6-Nitropiperonal (LXII) was prepared by the method of Parijs,[40] m.p. 98–98.5°, in 51% yield (lit.[40] m.p. 98°).

6-Aminopiperonal (LXIII) was prepared by the method of Campbell,[41] m.p. 106–108°, in 62% yield (lit.[41] m.p. 107–108°).

6-Iodopiperonal (LXIV) was prepared by the method of Rilliet and Kreitmann,[42] m.p. 112–113°, in 52% yield (lit.[42] m.p. 111°).

2-Carbomethoxy-2′-iodo-4′,5′-methylenedioxy-α-nitro-*cis*-stilbene (LXVI).—In a 5-ml. erlenmeyer flask was placed a mixture of 2-carbomethoxyphenylnitromethane (XXII, 0.098 g., 0.0005 mole, m.p. 64–65°), *n*-propylidene base of 6-iodopiperonal (LXV, 0.150 g., 0.0005 mole), and glacial acetic acid (4 ml.). The mixture was heated on a hot plate and the acetic acid was evaporated almost to dryness. The resulting dark brown oil was chromatographed on silica gel $HF_{254+366}$ plates (chloroform elution) and gave, after appropriate work-up, yellow-orange prisms (0.072 g., 32%), m.p. 118–119°. An analytical sample was prepared by recrystallization from ethanol: m.p. 118–119°; $\lambda_{\max}^{CHCl_3}$ 5.82, 6.56, 7.50, 10.70 μ; $\lambda_{\max}^{EtOH}$ 370 mμ (ε 8700).

Anal. Calcd. for $C_{17}H_{12}INO_6$: C, 45.06; H, 2.67; N, 3.09. Found: C, 45.14; H, 2.78; N, 3.15.

1-Carbomethoxy-6,7-methylenedioxy-10-nitrophenanthrene (LXVII). — 2-Carbomethoxy-2′-iodo-4′,5′-methylenedioxy-α-nitro-*cis*-stilbene (LXVI, 0.0720 g., 0.00016 mole, m.p. 118–119°) was photolyzed under the usual conditions for 3 hr. The cyclohexane (1000 ml.) and traces of iodine were removed under reduced pressure affording a brown oily residue (0.039 g.). Preparative t.l.c. on silica gel $HF_{244+366}$ (chloroform elution) afforded fine yellow needles (0.020 g., 39%): m.p. 254–255°; $\lambda_{\max}^{KBr}$ 5.85, 6.58, 7.45, 10.65 μ; $\lambda_{\max}^{EtOH}$ 234 mμ (ε 18,400), 268 (20,300), 282 (17,800), 357 (4900).

Anal. Calcd. for $C_{17}H_{11}NO_6$: C, 62.77; H, 3.41; N, 4.31. Found: C, 62.69; H, 3.61; N, 4.29.

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[40] A. H. Parijs, *Rec. trav. chim.*, **49**, 17 (1930).

[41] K. N. Campbell, *J. Org. Chem.*, **16**, 1736 (1951).

[42] A. Rilliet and L. Kreitmann, *Helv. Chim. Acta*, **4**, 588 (1921).

Synthesis of Polyferrocenylene[1]

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Polyferrocenylene was formed when cobaltous chloride or an organic halide was added to lithiated ferrocene. The direct bonding of ferrocene nuclei in the polymerization reactions is accounted for by coupling of ferrocenyl radicals. Identification of ferrocene derivatives by low and high voltage mass spectrometry is demonstrated.

Biferrocenyl was first detected in the reaction products of trialkylchlorosilanes with lithiated ferrocene.[2,3] Since then biferrocenyl has been synthesized using Ullmann coupling, reaction of diferrocenylmercury with silver, ferrocenylmagnesium bromide with cobaltous chloride, and other methods.[4] Korshak and co-workers[5] obtained polyferrocenylene by heating ferrocene with *t*-butyl hydroperoxide. Rausch[6] reported polyferrocenylene in thermal decomposition products of mercury-bridged ferrocenes $(C_{10}H_{10}FeHg)_x$. Nesmeyanov and co-workers[7] obtained some polyferrocenylene in an Ullmann coupling where bromo- and 1,1′-dibromoferrocene were used.

In this paper we report that lithioferrocenes react readily with cobaltous chloride in the absence of any organic halide. The reaction gave polyferrocenylene. We also found that ferrocenyl coupling takes place when organic halides are added to lithiated ferrocene. Benzyl chloride was especially effective for promoting polyferrocenylene formation. Such polyferrocenylenes were found to consist of biferrocenyl and higher ferrocenyl coupling products.

Lithiated Ferrocene and Cobaltous Chloride.—Exothermic reaction of anhydrous cobaltous chloride with lithioferrocenes[8] in ether–tetrahydrofuran, followed by stirring at room temperature and hydrolysis, resulted in polyferrocenylene (I). Lithioferrocenes which had

$$C_5H_5FeC_5H_5 \xrightarrow{\substack{1.\ n\text{-}C_4H_9Li \\ 2.\ CoCl_2 \\ 3.\ H_2O}} H\!\left(C_5H_4FeC_5H_4\right)_nH$$

I

$n \geq 2$

been synthesized by using the largest excess of *n*-butyllithium gave the highest yield (74.6%) of polyferrocenylene (Table I).

TABLE I

EFFECT OF REAGENT CONCENTRATION ON POLYFERROCENYLENE YIELDS. LITHIOFERROCENES AND COBALTOUS CHLORIDE REACTIONS

Moles of reagents				Polyferrocenylene	
Ferrocene	*n*-Butyllithium	Cobaltous chloride	Ferrocene recovery, %	Yield,[a] %	Av. mol. wt.
0.1	1.0	0.2	21.6	74.6	985
0.1	0.5	0.2	35.0	51.5	1434
0.1	0.37	0.3	29.8	33.8	455
0.1	0.25	0.2	43.0	21.6	512

[a] The calculation of yields is based on ferrocene.

Earlier in this laboratory we found that low voltage mass spectrometry of ferrocene and many of its derivatives gives intense molecule ion peaks with little or no fragmentation.[9] The method was useful for identification of ferrocene derivatives also in this work. Within the working range (up to a mass of about 700), I gave the following molecular ion peaks: ferrocene (*m/e* 186), cyclopentadienylferrocene (*m/e* 250), biferrocenyl (*m/e* 368, 370, 371, and 372), and terferrocenyl (*m/e* 554) (Table II).

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[1] Presented in part before the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964.

[2] M. D. Rausch, M. Vogel, H. Rosenberg, D. Mayo, and P. Shaw, ASTIA Document No. 150979, 1958.

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

[4] For a review of the literature, see M. D. Rausch, *Can. J. Chem.*, **41**, 1289 (1963).

[5] V. V. Korshak, S. L. Sosin, and V. P. Alexseeva, *Dokl. Akad. Nauk SSSR*, **132**, 360 (1960).

[6] M. D. Rausch, *J. Org. Chem.*, **28**, 3337 (1963).

[7] 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*, **4**, 667 (1963).

[8] All work was done with a lithiated ferrocene mixture consisting of lithio- and 1,1′-dilithioferrocene.

[9] D. J. Clancy and I. J. Spilners, *Anal. Chem.*, **34**, 1839 (1962).

CHART I

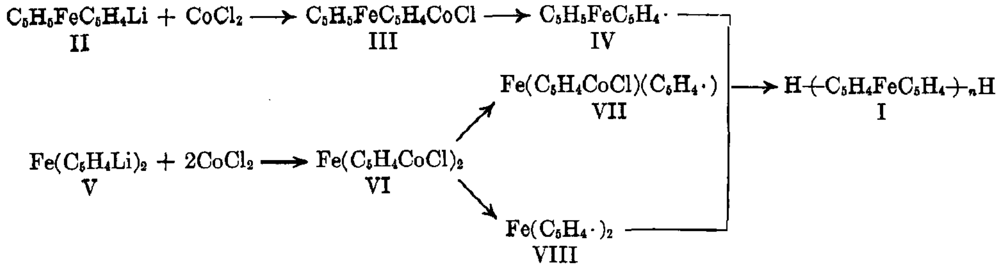

TABLE II

LOW VOLTAGE MASS SPECTROMETRY.[a] POLYFERROCENYLENE FROM LITHIOFERROCENES AND COBALTOUS CHLORIDE REACTIONS

	Intensities[b,c]		
m/e	A	D	Molecular ions[d]
186	6.0	6.0	$C_5H_5Fe^{56}C_5H_5$
250	10.2	...	$C_5H_5Fe^{56}C_5H_4\text{–}C_5H_5$
366	4.1	3.8	$C_5H_4Fe^{56}C_5H_4\text{–}C_5H_4Fe^{54}C_5H_4$
368	17.7	14.4	$C_5H_5Fe^{56}C_5H_4\text{–}C_5H_4Fe^{54}C_5H_5$, $C_5H_4Fe^{56}C_5H_4\text{–}C_5H_4Fe^{56}C_5H_4$
370	103.8	88.4	$(C_5H_5Fe^{56}C_5H_4)_2$
371	28.0	23.9	$C_5H_5Fe^{56}\text{–}C_5H_4\text{–}C_5H_4Fe^{57}C_5H_5$
372	4.2	5.2	$(C_5H_5Fe^{57}\text{–}C_5H_4)_2$
554	33.9	19.0	$H(C_5H_4Fe^{56}C_5H_4)_3H$

[a] Ionizing voltage 8 e.v. [b] Intensities of ions from two separately synthesized polyferrocenylene samples, A and D in Experimental Section. Differences in intensities may be due to differences in the sizes of the samples introduced in the spectrometer and not only due to relative abundances of ions. [c] Chart divisions. [d] The molecular ions are species where the positive charge is probably located on the iron atom. The C^{13} and lesser iron isotopic contributors are not listed as examples.

The intensities in Table II were compared with values calculated for a normal isotope distribution of iron and carbon which would give several molecular ion peaks of varying intensities. One feature of the low voltage spectrum is the absence of molecular ion peaks of the less abundant isotopic contributors. Apparently, unit masses for minor constituents and for some high molecular weight constituents, *e.g.*, terferrocenyl, are not detected because of lower sensitivity of the spectrometer at the low voltages used. For terferrocenyl the low voltage (8 e.v.) mass spectrum showed only the principal parent molecular ion peak (mass 554). However, in the high voltage (70 e.v.) spectrum, the three most abundant terferrocenyl molecule ion peaks (*m/e* 552, 554, and 555) were present. The higher sensitivities at the high voltage also allowed determination of all isotopic ferrocene and cyclopentadienylferrocene molecule ion peaks.)

Some deviations from the expected intensities for biferrocenyl—high intensities of the 366 and 368 and low intensity of the 372 mass peak compared with the principal (*m/e* 370) peak of the parent molecule—can be attributed to the presence of biferrocenylene. The 70- and 8-e.v. spectra of the two polyferrocenylenes (Table II) were found to have the same relative intensities for the peaks in the *m/e* range of 366 to 372, suggesting that fragmentation or splitting off of hydrogen is insignificant. It also indicates that *m/e* 366, 368, 369, and 370 peaks must be partly due to another compound, such as heteroannularly or homoannularly linked biferrocenylene, $C_{24}H_{16}Fe$.[10]

Ferrocene and cyclopentadienylferrocene may be present as minor impurities or are formed in the spectrometer.[11] However, a decrease of the ionization potential in the spectrometer (from 8 to 5.5 e.v.) did not eliminate the cyclopentadienylferrocene peak. This indicates that it was not a fragment formed upon electron bombardment in the spectrometer.

The other significant peaks found only in the 70-e.v. spectrum correspond to fragment ions which resulted from cyclopentadienyl–cyclopentadienyl and cyclopentadienyl–iron bond breaking in polyferrocenylene: C_5H_5Fe (*m/e* 121), $C_5H_4\text{–}C_5H_4$ (*m/e* 128), $C_5H_4FeC_5H_4$ (*m/e* 184), $C_5H_5FeC_5H_4$ (*m/e* 185), $C_5H_5FeC_5H_4\text{–}C_5H_4$ (*m/e* 249), $C_5H_4FeC_5H_4\text{–}C_5H_4Fe$ (*m/e* 304), and $C_5H_5FeC_5H_4\text{–}C_5H_4Fe$ (*m/e* 305).

Elemental analysis of the benzene-soluble polyferrocenylene showed somewhat high values for carbon and hydrogen and low values for iron. This may indicate that cyclopentadienyl-substituted polyferrocenylenes are present, as does the mass peak of 250 corresponding to the mass of cyclopentadienylferrocene (Table II). Possibly, these resulted from an oxidative cleavage of a ferrocenyl group in a polyferrocenylene molecule.

The formation of polyferrocenylene from lithiated ferrocenes (II and V), in the presence of sufficient cobaltous chloride to displace all lithium on lithiated ferrocene, may be accounted for by an initial formation of ferrocenylcobalt chlorides, III and VI. Decomposition of the latter may give ferrocenyl radicals, such as IV, VII, and VIII, which will couple to form polyferrocenylene (I).[12] (See Chart I.)

Ferrocenyl radical coupling was proposed earlier by Shechter and Helling.[13a] They obtained biferrocenyl by adding cobaltous chloride to ferrocenylmagnesium bromide in the presence of ethylene bromide.[13b] Wittig and Bickelhaupt[14] achieved phenyl coupling by adding cobaltous chloride to *o*-dilithiobenzene in the absence of organic halides. This work showed that cobaltous chloride may react similarly, in the absence of organic halides, with lithioferrocenes to give ferrocenyl coupling.[15]

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[10] The mass 369 peak was detected only in the 70-e.v. spectrum which affords higher sensitivities.

[11] We have found a mass 250 peak as a minor impurity in some other products where lithioferrocenes had been used in the synthesis. One sample of polyferrocenylene, however, does not have any 250 mass peak (Table II, D).

[12] I is shown as a polymer formed by heteroannular coupling. However, the analysis does not exclude the presence of structures formed by homoannular coupling, *e.g.*, $H_2\text{–}(\text{–}C_5H_3FeC_5H_5)_n$.

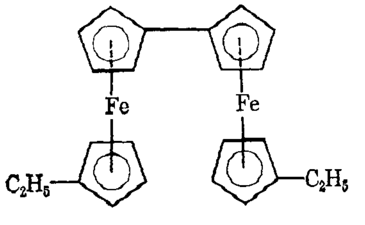
[13] (a) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961). (b) Ferrocenylmagnesium bromide was synthesized from magnesium and bromoferrocene in the presence of ethylene bromide as entrainer.

[14] G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958).

[15] No attempt was made to separate the proposed unstable ferrocenylcobalt chloride intermediate.

Lithiated Ferrocene and Organic Halides.—Ferrocenyl coupling by the addition of organic halides to lithioferrocenes was first indicated when biferrocenyl was isolated in a very small amount from lithioferrocenes and trialkylhalosilane reaction products.[2,3]

We have found that coupling of ferrocenyl groups in reactions of lithioferrocenes and organic halides is general. Thus, from the reaction products of lithioferrocenes with ethyl iodide and ethyl bromide, we could separate biferrocenyl and bis[1-(1′-ethylferrocenyl)] (IX). However, the major products were ethylferrocene and 1,1′-diethylferrocene. Also, the presence of triethylferrocene, ethylbiferrocenyl and triethylbiferrocenyl was detected by low voltage mass spectrometry.



IX

The reaction of lithioferrocenes with benzyl chloride at 40° gave polyferrocenylene. The highest yield (42%) of polyferrocenylene was obtained when a molar excess of benzyl chloride was added. However, the elemental analysis and low voltage mass spectrometry indicated that it also contains some benzylated ferrocenes (Table III). In addition, this polyferrocenylene gave a high *m/e* 368 peak intensity which indicates the presence of biferrocenylene. Except for the presence of peaks due to benzylated ferrocene, this polyferrocenylene has the same ferrocenyl coupling product ion peaks in both high and low voltage spectrum as the samples listed in Table II.

TABLE III

LOW VOLTAGE MASS SPECTROMETRY.[a] POLYFERROCENYLENE[b] FROM LITHIOFERROCENES AND BENZYL CHLORIDE REACTION

m/e	Intensities[c]	Molecular ions[d]
186	6.7	$C_5H_5Fe^{56}C_5H_5$
250	6.0	$C_5H_5Fe^{56}C_5H_4–C_5H_5$
276	6.0	$C_5H_5Fe^{56}C_5H_4–CH_2C_6H_5$
366	11.0	$C_6H_5CH_2C_5H_4Fe^{56}C_5H_4CH_2C_6H_5$, $(C_5H_5Fe^{54}C_5H_4)_2$
368	107.1	$C_5H_5Fe^{54}C_5H_4–C_5H_4Fe^{54}C_5H_5$, $\overbracket{C_5H_4Fe^{56}C_5H_4—C_5H_4Fe^{56}C_5H_4}$
370	447.0	$(C_5H_5Fe^{56}C_5H_4)_2$
371	120.3	$C_5H_5Fe^{56}C_5H_4Fe^{57}C_5H_5$
372	18.0	$(C_5H_5Fe^{57}C_5H_4)_2$
458	10.0	$C_5H_5Fe^{56}C_5H_4–C_5H_4Fe^{54}C_5H_4–CH_2C_6H_5$
460	53.8	$C_5H_5Fe^{56}C_5H_4–C_5H_4–Fe^{56}–C_5H_4CH_2C_6H_5$
550	10.3	$(C_6H_5CH_2–C_5H_4Fe^{56}C_5H_4)_2$
552	18.0	$H(C_5H_4Fe^{56}C_5H_4)_2C_5H_4–Fe^{54}C_5H_5$
554	82.4	$H(C_5H_4Fe^{56}C_5H_4)_3H$
665	8.6	$H(C_5H_4Fe^{56}C_5H_4)_3CH_2C_6H_5$

[a] Ionizing voltage e.v. [b] Sample A in Experimental Section. [c] Chart divisions. [d] The C^{13} and lesser iron isotopic contributors are not listed as examples.

A lower yield (13.5%) of polyferrocenylene was obtained when a fourfold excess of lithiated ferrocene was used; the polyferrocenylene contains no benzylated ferrocenes. When the addition of benzyl chloride to lithioferrocenes was carried out at 10°, the yield of polyferrocenylene was considerably lower (8.6%). Also, addition of lithioferrocenes to benzyl chloride (inverse addition) decreased the extent of ferrocenyl coupling (10% yield).

In the reactions carried out, the coupling of benzyl chloride with lithioferrocenes was not extensive. The added benzyl chloride, however, reacted completely, and some bibenzyl and stilbene were separated from the reaction mixtures.

No chloroferrocene was detected by the low voltage mass spectrometry in the crude reaction products, indicating that no chlorine and lithium exchange between benzyl chloride and lithioferrocenes took place. Simultaneous addition of benzyl chloride and carbon dioxide gave poly(ferrocenyl ketone).[16,17] Since no phenylacetic acid was obtained, no benzyllithium appeared to have been present.

Also benzyl iodide, iodobenzene, and 1,2-dibromoethane were added to lithioferrocenes. The crude products were found by the infrared, ultraviolet, and low voltage mass spectrometry analyses to contain polyferrocenylenes. However, no ferrocenyl coupling products were found to have been formed when lithiated ferrocenes were warmed in the absence of a halide.

These data indicate that, also in the presence of organic halides, lithioferrocenes may give ferrocenyl radicals which couple to produce polyferrocenylenes.

Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were determined with a Perkin-Elmer 137 B spectrophotometer. Ultraviolet spectra were obtained using a Beckman DK spectrophotometer. N.m.r. spectra were determined with a Varian (Model 4300 A, 40 Mc.) instrument. The chemical shifts are relative to tetramethylsilane as an internal standard. Mass spectra were obtained using a Consolidated Electrodynamics Corp., Model 21-103, mass spectrometer with an inlet temperature of 350° and a nominal ionizing voltage of 8 or 70 e.v. The working range of the spectrometer up to the mass of about 700 was used. Intensities are reported in chart divisions. Molecular weights were determined by vapor pressure osmometry.

Lithiation of Ferrocene.—Ferrocene was dissolved in tetrahydrofuran, and an excess of *n*-butyllithium[18] was added in about 2 hr. while the temperature was kept below 35°. The mixture was stirred at room temperature and under nitrogen overnight.

Polyferrocenylene from Lithioferrocenes and Cobaltous Chloride. A.—*n*-Butyllithium, from 15.9 g. (2.3 g.-atoms) of lithium and 92.5 g. (1 mole) of *n*-butyl chloride, in 400 ml. of ether was used to lithiate 18.6 g. (0.1 mole) of ferrocene in 1 l. of tetrahydrofuran. Anhydrous cobaltous chloride (26.0 g., 0.2 mole) was added gradually in 1 hr. to maintain the temperature of the mixture at about 35°. Addition of the last 3 g. of cobaltous chloride did not raise the temperature of the mixture. Stirring of the dark brown mixture was continued at room temperature for 3 hr. Then the mixture was hydrolyzed by pouring it on

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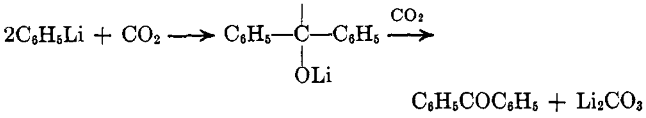
(16) J. Thiec [*Ann. chim.* (Paris), [12] **9**, 51 (1954)] similarly converted phenyllithium to the diaryl ketone by passing CO_2 over the surface of the ether solution.



$$2C_6H_5Li + CO_2 \longrightarrow C_6H_5—\overset{\displaystyle OLi}{\underset{\displaystyle OLi}{C}}—C_6H_5 \xrightarrow{CO_2} C_6H_5COC_6H_5 + Li_2CO_3$$

(17) Poly(ferrocenyl ketone) can be produced by passing CO_2 over warm (40–50°) ether–tetrahydrofuran solutions of lithioferrocenes (I. J. Spilners and J. P. Pellegrini, Jr., unpublished studies).

(18) Prepared according to the method of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

ice and water, extracted with benzene, washed with dilute aqueous hydrochloric acid and water, and filtered. The solvent was removed with a flash evaporator. The residue was heated in a sublimator to remove unreacted ferrocene (4 g., 21.6%). The remaining finely divided polyferrocenylene (I, 13.8 g., 74.6%) was dissolved in benzene, filtered, and precipitated by addition of petroleum ether (b.p. 30–60°). The analytical sample was obtained by passing the benzene solution through a column of activated alumina. The orange crystalline polyferrocenylene (av. mol. wt. 985) decomposes in air at about 240°.

The infrared spectrum (Nujol) of I has a strong doublet at 1110 cm.$^{-1}$, strong singlets at 1030 and 1000 cm.$^{-1}$, and a strong absorption around 815 cm.$^{-1}$. Weaker absorption bands are at 3120, 1700–1600, 860, 845, 722, and 675 cm.$^{-1}$. The ultraviolet spectrum (in cyclohexane) has absorption maxima at 222 mμ ($E_{1\,\mathrm{cm}}^{1\%}$ 1.12 × 10^3) and at 298 mμ ($E_{1\,\mathrm{cm}}^{1\%}$ 2.18 × 10^2).[3,19] The curve has a shoulder at 250 mμ. The n.m.r. spectrum (in CS_2) has one intense singlet at τ 6.17 (unsubstituted ring protons), weaker doublets at τ 5.77 and 5.98 (substituted ring protons),[20] and apparent singlets at τ 6.03 and 6.21. The low voltage mass spectrometry results are given in Table II (A).

Anal. Calcd. for $C_{10}H_9Fe$: C, 64.93; H, 4.87; Fe, 30.19. Calcd. for $C_{10}H_8Fe$: C, 65.29; H, 4.35; Fe, 30.36. Found: C, 65.56; H, 5.06; Fe, 29.25.

B.—The same reaction conditions as in A were used except that ferrocene (0.1 mole) was lithiated with *n*-butyllithium prepared from 8 g. (1.16 g.-atoms) of lithium and 46.3 g. (0.5 mole) of *n*-butyl chloride. Ferrocene (6.5 g., 35.0%) was recovered by sublimation. Polyferrocenylene (9.5 g., 51.5%) had an average molecular weight of 1434 and it decomposes at 230–240°. The infrared spectrum was identical with the spectrum in A.

Anal. Found: C, 65.60; H, 5.12; Fe, 29.21.

C.—Ferrocene (18.6 g., 0.1 mole) was lithiated with *n*-butyllithium prepared from 7 g. (1 g.-atom) of lithium and 34.3 g. (0.37 mole) of *n*-butyl chloride. Other conditions were the same as in A, except that 39 g. (0.3 mole) of cobaltous chloride was used. Ferrocene (5.5 g., 29.8%) and polyferrocenylene (6.3 g., 33.8%, av. mol. wt. 455, decomposed above 230°) were obtained.

Anal. Found: C, 65.60; H, 5.20; Fe, 29.22.

D.—Ferrocene (18.6 g., 0.1 mole) was lithiated with *n*-butyllithium prepared from 6 g. (0.86 g.-atom) of lithium and 23.1 g. (0.25 mole) of *n*-butyl chloride. Other conditions were as in A. Ferrocene (8.1 g., 43.0%) and polyferrocenylene (4.0 g., 21.6%, av. mol. wt. 512, decomposes above 230°) were obtained. The low voltage mass spectrometry results are given in Table II (D).

Anal. Found: C, 65.62; H, 5.29.

Reaction of Lithioferrocenes with Ethyl Iodide.—Lithioferrocenes were prepared in ether–tetrahydrofuran from 10 g. (1.45 g.-atoms) of lithium, 46.3 g. (0.5 mole) of *n*-butyl chloride, and 37 g. (0.2 mole) of ferrocene. Then 62.5 g. (0.4 mole) of ethyl iodide in 250 ml. of tetrahydrofuran was added in 90 min. The temperature initially rose to 40°. The mixture was stirred overnight and then poured on ice and water. The organic layer was filtered, washed with water, and dried. Solvent was removed with flash evaporator. Cold petroleum ether was added to the oily residue. The precipitate formed was separated by filtration and washed with cold petroleum ether. Sublimation gave 9.5 g. (25.7%) of ferrocene. In the residue was 3.5 g. (9.5%) of biferrocenyl (mol. wt. 375, decomposes at 235°). Distillation of the petroleum ether soluble oil gave 6.5 g. (15%) of ethylferrocene, b.p. 96° (2.8 mm.), $n^{25}D$ 1.5977 [lit.[21] b.p. 121–123° (10 mm.), $n^{20}D$ 1.6019], and 6.0 g. (12.4%) of 1,1′-diethylferrocene, b.p. 110° (2.8 mm.), $n^{25}D$ 1.5757 [lit.[22] b.p. 87–89° (0.15 mm.), $n^{25}D$ 1.5761].

Extraction of the distillation residue with petroleum ether gave 1.8 g. of orange crystalline material. The low voltage spectrum of this showed peaks corresponding to ethylbiferrocenyl (*m/e* 398, intensity 16.0), diethylbiferrocenyl (*m/e* 426, intensity 120.0), and triethylbiferrocenyl (*m/e* 454, intensity 0.6). The mixture was chromatographed on alumina. Recrystallization of the first petroleum ether cut from methanol gave 0.6 g. of orange crystalline bis[1-(1′-ethylferrocenyl)] (IX), m.p. 90° (lit.[5] m.p. 90–91°), from ethanol m.p. 96.5–97°.

The infrared spectrum, which was identical with the reported[5] spectrum, has strong 1110-, 1030-, 1020-, 855-, and 810-cm.$^{-1}$ bands. Weak bands are at 1225, 1000, 910, 840, and 725 cm.$^{-1}$.

The n.m.r. spectrum has a singlet at τ 6.26 (probably due to protons on ethylcyclopentadienyl rings),[23] multiplet at τ 5.93 (cyclopentadienyl protons), quadruplet at τ 7.97 (methylene protons), and triplet at τ 8.99 (methyl protons) with relative intensities of 8:8:4:6, respectively.

Anal. Calcd. for $C_{24}H_{26}Fe_2$: C, 67.66; H, 6.11; Fe, 26.22. Found: C, 67.79; H, 6.19; Fe, 26.30.

Reaction of Lithioferrocenes with Ethyl Bromide.—The same reaction conditions as in the reaction of lithioferrocenes with ethyl iodide were used. Ferrocene (23%), ethyl- and 1,1′-diethylferrocene (18%), biferrocenyl (2%), and ethylbiferrocenyls (5%) were obtained.

Polyferrocenylene from Lithioferrocenes and Benzyl Chloride. A.—*n*-Butyllithium, from 8 g. (1.16 g.-atoms) of lithium and 46.3 g. (0.5 mole) of *n*-butyl chloride, in 200 ml. of ether was used to lithiate 37 g. (0.2 mole) of ferrocene in 300 ml. of tetrahydrofuran. Benzyl chloride (50.8 g., 0.4 mole) was added gradually in 2 hrs. so that the temperature of the mixture remained at about 40°. The mixture was stirred for 30 min. longer, poured on ice and water, extracted with benzene, filtered, and washed with dilute aqueous hydrochloric acid and water. After removal of the solvent, sublimation of the residue gave 4 g. (11%) of ferrocene and 15.5 g. (42%) of finely divided light brown polyferrocenylene (decomposes above 200°).

The infrared spectrum (Nujol) has a strong doublet at 1110 cm.$^{-1}$, strong bands at 1030 and 1000 cm.$^{-1}$, and a strong absorption around 820 cm.$^{-1}$. Weaker absorption bands are at 3120, 1700–1600, 1410, 878, 845, 805, 720, and 700 cm.$^{-1}$. The ultraviolet spectrum (in cyclohexane) has absorption maxima at 222 mμ ($E_{1\,\mathrm{cm}}^{1\%}$ 1.06 × 10^3) and at 298 mμ ($E_{1\,\mathrm{cm}}^{1\%}$ 2.02 × 10^2). The curve has a shoulder at 250 mμ. The n.m.r. spectrum (in CCl_4) has an intense singlet at τ 6.17 which is surrounded by unresolved multiplets. The low voltage mass spectrometry results are given in Table III.

Anal. Calcd. for $C_{10}H_9Fe$: C, 64.93; H, 4.87; Fe, 30.19. Calcd. for $C_{10}H_8Fe$: C, 65.29; H, 4.35; Fe, 30.36. Found: C, 66.15; H, 5.12; Fe, 28.91.

The molecular weights are 489 for the ethanol-soluble fraction (34%) and 1048 for the ethanol-insoluble fraction (66%) of polyferrocenylene.

B.—The same reaction conditions as in A except that only 6.3 g. (0.05 mole) of benzyl chloride was used. Ferrocene (17.4 g., 47.3%) and polyferrocenylene (5.0 g., 13.5%, mol. wt. 561) were obtained. The infrared and ultraviolet spectra were as described in method A of the preparation of polyferrocenylene from lithioferrocenes and cobaltous chloride.

Anal. Found: C, 64.91; H, 5.06; Fe, 30.29.

C.—The same reaction conditions were used as in A, except that benzyl chloride was added to lithioferrocenes at 10°. Ferrocene (21.5 g., 58%) and polyferrocenylene (3.2 g., 8.6%) were obtained. The benzene-soluble portion of polyferrocenylene (1.6 g., decomposes above 180°) was found to have the following low voltage mass spectrum peaks, *m/e* (intensity): ferrocene, 186 (10.0); cyclopentadienylferrocene, 250 (8.3); benzylferrocene, 276 (8.0); benzylcyclopentadienylferrocene, 340 (6.1); biferrocenyl and biferrocenylene, 366 (11.0), 368 (76.1), 370 (76.3), 371 (20.3); benzylbiferrocenyl, 460 (18.3); and terferrocenyl, 554 (10.0).

Anal. Found: C, 66.03; H, 5.03; Fe, 28.61.

The benzene-insoluble portion of the polyferrocenylene (1.6 g., decomposes above 200°) was found to decompose in the spectrometer. The following low voltage spectrum mass peaks, *m/e* (intensity) were present: $C_5H_4Fe^{56}C_5H_4–C_5H_4Fe^{54}C_5H_4$, 366 (1.4); $(C_5H_4Fe^{56}C_5H_4)_2$, 368 (12.0); and $C_5H_4Fe^{56}C_5H_4C_5H_4Fe^{57}C_5H_4$, 369 (3.6). Analysis showed that carbon–hydrogen–iron ratio is 10.0:8.3:0.95.

Reaction of Lithioferrocenes, Benzyl Chloride, and Carbon Dioxide.—The reaction between lithioferrocene and benzyl chloride (A) was repeated, except that carbon dioxide was slowly passed into the flask during addition of benzyl chloride. The reaction

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(19) The infrared and ultraviolet spectra resemble the respective biferrocenyl spectra.

(20) S. I. Goldberg, D. W. Mayo, and J. A. Alford, *J. Org. Chem.*, **28**, 1708 (1963). The appearance of the substituted ring protons at a lower field is explained by the mutual shielding effect of the directly bonded ferrocene nuclei on all protons present.

(21) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

(22) M. Vogel, M. Rausch, and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957).

(23) Alkylated cyclopentadienyl ring protons in ferrocene appear as singlets: Y. Nagar, J. Hooz, and R. A. Benkeser, *Bull. Chem. Soc. Japan*, **37**, 53 (1964).

mixture turned red and warmed up to 50°. After the reaction was complete, the mixture was extracted with aqueous sodium carbonate. Acidification of the extracts gave 2.4 g. of dark red crystals. The infrared spectrum of this acid resembles the spectrum of an authentic sample of mixed ferrocenecarboxylic and 1,1′-ferrocenedicarboxylic acids.

The material which was insoluble in the base gave by sublimation 6.0 g. (16.2%) of ferrocene. In the sublimation residue remained 20.5 g. of red crystalline poly(ferrocenyl ketone). The poly(ferrocenyl ketone) was extracted with benzene and then with chloroform.

The benzene-soluble poly(ferrocenyl ketone), 10 g., decomposes above 200°, av. mol. wt. 1114, has infrared and ultraviolet spectra very similar to the spectra of an authentic sample of diferrocenylketone.[24] The infrared spectrum (Nujol) has strong bands at 1625, 1290, 1110, 1065, 1000, 850–810, 807, and 772 cm.$^{-1}$. Weaker bands are at 3120, 1200, 1050, 1025, 900, and 700 cm.$^{-1}$. The ultraviolet spectrum (in $CHCl_3$) has a wide absorption maximum between 250 and 280 mμ ($E_{1\,cm}^{1\%}$ 4.18 × 10^2) and an absorption maximum at 365 mμ ($E_{1\,cm}^{1\%}$ 89.5). Low voltage mass spectrometry gave only a mass peak corresponding to the molecular ion of diferrocenyl ketone (*m/e* 398).

The 70-e.v. mass spectrum has additional peaks which correspond to the following fragment ions: $C_5H_5Fe^{56}$ (*m/e* 121), C_5H_4-C_5H_4 (*m/e* 128), C_5H_4–C_5H_5 (*m/e* 129), $Fe^{56}C_5H_3CO$ (*m/e* 147), $C_5H_5Fe^{56}C_5H_4CO$ (*m/e* 213), $C_5H_5FeC_5H_4COC_5H_4$ (*m/e* 277), $C_5H_4Fe^{56}C_5H_4C_5H_4Fe^{56}$ or $C_5H_5Fe^{56}C_5H_4COC_5H_3CO$ (*m/e* 304), $C_5H_5Fe^{56}C_5H_4C_5H_4Fe$ (*m/e* 305), and $C_5H_4Fe^{56}C_5H_4COC_5H_4Fe^{56}$-$C_5H_4CO$ (*m/e* 424). Analysis showed that the carbon–hydrogen–oxygen–iron ratio is 11.0:10.5:0.8:0.8.

The chloroform-soluble portion (7 g., decomposes above 200°) has an infrared spectrum (Nujol) similar to that for the benzene-soluble ketone, except that the 1110- and 1000-cm.$^{-1}$ bands are weaker. Analysis showed that carbon–hydrogen–oxygen–iron ratio is 11.0:10.2:1.4:0.9.

In the insoluble residue remained 3.5 g. of the polyketone.

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[24] An authentic sample of diferrocenyl ketone was prepared by reacting ferrocene with phosgene and aluminum chloride.

Synthetic Utility of Alkali Metal Adducts of Diaryl Ketones

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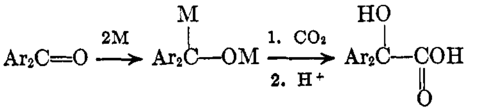
Reaction conditions for the preparation and use of dimetallo adducts (II) of benzophenones have been investigated. Two solvents (ammonia and dimethoxyethane), the three common alkali metals, and several substituted ketones were employed to prepare these organometallic reagents (II). Included in the discussion of uses of these reagents are new preparations of benzoins and benzilic acid esters, further studied preparations of glycols and benzilic acids, and a brief summary of other preparations previously reported.

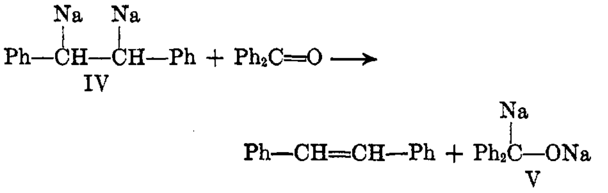
For an investigation[2] of the benzilic ester rearrangement a synthesis of this type of ester labeled with C^{14} was needed. One possibility (which could utilize readily available C^{14}-labeled carbon dioxide) conceived for synthesis (1) of the corresponding benzilic acid (III) involved carbonation of the dimetallo adduct II produced by reaction of a diaryl ketone (I) with alkali metal (M). To evaluate this possibility a fairly extensive study was made of the optimum conditions for preparation of, and the various possible reactions of, these metallo adducts (II). While our investigation of the benzilic ester rearrangement was in progress, Hamrick and Hauser reported certain other synthetic utilizations of adducts like II.[3] Our study, which complements that of Hamrick and Hauser, and a brief summation of earlier studies are recorded here to indicate that these adducts are conveniently accessible reagents of utility in several types of preparations.[4]



$$\mathrm{Ar_2C{=}O} \xrightarrow{2M} \mathrm{Ar_2}\overset{M}{\overset{|}{\mathrm{C}}}\mathrm{{-}OM} \xrightarrow[2.\ H^+]{1.\ CO_2} \mathrm{Ar_2}\overset{HO}{\overset{|}{\mathrm{C}}}\mathrm{{-}}\underset{O}{\underset{\|}{\mathrm{C}}}\mathrm{OH} \qquad (1)$$

I II III

The disodio adducts (II, M = Na) were first formed by Schlenk and co-workers[5] using ether as solvent and later by Wooster[6] using liquid ammonia. Brook, Cohen, and Wright[7] effected a novel preparation of the disodio adduct of benzophenone (V) by transfer of sodium from the analogous adduct of stilbene (IV).



$$\mathrm{Ph{-}}\overset{Na}{\overset{|}{\mathrm{C}}}\mathrm{H{-}}\overset{Na}{\overset{|}{\mathrm{C}}}\mathrm{H{-}Ph} + \mathrm{Ph_2C{=}O} \longrightarrow \mathrm{Ph{-}CH{=}CH{-}Ph} + \mathrm{Ph_2}\overset{Na}{\overset{|}{\mathrm{C}}}\mathrm{{-}ONa} \qquad (2)$$

IV V

Benzilic Acid Synthesis.—The usual time required for adduct II formation in ether was reported to be several days.[5] Since facile formation of other types of organometallics by direct reaction of sodium metal in 1,2-dimethoxyethane has been reported,[7,8] this was the first solvent we evaluated as a medium for reaction of alkali metals and diaryl ketones. In exploratory experiments, mixtures of benzophenone and 2 equiv. of alkali metal in dimethoxyethane were allowed to react and then treated with carbon dioxide (eq. 1). Some of the results are summarized in Table I.

When sodium was employed as a suspension, the densely colored (purple) adduct formed rapidly and, after carbonation, a 60–65% yield of benzilic acid was obtained. The adduct formed rapidly even when the metal was present in small chunks; the yield of benzilic acid was approximately the same (45–60%)

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[1] Union Carbide Nuclear Corp. Fellow, 1958–1959.

[2] J. F. Eastham and S. Selman, *J. Org. Chem.*, **26**, 293 (1961).

[3] P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 493 (1959).

[4] Accessibility of adducts II stems from the variety of syntheses available for preparation of diaryl ketones, *e.g.*, Friedel–Craft reactions, polyphosphoric acid and hydrogen fluoride acylations.

[5] W. Schlenk and T. Weickel, *Ber.*, **44**, 1183 (1911); W. Schlenk and A. Thal, *ibid.*, **46**, 2840 (1913); W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *ibid.*, **47**, 473 (1914); W. Schlenk and E. Bergmann, *Ann.*, **464**, 26 (1928).

[6] C. B. Wooster, *J. Am. Chem. Soc.*, **50**, 1388 (1928); see also C. A. Kraus and G. F. White, *ibid.*, **45**, 771 (1923).

[7] A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953).

[8] N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).