solid residue. This was treated with Girard T reagent to remove benzophenone. The residual material was refluxed with aqueous sodium hydroxide (25 ml. of 10% solution) to hydrolyze the anhydride or any ethyl or methyl ester that might have formed during the work-up. Acidification with concentrated hydrochloric acid gave β-naphthoic acid. The base-insoluble portion was chromatographed over alumina to yield tritane, 9-phenylfluorene, and polymer A. The products are listed in Table I.

Polymer A.—This material was soluble in ethanol and could be separated into different fractions by fractional precipitation from an ethanolic solution with water. Melting ranges of fractions varied from 80–144°. The polymer softened to a glassy bead which could be tapped from the melting point capillary tube. Molecular weight determination[14] on a fraction with melting range of 132–144° gave values of 598–600 in benzene solution; infrared spectrum (KBr): 3030, 1600, 1492, 1449, 1034, 744, and 700 cm.$^{-1}$.

Anal. Calcd. for an empirical formula $C_{19}H_{14}$: C, 94.01; H, 5.78. Found: C, 93.66; H, 5.78.

Polymer B.—Fractions with melting ranges varying from 150–300° were isolated during the work-up; infrared spectrum (KBr): 3030, 1739, 1600, 1492, 1449, 1279, 1187, 1034, 744, and 700 cm.$^{-1}$.

Anal. Found for fraction melting at 233–252°: C, 88.96; H, 5.18. Found for fraction melting above 300°: C, 91.75; H 5.25.

Pyrolysis of Trityl β-Naphthoate Using Oxygen.—Pyrolysis was effected in the same system as above with the exception that oxygen was bubbled into the melt. Traces of naphthalene were detected as sublimate in the condenser. After cooling, the residue was dissolved in benzene and extracted with cold sodium bicarbonate to remove the free acid. The anhydride was hydrolyzed and removed by boiling the solution with aqueous sodium hydroxide solution. V.p.c. analysis of the solution showed only benzophenone and tritane as the volatile components. Benzophenone was leached by treatment with Girard T reagent, and tritane was isolated by chromatography on alumina. The final residue was chiefly polymer C. Table VI contains all products.

Pyrolysis of β-Naphthoic Acid.—β-Naphthoic acid was pyrolyzed in the same system. After removal of the free acid by extraction with cold sodium bicarbonate, the residue was characterized and shown to be β-naphthoic anhydride, m.p. 136–137°, lit.[15] m.p. 133–134°.

Pyrolysis of β-Naphthoyl Peroxide.[16]—The flask containing the peroxide was heated cautiously to 107° in an oil bath. The contents softened slightly and decomposed vigorously after heating at 107–109° for 10 min. Heating was stopped and the oil bath was removed. β-Naphthoic acid was extracted with base and left an orange solid containing a trace of naphthalene and an unknown substance which showed carbonyl absorption at 1724 and 1695 cm.$^{-1}$ in the infrared spectrum. This material resisted all attempts at purification by recrystallization or sublimation. Table II shows all products.

Pyrolysis of β-Naphthoyl Peroxide with Tritane.—The two components in the molar ratio 1:2 were carefully powdered and transferred to the pyrolysis flask. The contents slowly were heated to 142° over a period of 1 hr. during which time some effervescence was observed. Further heating for 1 hr. was done at 142–145°. After removal of the acid, the base-insoluble residue was chromatographed over alumina. The various products are listed in Table V.

Photolysis of Trityl β-Naphthoate.—Photolysis of the ester in benzene with oxygen bubbling into the solution was studied over a period of 72–93 hr. A type 30620 Hanovia lamp (140 watts) was used. The infrared spectrum of the crude photolysate indicated β-naphthoic acid. The contents then were refluxed with a solution of 5 g. of sodium hydroxide in 50 ml. of water. The nonacid portion was found to be tritanol containing a small quantity of benzophenone as identified by v.p.c.

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[14] We acknowledge our thanks to Dr. Paul O. McCoy, Department of Chemistry, University of Oklahoma, Norman, Okla., for the molecular weight determination.

[15] O. Hausamann, *Ber.*, **9**, 1515 (1876).

[16] Crude peroxide melting at 120–125° was used. Pure peroxide decomposes explosively at 138°.

Multinuclear Ferrocenes. III. Acetylation of Biferrocenyl[1-3]

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Acetylation of biferrocenyl with acetic anhydride in the presence of polyphosphoric acid provides all three possible monoacetylbiferrocenyl position isomers as well as three isomeric diacetylbiferrocenyls. Structure assignments for all products are made on the basis of n.m.r. analysis, while previous infrared and ultraviolet spectral correlations for disubstituted ferrocenes are examined. In spite of the fact that the ferrocenyl group has been established as a strong electron donator, competitive acetylation of ferrocene and biferrocenyl in the present work shows that biferrocenyl is less susceptible to electrophilic substitution than is ferrocene. This apparent inconsistency is explicable in terms of a rapid equilibrium in which the iron atom of one ferrocene nucleus in biferrocenyl is bonded to electrophile, thus deactivating the molecule.

With the availability of methods of synthesis much better than that used in its initial preparation,[4] notably the Ullmann-type coupling of iodoferrocene,[5,6] study of biferrocenyl became a practical undertaking, and we began investigations into the chemistry of this molecule. Since the biferrocenyl molecule may be viewed as a ferrocene nucleus bearing a ferrocenyl substituent, we were interested initially in learning its reactivity relative to ferrocene itself as well as the possibility of obtaining information regarding the existence of any preferred pattern of orientation during electrophilic substitution.

Results and Discussion

A. Relative Reactivity.—In several instances the ferrocenyl group has been shown to possess strong electron-donating ability. Thus, ferrocenylbenzoic acids and ferrocenylphenols are weaker acids than benzoic acid and phenols, respectively, and *m*- and *p*-ferrocenylanilines are stronger bases than aniline itself.[7] The remarkable stability of a ferrocenylcarbinyl

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[1] Previous paper: S. I. Goldberg and R. L. Matteson, *J. Org. Chem.*, **29**, 323 (1964).

[2] We are pleased to acknowledge generous support of this work by the National Science Foundation, Grant G-24083. We also wish to express additional thanks to that agency for the institutional grant which made possible the purchase of the n.m.r. spectrometer used in this work.

[3] Taken in part from the M.S. thesis of J. S. Crowell, University of South Carolina, 1963.

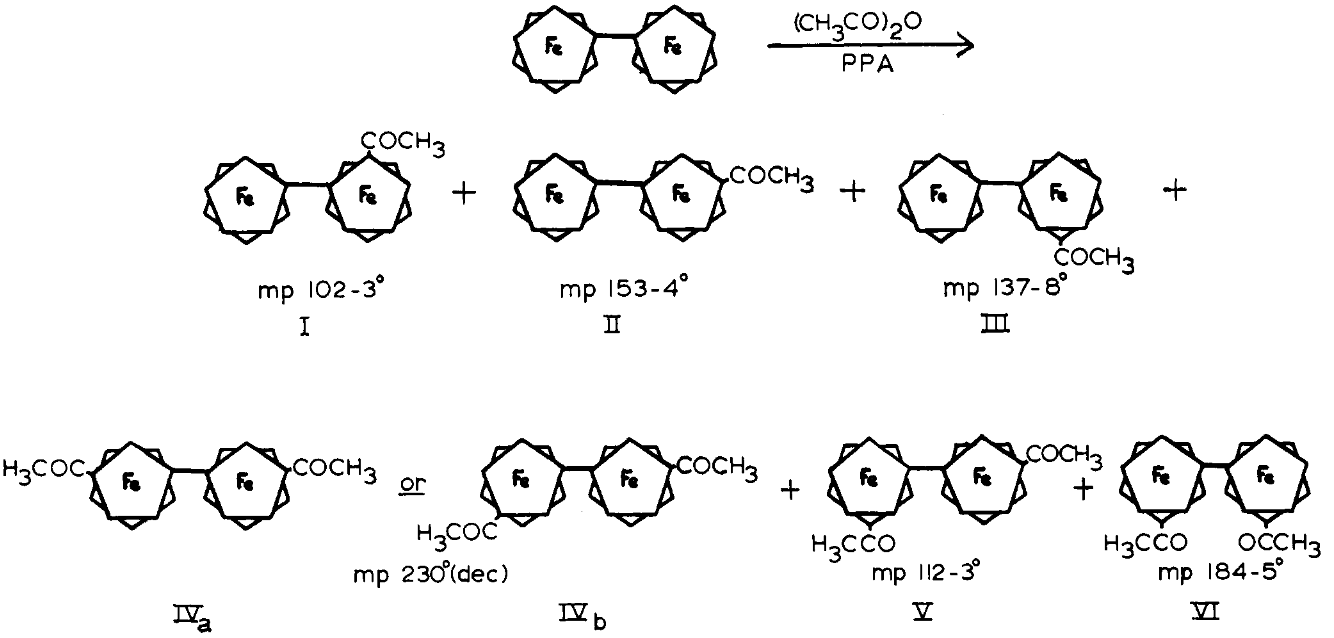
[4] S. I. Goldberg and D. W. Mayo, *Chem. Ind.* (London), 671 (1959).

[5] E. G. Perevalova and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **132**, 1093 (1960).

[6] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[7] A. N. Nesmeyanov, E. G. Perevalova, and R. V. Golovnya, *Dokl. Akad. Nauk SSSR*, **103**, 81 (1958); *cf.* A. N. Nesmeyanov, *Proc. Roy. Soc.* (London), **246**, 495 (1958).

SCHEME I

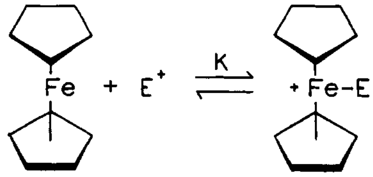


carbonium ion[8] also may be taken as an indication of the strong electron-donating ability of the ferrocenyl group; and the fact that the oxidation potential of biferrocenyl falls in between that of ethylferrocene and methoxyferrocene[9] is also in accord with this view. It was, therefore, expected that biferrocenyl would be found to be more susceptible to electrophilic substitution than ferrocene, and we were surprised to find this expectation not to be met by experimental trial.

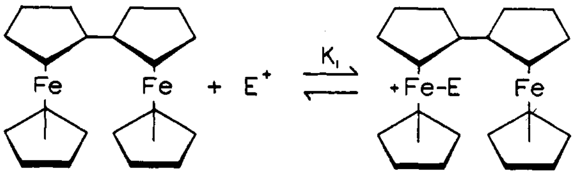
Equal molar amounts of ferrocene and biferrocenyl were allowed to compete for a molar equivalent amount of acetyl chloride in the presence of aluminum chloride under mild conditions. Careful work-up of the reaction mixture provided 92% recovery of biferrocenyl, but only 64% recovery of ferrocene. In addition, it was shown that acetylferrocene comprised 61% (by weight) of the acetylated material obtained from the reaction.

A further indication of the greater substitution ability of ferrocene is the fact that 51% of biferrocenyl was recovered from the acetylation mixture of acetic anhydride and polyphosphoric acid under conditions in which ferrocene gives rise to 71% yield of acetylferrocene.[10]

Thus, in spite of the fact that the ferrocenyl group is strongly electron donating, a ferrocene nucleus bearing a ferrocenyl group (biferrocenyl) undergoes electrophilic substitution to a lesser extent than does ferrocene. Yet, this is not inconsistent, when viewed in terms of an interpretation (eq. 1 and 2) which recognizes the strong electron-donating ability of the ferrocenyl group, in that biferrocenyl is *more* susceptible to electrophilic attack than ferrocene, but initial attack is on *iron*,[11a] and the biferrocenyl nucleus is rendered less prone to substitution on carbon. Since attack on iron is presumably an equilibrium step,[11a] the rate of substitution on carbon will be governed by the equilibrium concentration of uncharged species. In other words, because of the greater nucleophilic character of biferrocenyl, K_1 would be expected to be larger than K, and the results of the competition experiment may be explained by the presence of a greater concentration of uncharged ferrocene available for electrophilic attack on carbon.



(1)



(2)

B. Substitution Products of Biferrocenyl.—While treatment of biferrocenyl with acetic anhydride in the presence of polyphosphoric acid during 10 min. in a boiling water bath afforded incomplete reaction of biferrocenyl (51% recovery of starting material), a variety of acetylated products was obtained.[11b] The mixture of products was submitted to elution chromatog-

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[8] E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

[9] E. G. Perevalova, A. N. Nesmeyanov, and S. P. Gubin, Abstracts A, XIXth International Congress of Pure and Applied Chemistry, London, 1963, p. 187.

[10] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

[11] (a) M. Rosenblum and J. O. Santer, *ibid.*, **81**, 5517 (1959); T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *ibid.*, **82**, 5249 (1960); A. Berger, W. E. McEwen, and J. Kleinberg, *ibid.*, **83**, 2274 (1961); W. F. Little, R. A. Berry, and P. Kannan, *ibid.*, **84**, 2525 (1962); M. Rosenblum, J. O. Santer, and W. G. Howells, *ibid.*, **85**, 1450 (1963). (b) NOTE ADDED IN PROOF.—Since submission of this paper an account of the work of A. N. Nesmeyanov, V. N. Drozd, V. A. Sazonova, V. I. Romanenko, A. K. Prokof'ev, and L. A. Nikonova [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 667 (1963)] has appeared [*Chem. Abstr.*, **59**, 7556*E* (1963)] containing a report of results obtained from acetylation of biferrocenyl. The Russian authors observed only three acetylation products: 3-acetylbiferrocenyl, 1',6'-diacetylbiferrocenyl (compounds II and VI of the present investigation—both previously obtained by independent synthesis[1]), and a triacetylbiferrocenyl, m.p. 143-144°.

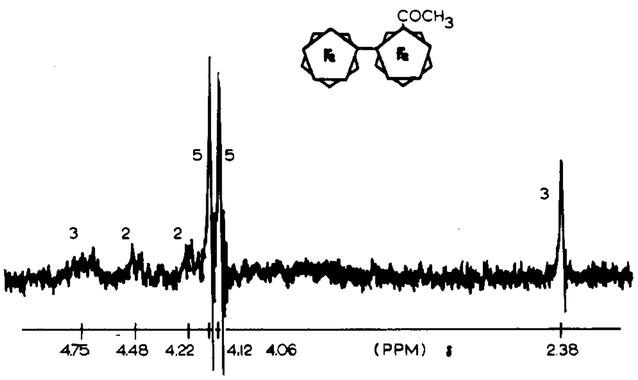

Figure 1

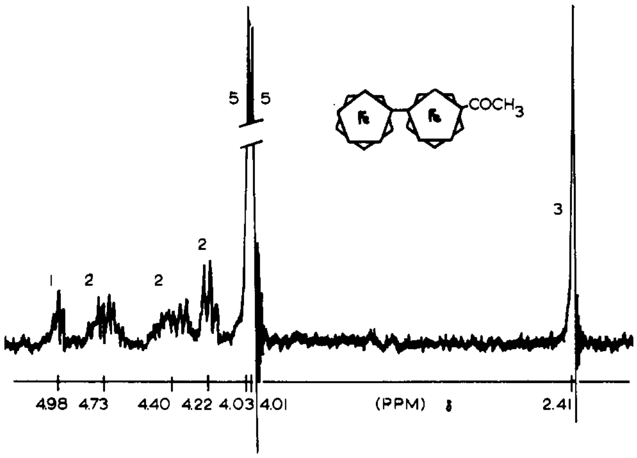

Figure 2

raphy on alumina, and each product was recrystallized to constant melting. Relatively easy separation of the monoacetylated products (I–III) from the diacetylated products (IV–VI) was obtained during column chromatography, but separation among the individual isomers of each group required very careful column development and elution. (See Scheme I.)

The first isomer to be eluted and the least abundant was assigned structure I, 2-acetylbiferrocenyl,[12] by means of comparison of the n.m.r. spectrum determined from it with that of the second eluted isomeric monoacetylated product, 3-acetylbiferrocenyl (II). In each spectrum (Fig. 1 and 2, respectively), the presence of two five-proton signals near δ 4, unsubstituted cyclopentadienyl ring, and one three-proton singlet near δ 2.4, methyl group in acetyl function, showed that each isomer possessed only one acetyl group (confirmed by combustion analysis) and that the acetyl group was contained in one of the directly bonded cyclopentadienyl of the biferrocenyl nucleus. The choice between the two isomeric possibilities was decided by the fact that the n.m.r. spectrum of the isomer melting at 153–154° (second to be eluted) gave rise to a low field one-proton triplet (δ 4.98) that must be due to a proton flanking the acetyl group but remote from the ring assembly, C-1. The lowest field signal present in the n.m.r. spectrum obtained from the isomer melting at 102–103° (first to be eluted) is a three-proton multiplet centered at δ 4.75 which must include the proton flanking the acetyl group and must be remote from C-1. Since the acetyl group may be expected to exert a greater deshielding effect on an adjacent proton when it is more remote from C-1, the higher melting isomer which gives rise to the lower field signal is assigned structure II, 3-acetylbiferrocenyl. This analysis is also consistent with the fact that the signal due to the methyl protons of the acetyl function of the higher melting isomer (II) occurs at slightly lower field (δ 2.41) than it does (δ 2.38) in the n.m.r. spectrum obtained from the lower melting isomer (I).

The remaining monoacetyl isomer, m.p. 137–138°, (third to be eluted) was assigned structure III, 1′-acetylbiferrocenyl. This material was shown to be identical with 1′-acetylbiferrocenyl, previously synthesized by an independent route, and the n.m.r. spectrum determined from III, as well as its analysis, are included in a separate account[1] of that work.

There have been several attempts to establish empirical generalizations based on properties of isomeric disubstituted ferrocenes. Among these is the order of elution of isomeric disubstituted ferrocenes from alumina which has been observed[13,14] to be 1,2- first, 1,1′-second, and 1,3- third. It will be noted that this sequence was not observed in the present work. This generalization, therefore, appears to be limited to disubstituted isomers possessing only one ferrocene nucleus. Empirical correlations based on infrared absorption also have been examined with the compounds encountered in this work. Utility of the reliable 9–10 rule[13,14–17] is extended by the present investigation to include substituted biferrocenyls: all of the compounds possessing at least one unsubstituted cyclopentadienyl ring (I, II, III, IV, and V) exhibit bands near 9 and 10 μ in their infrared spectra.

While correlation of infrared spectra of bands in the 10.9–11.3-μ region advanced by Rosenblum[18] as an aid in distinguishing between 1,2- and 1,3-disubstituted ferrocenes does not appear to be applicable in the present work, a similar correlation of bands in the region 1270–1300 cm.$^{-1}$ [13,16,19,20] appears to include the monoacetyl isomers, I and II.

Thus, 2-acetylbiferrocenyl (I) possesses a band at 1270 but not near 1290 cm.$^{-1}$, while 3-acetylbiferrocenyl (II) gives rise to a doublet of equal intensity at 1304 and 1292 cm.$^{-1}$ with no absorption near 1270 cm.$^{-1}$.

It is significant that the correlation of ultraviolet absorption in the region near 220 mμ previously suggested[13] for substituted acylferrocenes is applicable here. 3-Acetylferrocene (II) displays the longest wave-

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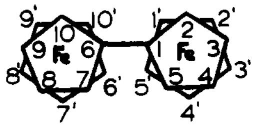
[12] In order to designate the individual isomers unambiguously, the numbering system shown below for biferrocenyl has been proposed.[1]



[13] K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

[14] M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *ibid.*, **84**, 2726 (1962).

[15] M. Rosenblum, Doctoral dissertation, Harvard University, 1953.

[16] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[17] A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin, and V. D. Vilchevskaya, *Dokl. Akad. Nauk SSSR*, **125**, 1037 (1959).

[18] M. Rosenblum and W. G. Howells, *J. Am. Chem. Soc.*, **84**, 1167 (1962).

[19] K. L. Rinehart, Jr., and K. L. Motz, *Chem. Ind.* (London), 1150 (1957).

[20] K. L. Rinehart, Jr., D. E. Bublity, and D. H. Gustafson, *J. Am. Chem. Soc.*, **85**, 970 (1963).

length maxima in this region, while 2-acetylferrocene (I) possesses the shortest (Fig. 3). It does not appear, however, that either the infrared correlation or the ultraviolet correlation is applicable to the isomeric diacetylated biferrocenyls obtained in this work.

Of the three isomeric diacetylbiferrocenyls obtained, the first eluted from alumina decomposed over a temperature range starting at about 230°. The n.m.r. spectrum determined from this material (Fig. 4) displayed a ten-proton singlet at δ 4.07, showing the presence of two unsubstituted cyclopentadienyl rings. The fact that the methyl groups of the two acetyl functions gave rise to a singlet signal (δ 2.42) indicated that the acetyl groups were equivalent, and the two-proton signal (probably a triplet) at δ 5.00 also meant that each acetyl group was located β to the ring assembly atoms of the biferrocenyl nucleus. This analysis, therefore, limits the structure possibilities to either 3,9-diacetylbiferrocenyl (IVa) or 3,8-diacetylbiferrocenyl (IVb). While it is not possible to distinguish between these two structures at the present time, the four-proton triplet at δ 4.80, in either case, must arise from the four protons which flank the ring assembly atoms.

The n.m.r. spectrum (Fig. 5) determined from the second diacetyl isomer eluted from alumina (m.p. 111–112°) shows the presence of one unsubstituted cyclopentadienyl ring (five-proton singlet at δ 4.02) and the presence of two nonequivalent acetyl groups. The three-proton singlet at δ 2.18 is due to an acetyl group present in a nondirectly bonded cyclopentadienyl ring (signal at δ 2.15 for acetyl groups in III and VI), while the lower field, three-proton singlet must be due to the acetyl group present in a bonded cyclopentadienyl ring and located β to the ring assembly atom because of the presence of the one-proton triplet at δ 4.98. This isomer is, therefore, assigned the structure of 3,6′-diacetylbiferrocenyl (V).

The last of the isomeric diacetyl biferrocenyls, m.p. 183–185°, to elute from alumina proved to be identical with 1′,6′-diacetylbiferrocenyl (VI), previously synthesized.[1]

While any attempt to correlate spectral properties with structure for these disubstituted isomers would be premature since the three isomers obtained here represent only a small fraction of the number of disubstituted biferrocenyls possible, it may be significant to note that adsorbability on alumina appears to increase with the degree of substitution in the nondirectly bonded cyclopentadienyl rings of biferrocenyl.

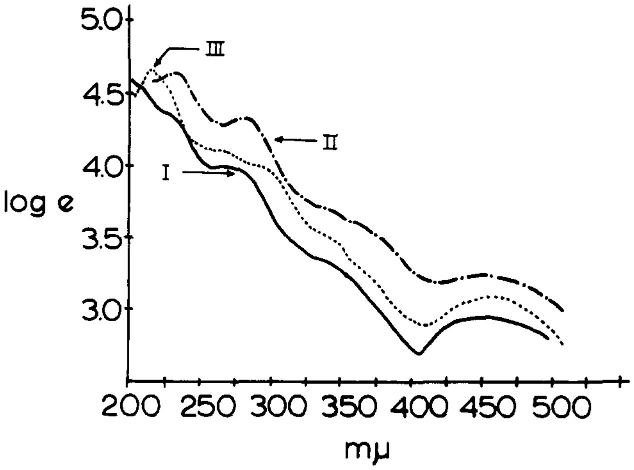


Figure 3

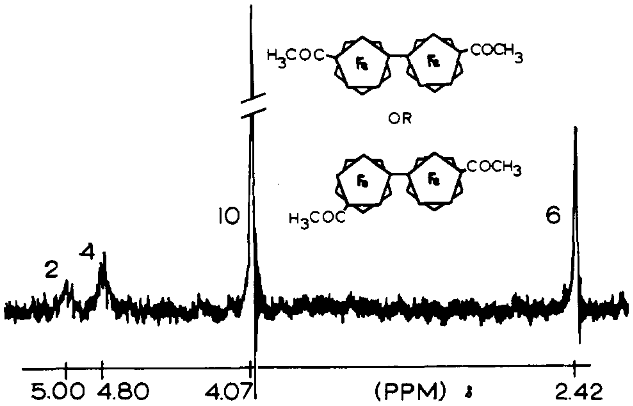


Figure 4

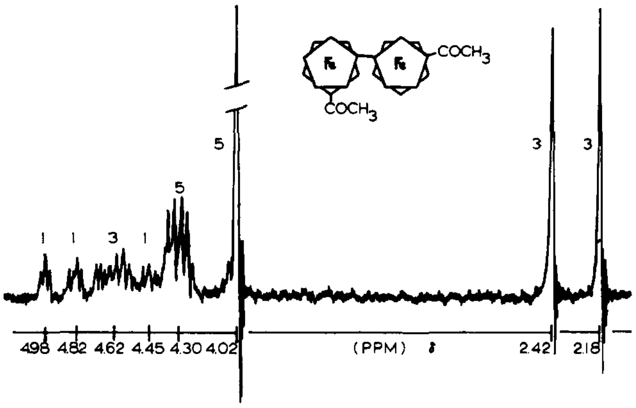


Figure 5

Experimental

Temperature measurements are reported uncorrected. N.m.r. spectra were determined with a Varian A-60 spectrometer at 60 Mc. with a room temperature probe, employing chloroform solvent containing approximately 5% (v./v.) tetramethylsilane as internal standard. Ultraviolet spectra were obtained in 95% ethanol with a Cary Model 14 recording spectrophotometer, while infrared spectra were determined in carbon tetrachloride solution, usually 5% (wt./wt.), with a Perkin-Elmer Model 21 recording spectrophotometer.

Combustion analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The biferrocenyl used in this work was prepared[21] by a procedure previously described.[1]

All column elution chromatography was carried out with Merck acid-washed alumina and purified elution solvents. The column chromatograms were wrapped with aluminum foil to protect them from light during development and elution.

Competitive Acetylation of Biferrocenyl and Ferrocene.—Ferrocene (186 mg., 1.00 mmole) and biferrocenyl (370 mg., 1.00 mmole) were dissolved in 100 ml. of dry methylene dichloride, and the resulting solution was cooled to approximately 0° by means of an external ice bath. While the solution was maintained under an atmosphere of purified nitrogen and agitated by means of a magnetically operated stirrer, a mixture of acetyl chloride (134 mg., 1.00 mmole) and anhydrous aluminum chloride (120 mg., 1.00 mmole), contained in 13 ml. of methylene dichloride, was added slowly to the cold, red solution during a 30-min. period. The reaction mixture immediately assumed a deep violet coloration upon initial introduction of the acid chloride–aluminum chloride addend.

After addition, the reaction was allowed to warm slowly (~1 hr.) to room temperature, and stirring was continued during an

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[21] We wish to acknowledge the very able assistance of Miss Patricia Mobley and Mr. John Alford in preparation of the biferrocenyl.

additional hour at room temperature. After the mixture was poured quickly onto 100 ml. of crushed ice and the ice was allowed to melt, the resulting hydrolysate was phase separated. The light blue aqueous phase was treated with ascorbic acid to discharge the blue color and then extracted with three 10-ml. portions of methylene dichloride. Combination, drying, and evaporation of all the methylene dichloride solutions yielded 583 mg. of a solid, orange-red material which was submitted to chromatography on 30 g. of Merck acid-washed alumina. Development with hexane gave rise to a large, yellow, diffuse band, which was eluted with hexane, and a smaller, orange-red area, which was eluted with ethyl acetate. Evaporation of the hexane eluent gave 504 mg. of orange solid which, by means of fractional crystallization from hexane,[1] was shown to consist of 339 mg. (92% recovered) of biferrocenyl and 119 mg. (64% recovered) of ferrocene.

Evaporation of the ethyl acetate eluent yielded 67 mg. of light red solid which was chromatographed on alumina. Development with ether produced a mobile salmon-colored band and several slower moving, darker red bands. The large, salmon-colored band was collected in ether and evaporated to 41 mg. of red, needle-shaped crystals of acetylferrocene, m.p. 84–87° (lit.[22] m.p. 85–86°), which was not depressed upon admixture melting with authentic acetylferrocene. This material also gave rise to an infrared spectrum (carbon tetrachloride) superimposable upon that determined from authentic acetylferrocene.

Acetylation of Biferrocenyl.—Biferrocenyl (20.0 g., 54.1 mmoles) was suspended and partially dissolved in a mixture containing 80 ml. of acetic anhydride and 20 ml. of polyphosphoric acid (two parts 85% orthophosphoric acid and one part phosphorus(V) oxide by weight). The heterogeneous reaction mixture was flushed with nitrogen and then immersed in a hot water bath (~95°) for 10 min. during which time the flask was constantly swirled. At the end of the 10-min. heating period, enough crushed ice was added to cause the temperature of the reaction mixture to fall rapidly to about 15°. After neutralization of the cooled reaction mixture by addition of saturated aqueous sodium carbonate solution, all of the solid material present was washed onto a Büchner funnel and sucked as dry as possible. The solid residue was triturated with three 25-ml. portions of ether, leaving 8.5 g. of biferrocenyl as residue. An additional 1.7 g. of recovered biferrocenyl was obtained from elution chromatography (see below), bringing the total recovered starting material to 10.2 g. (51%). The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated to an orange-red, solid residue. An infrared spectrum (carbon tetrachloride) determined from this crude mixture indicated the presence of acetylation product (broad band near 6 μ). The material then was submitted to a slow, careful chromatographic separation on alumina.

Chromatographic Separation of Biferrocenyl Acetylation Mixture.—The solid, ether-soluble residue described above was dissolved in a minimum volume of hot chloroform and transferred to a column containing 600 g. of Merck acid-washed alumina. The column of alumina, 3 ft. high and 1 in. in diameter, previously was carefully packed in hexane solution. The dark red chloroform solution was run onto the top of the alumina column in a narrow uniform band, and development of the column was begun with hexane. The initially narrow band of material widened quickly while the chloroform was washed through, but then only slow and steady movement of a diffuse, yellow band, which had developed out of the dark red solution, was observed. Elution with hexane was continued until all of the mobile, yellow region was collected.

Evaporation of the hexane eluent yielded an additional 1.7-g. portion of unreacted biferrocenyl which was identified by means of a mixture melting point with authentic biferrocenyl.

Development of the column then was continued with 1:1 (v./v.) hexane–benzene. The remaining material separated into two major regions: a dark orange band moving downward just perceptively and a red region remaining stationary. Continued elution with 1:1 hexane–benzene eventually gave rise to a separation of the mobile, orange area into two component orange bands.

2-Acetylbiferrocenyl (I).—Just before any of the material in the faster-moving, orange band had reached the end of the column, there was collected a volume (~300 ml.) of faintly yellow eluent. The yellow material in the eluent was not visible on the column. Evaporation of the eluting solvent mixture, followed by recrystallization of the residue from hot hexane, gave rise to 13 mg. (0.12% yield[23]) of an orange-red crystalline material, m.p. 102–103°, which was assigned the structure of **2-acetylbiferrocenyl** (I) on the basis of the spectral data (see text) determined from it.

Anal. Calcd. for $C_{22}H_{20}Fe_2O$: C, 64.12; H, 4.89. Found: C, 63.81; H, 5.10.

3-Acetylbiferrocenyl (II).—Elution of the column was continued with 1:1 hexane–benzene, and the faster-moving, orange band was collected. The eluting solvent mixture was evaporated *in vacuo*, and the crystalline, orange residue obtained was recrystallized from hot hexane to yield 70 mg. (0.64% yield[23]) of **3-acetylbiferrocenyl** (II) as needle-shaped crystals, m.p. 153–154° (see text for discussion of structural assignment).

Anal. Calcd. for $C_{22}H_{20}Fe_2O$: C, 64.12; H, 4.89. Found: C, 63.82; H, 5.04.

1′-Acetylbiferrocenyl (III).—The slower-moving, orange band was eluted next with the same solvent mixture, 1:1 hexane–benzene. Evaporation of the eluent to dryness *in vacuo* provided a crystalline, orange residue. Recrystallization of this material from hot hexane solution gave 550 mg. (5.1% yield[23]) of pure **1′-acetylbiferrocenyl** (III) as dark orange, needle-shaped crystals, m.p. 137–138°, which was undepressed upon melting in admixture with 1′-acetylbiferrocenyl previously obtained by means of an independent synthesis.[1] For additional comments concerning the structural assignment and spectral properties of this compound, see ref. 1.

Anal. Calcd. for $C_{22}H_{20}Fe_2O$: C, 64.12; H, 4.89. Found: C, 64.23; H, 4.90.

3,9- or 3,8-Diacetylbiferrocenyl (IVa or IVb).—Since very little development of the red region at the top of the column occurred during the large volume of solvents used for elution of unreacted biferrocenyl and the monoacetylbiferrocenyls, the eluting solvent was changed to pure benzene. Column development with this solvent caused a diffuse, light red band to move slowly out of the major dark red area. This band was collected in eight fractions of approximately equal volume, and each fraction was evaporated to dryness *in vacuo*. Crystallization and recrystallization of the combined residues obtained from the first three fractions gave 100 mg. (0.85% yield[23]) of **3,9- or 3,8-diacetylbiferrocenyl** as yellow crystals which were observed to decompose steadily over the temperature range 230–250°, when melting was attempted. See text for spectral data and discussion concerning the two structural possibilities for this compound.

Anal. Calcd. for $C_{24}H_{22}Fe_2O_2$: C, 63.47; H, 4.88. Found: C, 63.55; H, 4.96.

3,6′-Diacetylbiferrocenyl (V).—The small amount of material left in the mother liquors of the crystallizations of the combined residue obtained from the first three fractions described above was added to the combined residues provided by evaporation of the remaining benzene eluents. This material was crystallized and recrystallized from a benzene–hexane mixture to give rise to 700 mg. (5.8% yield[23]) of **3,6′-diacetylbiferrocenyl** (V) as red, needle-shaped crystals, m.p. 112–113°. See text for spectral data pertinent to the structural assignment made to this compound.

Anal. Calcd. for $C_{24}H_{22}Fe_2O_2$: C, 63.47; H, 4.88. Found: C, 63.86; H, 4.89.

1′,6′-Diacetylbiferrocenyl (VI).—While elution with pure benzene gave rise to the diffuse, light red band described above, the slower-moving, darker red band remained close behind and appeared to be homogenous throughout its movement down the column. The major portion of this band was eluted from the column with 20:1 (v./v.) benzene–ether which carried it off the column a little faster than did pure benzene. The crystalline residue obtained from the eluents was recrystallized from hot benzene to yield 200 mg. (1.8% yield[23]) of **1′,6′-diacetylbiferrocenyl** (VI) as dark red, needle-shaped crystals which melted at 184–185°, undepressed on admixture with 1′,6′-diacetylbiferrocenyl previously prepared by an independent route.[1] For spectral data and addition comments regarding the structural assignment to this material, see ref. 1.

Anal. Calcd. for $C_{24}H_{22}Fe_2O_2$: C, 63.47; H, 4.88. Found: C, 63.41; H, 4.56.

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(22) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, *Dokl. Akad. Nauk SSSR*, **97**, 459 (1954).

(23) Yield calculation was based on 9.8 g. of unrecovered biferrocenyl.