of the blue color was noted. For the introduction of iron, aliquots of a stock solution of 0.1 g. of anhydrous ferric chloride in 100 ml. of tetrahydrofuran were added. Thus for example, in one experiment using *t*-butyl alcohol, 1 ml. of this solution was added; assuming that the liquid volumes are additive, this is equivalent to 0.001 mg. of iron per ml. of reaction mixture which we regard, for convenience, as equivalent to 1 p.p.m. Corresponding aliquots were taken for other iron concentrations and experiments using the other alcohols. In cases where the reaction times were very short (<10 min.), the alcohol and/or ferric chloride were added last to the other reagents so as to avoid the time normally required for the metal to "melt" in the reaction mixture.

The effect of iron on the Birch reduction of estradiol 3-methyl ether was studied using 6.5 g. of the steroid and the quantities of other reagents (*t*-butyl alcohol as proton donor) given directly above. Likewise the addition of definite amounts of iron was done in a fashion similar to that described. The products were isolated and analyzed for unreduced starting material as described earlier.

CHICAGO 80, ILL.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

Preparation of Substituted Ferrocenes from Fulvenoid Compounds[1]

WILLIAM F. LITTLE AND ROBERT C. KOESTLER[2]

Received January 18, 1961

1,2-Diaroylcyclopentadienes readily form substituted cyclopentadienide ions with bases, but these anions do not react with ferrous chloride to yield substituted ferrocenes. However, prior reduction of the carbonyl groups with lithium aluminum hydride followed by treatment with ferrous chloride yields 1,1′,2,2′-tetrabenzylferrocenes. Unsubstituted tetrabenzylferrocene and a series of substituted tetrabenzylferrocenes were prepared. The substituents, on all four benzyl groups in each case, included *p*-methyl, *p*-fluoro, *o*-chloro *p*-chloro, *m*-bromo, and *p*-bromo.

Fulvenes have proved to be useful starting materials for preparation of unusual heteroannular disubstituted ferrocenes[3-6] by addition of reagents such as phenyllithium, lithium aluminum hydride, and sodium to the *exo* double bonds of alkyl and aryl fulvenes to generate substituted cyclopentadienide ions that will "sandwich" with ferrous chloride. Knox[7] has added phenyllithium to the fulvenoid compound, diazocyclopentadiene, and has prepared phenylazoferrocenes similarly.

Acylcyclopentadienes may be considered as fulvenoid compounds in that enolization of these systems produces α-hydroxyfulvenes; in fact, some acylcyclopentadienes have been demonstrated to exist principally as enols.[8] This consideration has suggested a likely approach to the preparation of additional ferrocenes of novel structure.

Linn and Sharkey[8] reported that aroyl halides react with cyclopentadiene to yield exclusively 1,2-diaroylcyclopentadienes. These substances were demonstrated to exist to an extent greater than 90% in the hydrogen bonded enol form, II.

Diaroylcyclopentadienes readily form salts with strong bases; this suggested a possible route to tetraaroylferrocenes, III, by reaction with ferrous ions. No difficulty was encountered in preparing salts of dibenzoylcyclopentadiene; however, the resulting anion failed in all attempts to "sandwich" with iron. The attempts employed as bases phenyllithium in ether, sodium ethoxide in ethanol, and diethylamine as both base and solvent. Only recovery of dibenzoylcyclopentadiene resulted with the phenyllithium and with sodium ethoxide, while diethylamine produced only tars. Apparently the *pi* electrons in the dibenzoylcyclopentadienide ion are too delocalized for effective sandwiching.

The failures of the above reactions were ascribed to excessive delocalization of the *pi* electrons for the sandwiching reaction with ferrous chloride. Accordingly, in order to circumvent this difficulty and to increase the availability of the ring electrons, the carbonyl groups of dibenzoylcyclopentadiene were reduced with lithium aluminum hydride prior to sandwiching. The reduction mixture in ether was directly introduced to anhydrous ferrous chloride in tetrahydrofuran, and from the resulting reaction was isolated 1,1′,2,2′-tetrabenzylferrocene, IVa, in 13% yield.

The generality of this procedure as a method for preparing tetrabenzylferrocenes of known substitution patterns was established by preparing similar derivatives starting with substituted benzoyl chlorides. Starting with *p*-methyl-, *p*-fluoro-, *o*-chloro-, *p*-chloro-, *m*-bromo-, and *p*-bromobenzoyl

---

(1) Presented at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov. 3-5, 1960.

(2) R. J. Reynolds Fellow, Feb.-June, 1960.

(3) R. C. Koestler and W. F. Little, *Chem. & Ind.* (*London*), 1589 (1958).

(4) P. L. Pauson and G. R. Knox, *Proc. Chem. Soc.*, 289 (1958).

(5) R. L. Pruett, personal communication; K. L. Rinehart, A. K. Frericks, P. A. Kittle, L. E. Westman, D. H. Gustafson, R. L. Pruett, and J. E. McMahon, *J. Am. Chem. Soc.*, **82**, 4111 (1960).

(6) W. F. Little and R. C. Koestler, in press.

(7) G. R. Knox, *Proc. Chem. Soc.*, 56 (1959).

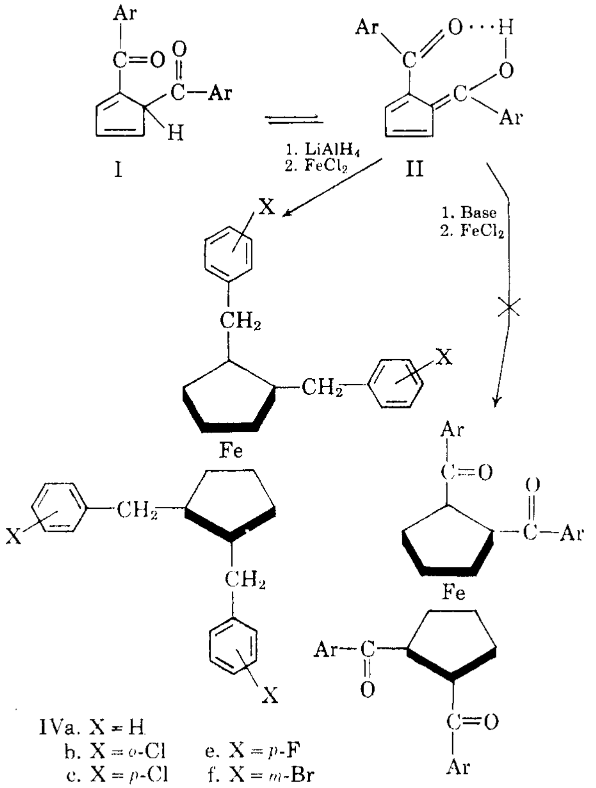
(8) W. J. Linn and W. H. Sharkey, *J. Am. Chem. Soc.*, 79, 4970 (1957).

TABLE I

DIAROYLCYCLOPENTADIENES

Compound	Yield,[a] %	M.P.	Formula	Calcd.		Found	
				C	H	C	H
1,2-Di(*p*-fluorobenzoyl)-cyclopentadiene	75	174–175	$C_{19}H_{12}O_2F_2$	73.54	3.90	73.84	4.18
1,2-Di(*m*-bromobenzoyl)-cyclopentadiene	74	139.5–140.5	$C_{19}H_{12}O_2Br_2$	52.81	2.80	53.44	2.66
1,2-Di(*p*-bromobenzoyl)-cyclopentadiene	15	172–174	$C_{19}H_{12}O_2Br_2$	52.81	2.80	52.35	2.81
1,2-Di(*p*-iodobenzoyl)-cyclopentadiene	65	192–193	$C_{19}H_{12}O_2I_2$	43.37	2 30	43.40	2.67

[a] Based on acid chloride.



chloride, the corresponding diaroylcyclopentadienes were prepared, and from these the corresponding substituted tetrabenzylferrocenes were obtained in yields usually ranging from 25–30%. All of the tetrabenzylferrocenes were yellow, easily crystallized solids. Only 1,2-di(*p*-iodobenzoyl)cyclopentadiene failed to yield sufficient amounts of the tetrabenzylferrocene to be characterized.

Table I lists the diaroylcyclopentadienes prepared that were not reported by Linn and Sharkey; Table II lists the tetrabenzylferrocenes.

EXPERIMENTAL

All melting points are uncorrected.

Analyses were performed by Microtech Laboratories, Skokie, Ill., and by Kenneth L. Shepard in this Department.

1,2,-Diaroylcyclopentadienes. The dibenzoylcyclopentadienes were prepared essentially by the method of Linn and Sharkey.[8] To a solution of phenyllithium (0.02 mole) was added an equimolar quantity of cyclopentadiene in dry ether solution. To this reaction mixture was then added dropwise an equivalent amount of the aromatic acid chloride at room temperature After stirring for 15 min., the mixture was treated with dilute acetic acid and the layers separated. The ether layer was extracted several times with dilute acetic acid, and the volume reduced to about half. Addition of about an equal volume of 90% ethanol, followed by further reduction of the volume at 55°, yielded, on cooling, yellow crystals of the diaroylcyclopentadiene. Most of the diaroylcyclopentadienes were recrystallized from petroleum ether (b.p. 60–110°).

Attempted preparations of tetrabenzylferrocene. Equimolar quantities of phenyllithium and dibenzoylcyclopentadiene in ether solutions were mixed and stirred for 1 hr. The mixture was added to an equivalent quantity of ferrous chloride (anhydrous) in tetrahydrofuran. After stirring for 1 hr., the mixture was filtered and treated with dilute hydrochloric acid. Evaporation of the solvent yielded only the starting dibenzoylcyclopentadiene.

A similar procedure was used with sodium ethoxide[9] in ethanol as the base. The reaction with ferrous chloride was allowed to reflux for 3 hr., but again only starting material was obtained.

The reaction between dibenzoylcyclopentadiene and ferrous chloride in diethylamine was allowed to stir overnight. Evaporation of the solvent after filtration yielded a black tar which was taken up in methylene chloride and was treated with sodium hydrosulfite. Evaporation of the solvent yielded a solid that appeared to be polymeric and contained no iron.

1,1′,2,2′-Tetrabenzylferrocene. To a solution of 1.32 g. (0.035 mole) of lithium aluminum hydride in 100 ml. of dry ether was added 7.0 g. (0.0255 mole) of solid dibenzoylcyclopentadiene. The reaction that ensued brought the system to reflux. After 2 hr. at reflux, the mixture, containing a yellow precipitate, was transferred under nitrogen to a mixture of anhydrous ferrous chloride (0.0127 mole) in tetrahydrofuran. The reaction mixture turned brown and was allowed to reflux for 2 hr. Water and dilute hydrochloric acid were added to hydrolyze the inorganic salts, and the ether layer was separated. The ether layer was washed three times with water and was dried over magnesium sulfate before the ether was evaporated. The residue was chromatographed on alumina with benzene–10% ethanol. The yellow crystals obtained were recrystallized from acetone. The yield was 0.92 g., 13%, m.p. 154.5–155.5°.

---

[9] W. F. Little, R. C. Koestler, and R. Eisenthal, *J. Org. Chem.*, **25**, 1435 (1960).

TABLE II

TETRASUBSTITUTED FERROCENES PREPARED FROM DIAROYLCYCLOPENTADIENES

Compound	Yield, %	M.P.	Formula	Calcd. C	Calcd. H	Found C	Found H
1,1′,2,2′-Tetrabenzylferrocene	13	154.5–155.5	$C_{38}H_{34}Fe$	83.51	6.27	83.20 83.44	6.22 6.33
1,1′,2,2′-Tetrakis(*p*-methylbenzyl)-ferrocene	25.5	101–102[a] 117–118	$C_{42}H_{42}Fe$	83.71	7.03	83.32	7.12
1,1′,2,2′-Tetrakis(*o*-chlorobenzyl)-ferrocene	10.7	163.5–164.5	$C_{38}H_{30}Cl_4Fe$	66.69	4.42	66.52	4.40
1,1′,2,2′-Tetrakis(*p*-chlorobenzyl)-ferrocene	25.7	169–171	$C_{38}H_{30}Cl_4Fe$	66.69	4.42	66.75 67.08	4.33 4.58
1,1′,2,2′-Tetrakis(*p*-fluorobenzyl)-ferrocene	30.5	142–143	$C_{38}H_{30}F_4Fe$	73.79	4.89	73.66	5.03
1,1′,2,2′-Tetrakis(*m*-bromobenzyl)-ferrocene	24.4	117.5–118	$C_{38}H_{30}Br_4Fe$	52.94	3.51	53.26	3.53
1,1′,2,2′-Tetrakis(*p*-bromobenzyl)-ferrocene	9.5	207–208	$C_{38}H_{30}Br_4Fe$	52.94	3.51	53.11	3.65

[a] Compound melts at 101°, resolidifies at 102°, and melts finally at 117–118°.

The other tetrabenzylferrocenes were prepared by almost identical procedures from diaroylcyclopentadienes prepared from the appropriately substituted benzoyl chlorides. The recrystallization solvents used with the substituted compounds were as follows: *p*-methyl, ethanol; *o*-chloro, ethyl acetate; *p*-chloro; acetone; *p*-fluoro, acetone-water; *m*-bromo, acetone; *p*-bromo, benzene.

Acknowledgment. The authors would like to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

Preparation of Heteroannular Disubstituted Ferrocenes from Fulvenes

WILLIAM F. LITTLE AND ROBERT C. KOESTLER

Received February 6, 1961

Lithium aluminum hydride was added to the *exo* double bonds of dimethylfulvene and diphenylfulvene, followed by treatment with ferrous chloride to produce heteroannular diisopropylferrocene and dibenzhydrylferrocene, respectively. Addition of phenyllithium to dimethylfulvene, followed by treatment with ferrous chloride similarly gave heteroannular bis(α,α-dimethylbenzyl)ferrocene. Phenyllithium addition to diphenylfulvene, however, did not give the expected bis-triphenylmethylferrocene upon treatment with ferrous chloride. The structure of the product obtained was not determined. Bistriphenylmethylferrocene was, however, obtained from triphenylmethylcyclopentadiene and ferrous chloride.

The aromatic nature of a cyclopentadienide ion endows the ring with a stability that enables fulvenes to react with several reagents as pseudo ketones, the five-membered ring with its ability to accommodate a negative charge performing as the carbonyl oxygen. Figure 1 summarizes four reactions of fulvenes that are analogous to ketone reactions. Lithium aluminum hydride adds to the *exo* double bond of alkyl- and arylfulvenes to yield substituted cyclopentadienide ions[1]; phenyllithium likewise adds to fulvenes[2] in an analogous manner to carbonyl addition. With strong bases such as triphenylmethide or sodium amide, alkylfulvenes lose protons[3] in a manner analogous to enolization; and with sodium metal,[4] reductive coupling occurs, as in pinacol formation from ketones, to form dianions.

All of these reactions offer routes to substituted ferrocenes, simply by treating the products with anhydrous ferrous chloride. The purpose of the present communication is to present the details of the use of the first two of these reactions for the production of ferrocenes. Concurrently, the authors[5] and Pauson[6] reported results of preparations of disubstituted ferrocenes by these routes in preliminary communication form. Pauson also reported the use of potassium amide on dimethylfulvene for preparation of dialkenylfulvenes, and Pruett[7] has found that the fourth reaction produced bridged ferrocenes whose

---

[1] (1) K. Ziegler, H. G. Gellet, H. Martin, and J. Schnider, *Ann.*, **589**, 91 (1954).

[2] (2) K. Ziegler and W. Schafer, *Ann.*, **511**, 101 (1934).

[3] (3) W. Schlenk and E. Bergmann, *Ann.*, **479**, 58 (1930).

[4] (4) W. Schlenk and E. Bergmann, *Ann.* **463**, 63 (1928); **479**, 42 (1930).

[5] (5) R. C. Koestler and N. F. Little, *Chem. & Ind.* (*London*), 1589 (1958).

[6] (6) P. L. Pauson and G. R. Knox, *Proc. Chem. Soc.*, 289 (1958).

[7] (7) R. L. Pruett, personal communication.