl), 3090, 3040, 1100, 998 (ferrocenyl), and 1630 cm⁻¹ (double bond). Attempts to prepare an analytical sample of the material were unsuccessful owing to its ease of decomposition, particularly during chromatography. Successful conversion to 1,2-diferrocenylcyclopentadiene (below) in good yield, however, clearly established that the material obtained from the sodium borohydride reduction was mainly the cyclopentenol.

The crude reduction product (orange oil) was dissolved in 15 ml of methylene chloride and allowed percolate through a narrow column (12 mm) which consisted of a 1.5-cm layer of alumina (Woelm, neutral) sandwiched between two 10-cm layers of silicic acid. The column was washed with methylene chloride until the effluent was colorless (total volume, about 200 ml). The combined effluent was then passed through another column containing a 10-cm section of silicic acid before the solvent was carefully evaporated in a nitrogen stream to leave 1,2-diferrocenyl-1,3-cyclopentadiene (4): orange oil; 385 mg (45.7% yield over two steps); ir (CH_2Cl_2) 3100, 3050, 1100, 998 (ferrocenyl), 3080, 2950, 2860, and 1660 cm⁻¹ (cyclopentadienyl); nmr ($CDCl_3$) δ 6.55 (1 H, doublet of triplets, J = 5.5 and 1.5 Hz, C_3 H), 6.17 (1 H, doublet of triplet, J = 5.5 and 1.5 Hz, C_4 H), 4.32 (4 H, two overlapped triplets, α-Fc H), 4.10 (4 H, two overlapped triplets, β-Fc H), 3.98 (5 H, s, unsubstd Fc H), 3.92 (5 H, s, unsubstd Fc H), and 3.33 (2 H, t, J = 1.5 Hz, CH_2) (see Figure 3); uv [EtOH–H_2O–CH_2Cl_2, 19:1:1 (v/v/v)] 220 nm (ε 20,000) and 320 (5500); mass spectrum[9] m/e (intensity relative to M⁺) 436 (M⁺ + 2, 8.0), 435 (M⁺ + 1, 34), 434 (M⁺, 100) 433 (M⁺ − 1, 7.0), 432 (M⁺ − 2, 16) [calcd[15] for $C_{25}H_{22}Fe_2$: 436 (M⁺ + 2, 5.7), 435 (M⁺ + 1, 32.2), 434 (M⁺, 100), 433 (M⁺ − 1, 3.6), and 432 (M⁺ − 2, 12.7)]; other prominent peaks 368 (16), 366 (16), 312 (19), 191 (38), 190 (42), 189 (54), 165 (20), and 121 (89).
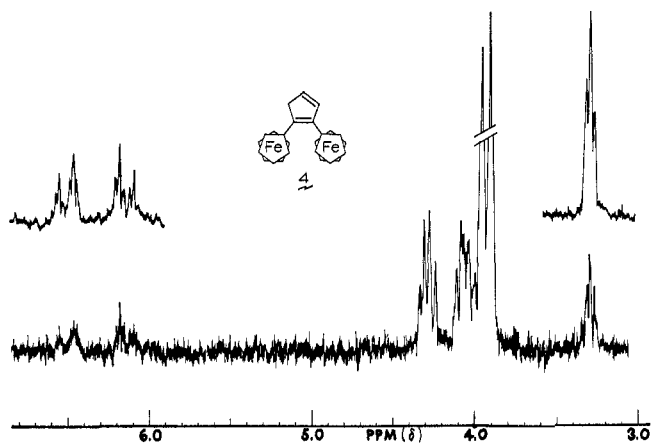
Figure 3.—Nmr spectrum of 1,2-diferrocenyl-1,3-cyclopentadiene.

1,2-Terferrocene (2).—In a thoroughly dried three-necked flask, equipped with a stirrer, nitrogen inlet, condenser, and a rubber septum injection port, was mixed a solution of 1,2-diferrocenyl-1,3-cyclopentadiene (4) (348 mg, 0.802 mmol) in 20 ml of anhydrous ether and a solution of n-butyllithium [4 ml (6 mmol) of a 15% (w/w) solution in hexane (Foote Mineral Co.)] in 100 ml of anhydrous ether. The mixture was stirred at room temperature for 1 hr before freshly prepared cyclopentadiene (3.3 g, 50 mmol) and n-butyllithium (10 ml, 16 mmol) were added. The mixture was stirred for an additional 3-hr period when iron-(II) chloride[16] (1.0 g, 7.9 mmol) was added, and the whole mixture was stirred overnight. After addition of 25 ml of 5% aqueous ammonium chloride solution, the separated aqueous phase was exhaustively extracted with ether, and the ether extracts were combined with the original ethereal phase before the whole mixture was dried (CaCl₂) and evaporated. The residue, a brown solid, was chromatographed on alumina (Merck, acid-washed). Elution with hexane gave ferrocene, 1.4 g. Further column development and elution with a mixture of hexane and benzene (1:1 (v/v)] produced 46 mg of crude 1,2-terferrocene (2) which was initially obtained as an orange-brown solid. This material was successively (five times) recrystallized from hexane–benzene

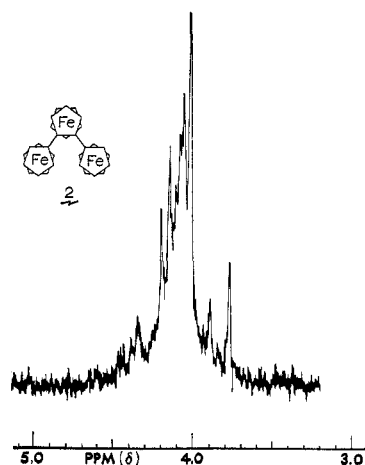(16) P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.,* **76,** 5491 (1954).

Figure 4.—Nmr spectrum of 1,2-terferrocene.

to yield a 10-mg orange crystalline, constant-melting (mp 191–193°, sealed, evacuated capillary) sample of 1,2-terferrocene which was chromatographically pure (R_f 0.90) and characterized by the following spectral properties: ir (CH₂Cl₂) 3100, 3050, 1100, and 1000 cm⁻¹; uv (EtOH) 215 nm broad (ε 24,000) and 290 sh (5000); nmr (CDCl₃) showed only a complex cluster of signals centered at δ 4.05 indicating the presence of only ferrocenyl protons (see Figure 4) [determination of the spectrum at 45° (near 36° initially) caused significant changes in the detailed structure of the signal complex indicating perhaps a rather facile and complex conformational equilibria]; mass spectrum[9] m/e (intensity relative to M⁺) 556 (M⁺ + 2, 8.5), 555 (M⁺ + 1, 38), 554 (M⁺, 100), 553 (M⁺ − 1, 7.3), and 552 (M⁺ − 2, 23) [calcd[15] for C₃₀H₂₆Fe₃: 556 (M⁺ + 2, 8.9), 555 (M⁺ + 1, 40), 554 (M⁺, 100), 553 (M⁺ − 1, 6.7), and 552 (M⁺ − 2, 19)].

Anal. Calcd for C₃₀H₂₆Fe₃: C, 65.03; H, 4.73. Found: C, 64.92; H, 4.86.

Registry No.—**2,** 12504-91-5; **4,** 12504-84-6; **5,** 12504-88-0; **7,** 12504-87-9; **8,** 12504-90-4; **9,** 12113-85-8; **10,** 12504-86-8; **11,** 12504-85-7; desoxy-ferrocoin, 12504-83-5.

A Facile Synthesis of 3-Acylaminoisocoumarins[1a]

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The synthesis of some 3-acylaminoisocoumarins is reported. Spectral data and chemical reactivity are discussed. 3-Aminoisocoumarin was prepared and acylated to afford 3-acylaminoisocoumarin by an alternative route.

During a program for the synthesis of some tetracyclic indole compounds, we had need of 5-(2-carboxy-5-chlorophenyl)levulinic acid (1) as a precursor. It was hoped that 3-carbethoxypropionic 5-chloro-α-cyano-2-toluic anhydride (2) could be condensed under basic conditions to form ethyl 5-(2-carboxy-5-chlorophenyl)-5-cyanolevulinate (3). Hydrolysis of 3 and subsequent decarboxylation would yield 1.

It was planned to synthesize 2 by the reaction of 5-chloro-α-cyano-2-toluic acid (4) with 3-carbethoxypropionyl chloride[2] in the presence of pyridine. Attempts

to prepare 4 by the reaction of 5-chlorophthalide,[3] with potassium cyanide utilizing Price's procedure,[4] yielded only tars. Adequate yields of 4 could be obtained when the reaction was carried out in dimethyl sulfoxide at 100–110°.

Upon reaction of 4 with 3-carbethoxypropionyl chloride[2] in the presence of 2 equiv of pyridine, no anhydride was isolated. Instead a high-melting solid, mp 198–199°, 5 was isolated in 39.6% yield. The infrared spectrum indicated loss of the nitrile and showed no absorption below 5.7 μ (the characteristic carbonyl

(2) I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p 384.

(3) L. P. Levy and H. Stephan, *J. Chem. Soc.,* 867 (1931).

(4) C. C. Price, *Org. Syn.,* **22,** 61 (1942).