nmr, mass spectrum, and vpc with an authentic sample: ir (CCl_4) 3090, 1655, 872 cm^{-1}; nmr (CCl_4) τ 5.21 and 5.50 (two singlets, 2 H), 7.55 (broad singlet, 1 H), 9.00 (s, 3 H), 9.10 (d, 6 H, J = 6 Hz); mass spectrum (80 eV) m/e (rel intensity) 204 (19 M$^+$), 189 (21), 161 (78), 108 (100).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.13; H, 11.95.

In a similar manner, olefin **23** was hydrogenated, oxidized, treated with methyllithium, and dehydrated to give a product which, by nmr, was a 45:55 mixture of copacamphene and sativene.

Acid-Catalyzed Rearrangement of (+)-Copacamphene.—In a manner similar to that described above for sativene, (+)-copacamphene[22] (100 mg) was isomerized by treatment with $Cu(OAc)_2 \cdot H_2O$ (25 mg) in 3 ml of refluxing glacial acetic acid, and the course of the reaction was followed by vpc. After 4 days, equilibrium was reached and the product consisted of a mixture of three isomeric compounds.

Fraction 1 (32%) was found to be (+)-cyclosativene (**7**), α_D +61° [*c* 0.46 (lit.[20] +67.8°)], by comparison of ir, nmr, and mass spectrum with an authentic sample.

Fraction 2 (7%) was found to be sativene by micro ir.

Fraction 3 (61%) was identified as isosativene by comparison of its ir, nmr, and mass spectrum with an authentic sample.

Registry No.—**7**, 30541-92-5; **8**, 22415-05-0; **12**, 29642-51-1; **18**, 29642-52-2; **19**, 30541-95-8; **20**, 29642-54-4; **21**, 29642-55-5; **22**, 30541-98-1; **23**, 30597-80-9.

Acknowledgment.—We thank the Alfred P. Sloan Foundation and the Petroleum Research Fund administered by the American Chemical Society for their support of this work.

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[22] We thank Dr. Westfelt for a generous sample of (+)-copaborneol, the precursor of (+)-copacamphene.

[*m*][*n*]Ferrocenophanes.[1] Derivatives Containing Tri-, Tetra-, and Pentamethylene Bridging Groups

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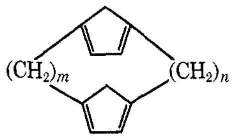
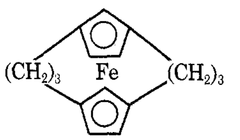
Received December 11, 1970

Doubly bridged ferrocenes ([*m*][*n*]ferrocenophanes) containing tri-, tetra-, and pentamethylene bridging groups have been synthesized and characterized. Ring closure reactions of [*m*]ferrocenophanylpropionic acids provide a convenient route to these compounds in contrast to schemes designed to form an interannular bridge by linking acetyl groups on different rings in diacetylferrocenophanes.

The possibility of using metallocenophanes as starting compounds for the synthesis of tricyclic tetraenes such as **1**, or positional isomers, led us to prepare a series of doubly bridged ferrocene derivatives.



1



2

The only examples of such ferrocenophenes reported[3] are those which have three atoms in each bridge. In a previous note[4] we contrasted the difficulty encountered in attempting to cleave [3][3]-1,3-ferrocenophane (**2**) with the ease of reducing 1,1′-dialkylferrocenes, which react vigorously with lithium in propylamine to form substituted cyclopentadienes.

Although no conclusive evidence exists concerning the mechanism of these reductive cleavage reactions, Trifan and Nicholas[5] suggested that two steps were involved in the reduction of ferrocene, the first being a one-electron transfer to form a cyclopentadienide ion and a cyclopentadieneiron radical. The second step was postulated to be another one-electron transfer to the radical forming a second cyclopentadienide ion and metallic iron. Clearly **2** is an unlikely candidate to undergo such a process because of the restrictions placed on the molecule by the two trimethylene bridges. An examination of molecular models suggested to us that ferrocenophanes **5a–f** which have more than three atoms in one or both bridges would be more likely to undergo reductive cleavage, and we have prepared a number of these compounds which we now report (see Scheme I).

Results and Discussion

Rinehart and coworkers showed[6] that β-ferrocenylpropionic acid reacts in the presence of trifluoroacetic anhydride (TFAA) to form [3]ferrocenophan-1-one (**14**) to the virtual exclusion of other possible products such as a fused ring ketone or intermolecular condensation product. We have found that identical conditions afford good yields of **4a–d** from β-ferrocenophenylpropionic acids **3g–j**. These acids were prepared from acetylferrocenophanes **3c–f**[7] *via* sodium hydride catalyzed condensation with ethyl carbonate, hydrogenolysis, and saponification.[6] Only in the ring closure reaction of **3i** was more than one product isolated, a small amount of **4g** being formed along with the major product, **4a**. Based on the fact that one product is formed in predominant amounts in all ring closure reactions, we initially assigned structures **4a–d** to the products. The possibility exists, however, in the case of the [3][5]- and [4][5]ferrocenophanes, of construct-

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[1] Ferrocenophane nomenclature conforms to that suggested by B. H. Smith ("Bridged Aromtic Compounds," Academic Press, New York, N. Y., 1964, pp 8–23) and used by T. H. Barr, W. E. Watts, and coworkers, in their recent papers which are cited. For a review, see W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

[2] Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, Calif. 93523.

[3] K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Amer. Chem. Soc.*, **85**, 970 (1963); K. Schlögl, M. Peterlik, and H. Seiler, *Monatsh. Chem.*, **93**, 1309 (1962).

[4] A. D. Brown, Jr., and H. Reich, *J. Org. Chem.*, **35**, 1191 (1970).

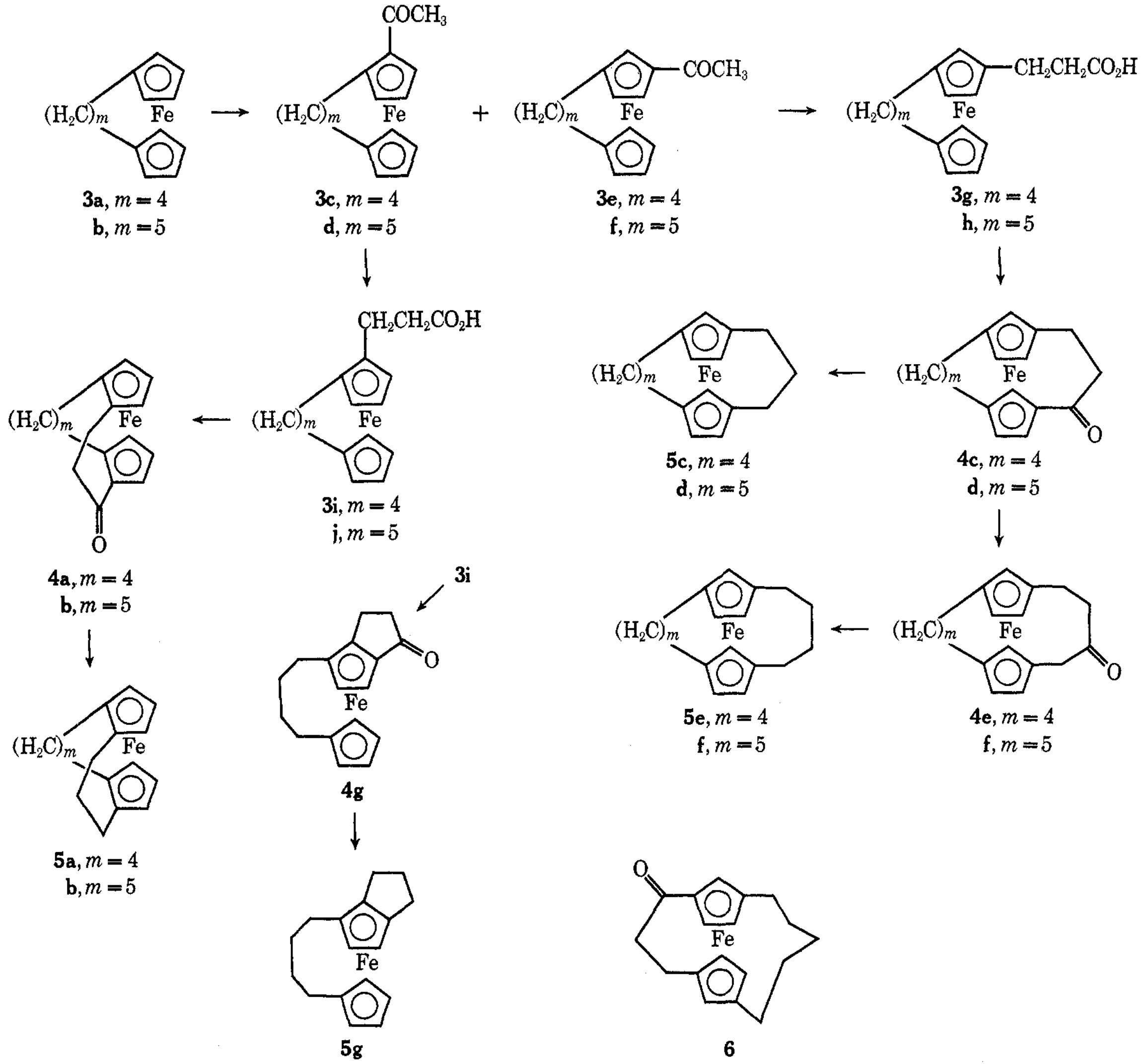
[5] D. S. Trifan and L. Nicholas, *J. Amer. Chem. Soc.*, **79**, 2746 (1957).

[6] K. L. Rinehart, Jr., R. J. Curby, Jr., D. H. Gustafson, K. G. Harrison, R. E. Bozak, and D. E. Bublitz, *ibid.*, **84**, 3263 (1962).

[7] T. H. Barr, E. S. Bolton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **25**, 5245 (1969).

SCHEME I

SUMMARY OF [m][n]FERROCENOPHANE SYNTHESES



ing models in which ring carbon atoms to which bridge ends are attached are not eclipsed, for example, **6**. The considerable flexibility of the pentamethylene bridge[7] could conceivably allow sufficient ring rotation for the propionic acid (**3h** or **3j**) ring closure to occur on one of two or three ring carbon atoms depending on the proximity of the bridging group to the propionic acid chain. Although we looked carefully for such compounds, none could be found. While formation of **6** and similar products appears possible, the alternate conformation of the pentamethylene bridge provides less interference between ring and bridge hydrogens and structures **4b** and **4d** should predominate. Models of [3][4]ferrocenophanes indicate that a [3][4] structure corresponding to **6** would be still less likely to form.

Additional evidence for the assigned structures comes from a simple and unique feature of the nmr spectrum of [3]ferrocenophane and many of its derivatives. Reduction of **4a–d** using lithium aluminum hydride and aluminum chloride[8] provided **5a–d**, each of which contains an interannular trimethylene bridge. The single sharp peak[9] which occurs between τ 7.8 and 8.12 characteristic of the trimethylene bridge is a major feature of the spectrum of **5a**, **5c**, and **5d**. Although the spectrum of **5b** does not show this peak as distinctly as do the other three, ring proton resonance patterns of **4a** and **4b**, precursors of **5a** and **5b**, are quite similar to each other and distinctly different from that of **4g**, the fused ring ketone. When the very small amount of **4g** available was reduced with lithium aluminum hydride–aluminum chloride, we obtained **5g** whose ring nmr spectrum appears as a broad unresolved band between τ 5.9 and 6.4 (6 H) and whose methylene proton spectrum is two broad bands centered at τ 7.64 and 8.17 (8 H and 6 H, respectively). Although we had insufficient material for complete characterization of **5g**, its nmr spectrum helps to confirm the structure of **4g**, since no singlet corresponding to an intermolecular trimethylene bridge is present in **5g** while the spectrum of **5a** does show this single peak. Next, in comparing ring proton spectra of **4a** and **4b** (Table II), we find six well-separated peaks (one proton each) in the spectrum of **4b** and five (one peak accounts for two protons) such peaks in **4a**. Chemical shift, apparent multiplicity, and peak shape are very similar for the ring protons in these two compounds. These points of similarity, the obvious presence of a heteroannular trimethylene bridge in **5a**, and

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[8] K. Schlögl, A. Mohar, and M. Peterlik, *Monatsh. Chem.*, **92**, 921 (1961).

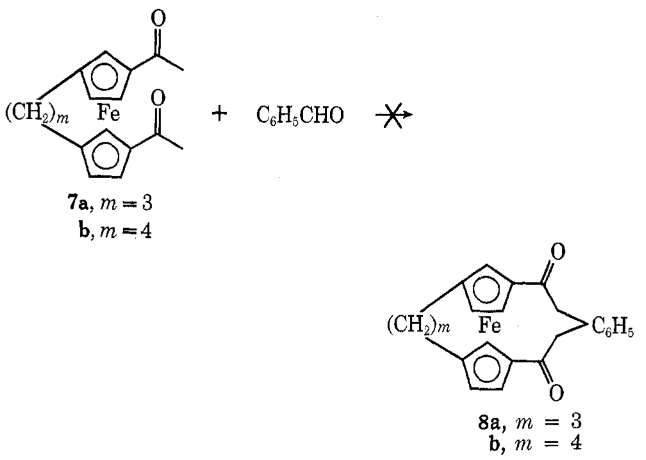
[9] T. H. Barr and W. E. Watts, *Tetrahedron*, **24**, 6111 (1968).

the observed product distribution leave little doubt that **4** and **5** are proper structures. The structures of ferrocenophanes **4e,f** and **5e,f** follow from **4a–d** and **5a–d**.

The method of Barr and Watts[10] was used to prepare **3b** from 1-acetyl-1′-β-chloropropionylferrocene, and **3a** was obtained *via* a ring enlargement[11] reaction in which diazomethane (generated *in situ* from Diazald[12]) reacted with **14**. The conversion of ketones **4c** and **4d** to **4e** and **4f** was also accomplished using diazomethane. This reaction could not be used, however, for the ring enlargement of the two α-dibridged ketones **4a** and **4b**. The Wolff–Kishner method was found to be suitable for reducing **4e** and **4f** to **5e** and **5f**, respectively.

We considered that alternate routes to [3][5]- and [4][5]ferrocenophanes might be possible *via* Scheme II.

SCHEME II[10,13]



7a, $m = 3$
b, $m = 4$

8a, $m = 3$
b, $m = 4$

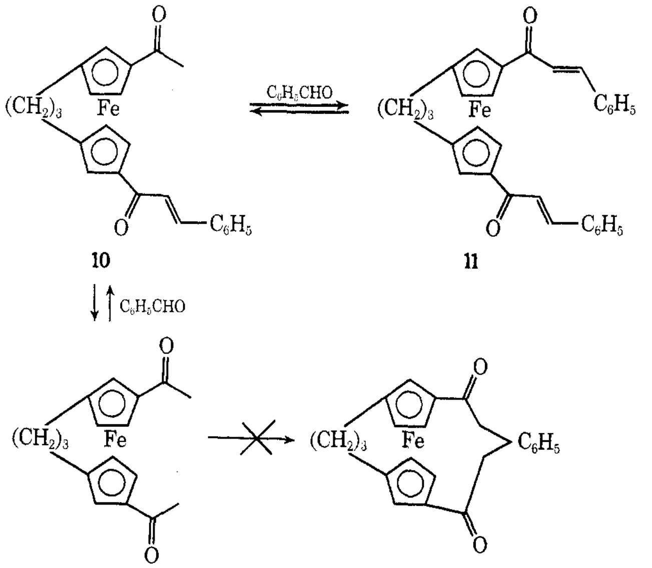
However, preparation of **7a** or **7b** would require isolation of specific diacetyl isomers of the parent ferrocenophane. While we have isolated and characterized five diacetyl isomers of [3]ferrocenophane (including **7a**) as well as several dicinnamoyl- and monoacetylmonocinnamoyl[3]ferrocenophanes[14] and found that the eclipsed diacetyl isomers are formed in exceedingly small yield and are difficult to purify, we have not succeeded in effecting Scheme II. The only diacetyl[3]ferrocenophane reported to date is **9**,[6] which we reacted with benzaldehyde and base, under the usual conditions for ring closure[13] (Scheme III). We obtained only **10** and **11**, which indicates that while mobile equilibria exist among **9**, **10**, and **11**, the formation of ring-closed product **12** is not favored.

Characterization of previously unreported compounds is provided in Tables I and II.

Experimental Section[15]

Single-Bridged Ferrocenes (3a,b).—[4]Ferrocenophane (**3a**) was prepared[9] from **14** by a modification of the method of Rosenblum, *et al.*[11] In a typical experiment 1 g of **14** (4.2 mmol) and 1.2 g of Diazald[12] were dissolved in a mixture of 80 ml of tetrahydrofuran and 20 ml of 95% ethanol and cooled to 0°. A solution of 0.3 g of potassium hydroxide in a small amount of ethanol-water (1:1) was added slowly and the mixture was stirred for 6 hr at 0°, after which the reaction was stopped by carefully acidifying the solution with 2 *N* HCl. The mixture was concentrated under vacuum and extracted thoroughly with CH_2Cl_2 and the extracts were dried ($MgSO_4$), evaporated, and chromatographed. The yield of [4]ferrocenophan-2-one (**13**) was 0.75 g (70%), mp 112–114° (lit.[11] 113.5–114.5°). Reduction of **13** by reported[11] methods gave **3a**, mp 66–68° (lit.[11] 63–64°).

SCHEME III



10 **11** **9** **12**

TABLE I
FERROCENOPHANES AND PRECURSORS[a]

Compd	Yield, %	Mp, °C	Ir,[e] cm^{-1}
4a	61[b]	123–125	1650
4b	76.7[b]	156–158	1680
4c	62.5[b]	83–84	1680
4d	58[b]	105–106	1660
5a	85.5[c]	78–80	
5b	89[c]	153–154	
5c	90[c]	72–73	
5d	98[c]	70–72	
5e	91[c]	114–116	
5f	65[c]	34.5–36	
4e	80[c]	89–91	1710
4f	50[c]	114–115.5	1700
3i	62[d]	98–101	1715
3g	60[d]	82–84	1720
3j	60.4[d]	126–129	1705
3h	82.2[d]	95–96	1705
4g	7.5[b]	127–129	1700
10		163–165	
11		205–207	

[a] All compounds in this table gave satisfactory (±0.4) analyses for C, H, and Fe. The analytical data were made available to the referees and to the Editor. [b] Yield based on ferrocenophanylpropionic acid. [c] Yield based on cyclic ketone. [d] Yield based on acetylferrocenophane. [e] Carbonyl, taken as mulls.

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[10] T. H. Barr and W. E. Watts, *Tetrahedron*, **24**, 3219 (1968).

[11] M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Amer. Chem. Soc.*, **85**, 316 (1963).

[12] *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide from Aldrich Chemical Co.

[13] T. A. Mashburn, C. E. Cain, and C. R. Hauser, *J. Org. Chem.*, **25**, 1982 (1960); M. Furdik, *et al.*, *Chem. Zvesti*, **16**, 45 (1961); *Chem. Abstr.*, **55**, 18692 (1961).

[14] The proof of structure of these diacylferrocenophanes is the subject of a communication now in preparation.

[15] Melting points were taken on a Kofler hot stage and are uncorrected. Nmr spectra were determined in $CDCl_3$ with tetramethylsilane as an internal reference on a Varian A-60 instrument and infrared spectra were recorded using a Beckman IR-4 spectrometer. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo.

TABLE II

NMR SPECTRA[a] OF β-FERROCENOPHANYLPROPIONIC ACIDS AND FERROCENOPHANES

Compd	Ring protons[b]	Bridge protons[b,c]
4a	m, 1, 5.15; m, 1, 5.61; m, 1, 5.78; m, 2, 5.82; m, 1, 6.14	m, 12, 6.33–8.53
4b	m, 1, 5.21; m, 1, 5.47; t, 1, 5.62; t, 1, 5.77; m, 1, 5.95; m, 1, 6.30	m, 14, 6.42–8.83
4c	m, 1, 5.15; m, 2, 5.35; m, 2, 5.63; m, 1, 6.06	s, 4, 7.14; m, 4, 7.80; m, 4, 8.26
4d	m, 1, 5.21; m, 1, 5.31; m, 1, 5.47; m, 1, 5.55; m, 1, 5.78; m, 1, 6.13	s, 4, 7.11; m, 4, 7.95; m, 6, 8.17
5a	m, 5, 6.07; m, 1, 6.21	m, 4, 7.30; s, 6, 7.89; m, 4, 7.99
5b	t, 2, 5.85; m, 4, 6.21	m, 16, 6.75–8.66
5c	m, 4, 5.99; m, 2, 6.17	m, 4, 7.80; s, 6, 8.10; m, 4, 8.26
5d	s, 6, 6.13	m, 16, 7.67–8.59[e]
5e	m, 6, 6.02	m, 8, 7.60; m, 8, 8.22
5f	m, 6, 6.14	m, 8, 7.73; m, 10, 8.20
4e	m, 6, 5.98	s, 2, 6.74; s, 4, 7.27; m, 4, 7.67; m, 4, 8.23
4f	m, 6, 6.04	s, 2, 6.71; s, 4, 7.26; m, 4, 7.77; m, 6, 8.14
3i[d]	m, 6, 5.95; m, 1, 6.20	m, 4, 7.37; m, 4, 7.58; m, 4, 8.10
3g[d]	m, 6, 5.96; m, 1, 6.19	s, 4, 7.39; m, 4, 7.60; m, 4, 8.18
3j[d]	m, 6, 6.00; m, 1, 6.35	m, 4, 7.37; m, 4, 7.70; m, 6, 8.20
3h[d]	m, 6, 6.03; m, 1, 6.27	s, 4, 7.39; m, 4, 7.72; m, 6, 8.11
4g	m, 2, 5.52; m, 1, 5.70; m, 2, 6.05; m, 1, 6.70	m, 2, 7.07; m, 2, 7.20; m, 4, 7.50; m, 4, 8.08
5g	m, 6, 6.12	m, 8, 7.58; m, 6, 8.10

[a] Taken in $CDCl_3$ using $(CH_3)_4Si$ as internal indicator. [b] Listed in order: observed multiplicity (s = singlet, t = triplet, m = multiplet), number of protons, chemical shift (τ). [c] Including aliphatic protons of propionic acids. [d] Acid protons appear at τ −1.1 to −1.7 and shift with dilution. [e] Including a sharp singlet at τ 8.08 assigned to the heteroannular trimethylene bridge.

[5]Ferrocenophane (**3b**) was prepared according to the method of Barr and Watts.[10]

Acetylferrocenophanes (3c–f).—Ferrocenophanes **3a** and **3b** were acetylated using acetic anhydride and boron trifluoride etherate. Two monoacetyl derivatives were obtained for each ferrocenophane with the β-acetyl isomers **3e** and **3f** being formed in larger quantities (1.5 to 2 times) than the α-acetyl compounds **3c** and **3d** (*cf.* ref 6). For example, to 5.5 g (0.023 mol) of **3a** and 4.6 g (0.045 mol) of acetic anhydride dissolved in 100 ml of dry methylene chloride under nitrogen and cooled to 0° was added slowly 9.6 g of boron trifluoride etherate. The mixture was stirred at 0° for 0.5 hr and at room temperature for 2 hr and then poured into ice water and extracted thoroughly with methylene chloride. The extracts were dried ($MgSO_4$), concentrated under vacuum, and chromatographed on deactivated Al_2O_3. The first fraction, **3c**, was eluted with a mixture of petroleum ether (bp 20–40°) and benzene (3:2), yield 2.1 g of a viscous red oil (34%). The second major band, **3e**, was removed from the column with chloroform and recrystallized from petroleum ether (bp 30–60°), yield 3.6 g (56%), mp 78–80° (lit.[7] 81–82°). By similar procedures were obtained **3d**, mp 99–100° (lit.[7] 98–99°), in 27% yield, and **3f**, mp 68–70° (lit.[7] 66–68°), in 57% yield.

β-Ferrocenophanylpropionic Acids (3g–j).—These acids were prepared by reported[6] procedures for synthesizing β-ferrocenylpropionic acids.

[3][*n*]Ferrocenophan-1-ones (4a–d).—The procedure used was a minor modification of reported[6] methods. Best yields were obtained as in the following scheme for the preparation of **4b**. A solution of 1.0 g of **3j** (3.2 mmol) in a small amount of dry methylene chloride was added slowly to a cold (ice bath) solution of 3.0 g of trifluoroacetic anhydride in 30 ml of methylene chloride under nitrogen. The mixture was stirred at 0° for 5 hr as the characteristic dark color developed, and then the flask was stoppered and allowed to stand at approximately −10° over the weekend. The solution was neutralized by pouring into cold sodium bicarbonate solution, the organic material was extracted with methylene chloride, and the extract was dried ($MgSO_4$) and concentrated under vacuum. Crystals formed which were dissolved in a mixture of benzene and hexane and the product was separated from a small amount of black tarry material by passing the mixture through a short column of deactivated Al_2O_3. The black material was retained at the top of the column and the pure product, eluted with benzene and recrystallized from benzene–hexane, melted at 154–156°. Subsequent recrystallization raised the melting point to 156–158°. Compounds **4a, 4c,** and **4d** were prepared similarly (Table I). Only in the reaction of **3i** by this procedure were two products formed, a small amount of **4g** being separated as a small band eluted after **4a** during purification by chromatography.

[4][*n*]Ferrocenophan-2-ones (4e and 4f).—The ring enlargement procedure for the preparation of **3a** was used to convert **4c** and **4d** to **4e** and **4f**. Ketones **4a** and **4b** did not react.

[*m*][*n*]Ferrocenophanes (5a–d).—Reduction of **4a–d** using lithium aluminum hydride and aluminum chloride according to reported[6,8] procedures gave **5a–d**, respectively (Table I).

[*m*][*n*]Ferrocenophanes (5e and 5f).—The Wolff–Kishner procedure described by Rosenblum and coworkers[11] and used by us to prepare **3a** converted **4e** into **5e** and **4f** into **5f**.

Reduction of 4g.—Lithium aluminum hydride and aluminum chloride[6,8] reduced **4g** to **5g**. Insufficient material precluded full characterization of **5g**.

Attempted Preparation of 12.—When **9**[9] was treated with an equimolar amount of benzaldehyde in the presence of aqueous base,[13] a mixture of **9** and **10** was obtained which could be separated by chromatography on deactivated neutral alumina (benzene or methylene chloride. **10** crystallized as orange plates from benzene–hexane (Table I). When excess benzaldehyde was used, the only product was **11**, no **12** being formed.

Acknowledgment.—We wish to express our appreciation to Mr. J. L. Pflug and Mrs. Antionette Austin, who took the spectra.