

Synthesis of Mono- and Disubstituent of Ferrocene and/or Biferrocene Derivatives

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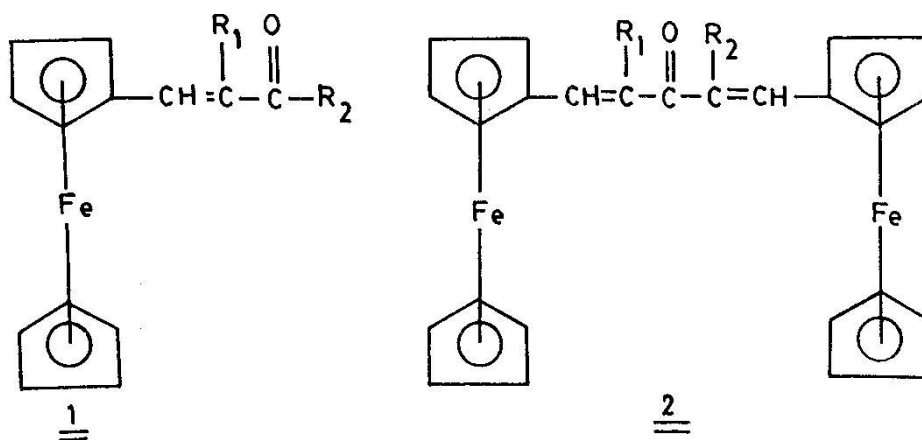
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Summary: Ferrocylidene ketones (1) and biferrocylidene ketones (2) were prepared by condensation of formyl ferrocene with ketones. Biferrocene (5-10) derivatives were obtained by treatment of lithioferrocene with phthalic anhydride, methyl benzoate and/or phenyl iodide respectively. The PMR and IR of these compounds are described.

Ferrocylidene ketones were prepared by condensation of formyl ferrocene with acetophenone by means of alkali has been well documented [1]. Ferrocylidene ketones (1a-c) biferrocylidene ketones (2a,b) were prepared by stirring a solution of formyl ferrocene in ethanol, ketones namely acetone, ethyl methyl ketone and/or diethyl ketone in the presence of sodium

hydroxide at 5°C. The structures of compounds (1) and (2) were inferred from their IR and PMR spectra as shown in Table 1.

On the other hand biferrocylidene ketones (2a,b) were prepared by heating at the boiling point the mixture of formylferrocene in ethanol, ketones namely acetone and/or ethyl methyl



- a) $\text{R}_1 = \text{H}$; $\text{R}_2 = \text{CH}_3$
 b) $\text{R}_1 = \text{H}$; $\text{R}_2 = -\text{CH}_2-\text{CH}_3$
 c) $\text{R}_1 = \text{CH}_3$; $\text{R}_2 = \text{CH}_2-\text{CH}_3$

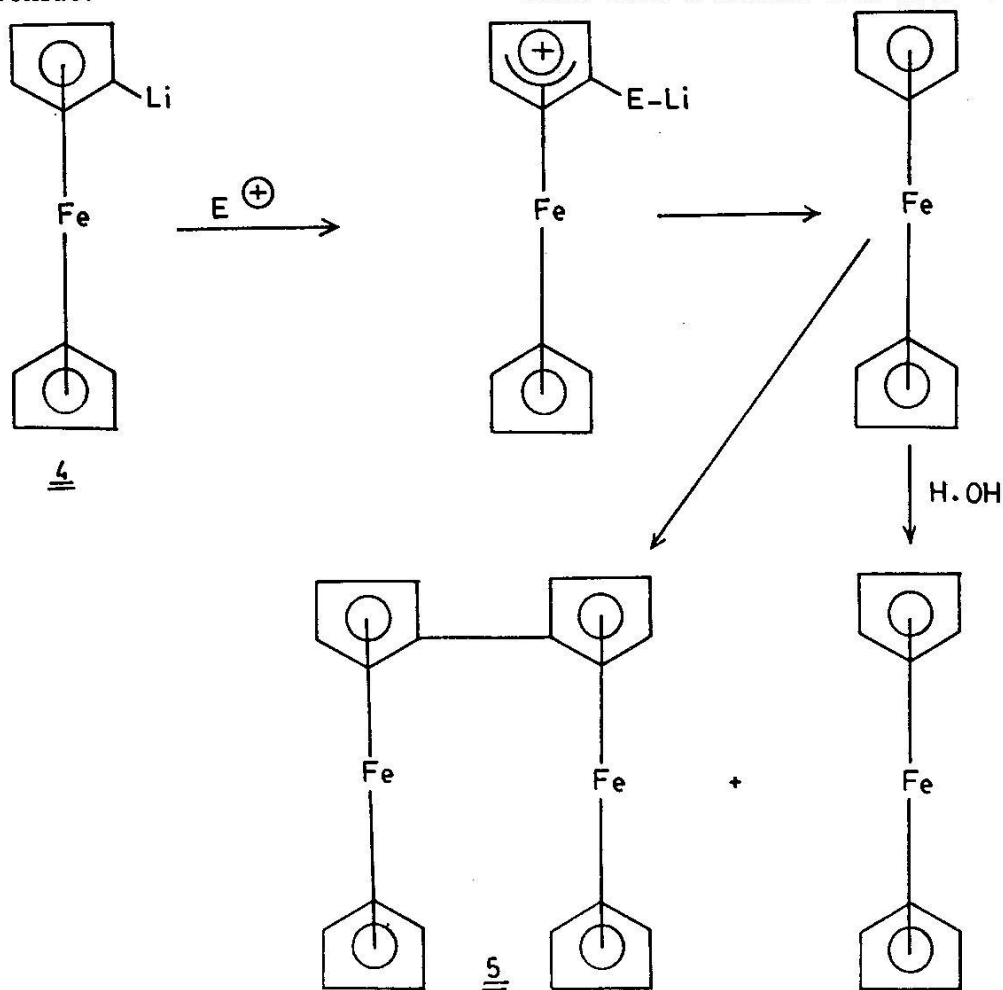
- a) $\text{R}_1 = \text{H}$; $\text{R}_2 = \text{H}$
 b) $\text{R}_1 = \text{H}$; $\text{R}_2 = \text{CH}_3$

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ketone in presence of sodium hydroxide. Also the compound (2a) was obtained if we take a mixture of mono ferrocylidene acetone (1a), formyl ferrocene and sodium hydroxide in ethanol and refluxed for 2 hours.

Biferrocene was first detected in the reaction products of trialkyl chlorosilanes with lithiated ferrocene [2,3]. Since the biferrocene has been synthesised using Ullmann coupling reaction of diferrocenyl mercury with silver, ferrocenyl magnesium bromide with cobaltous chloride, and other methods [4,5]. Korshak and co-workers [6] obtained polyferrocene by heating ferrocene with *t*-butyl hydroxide.

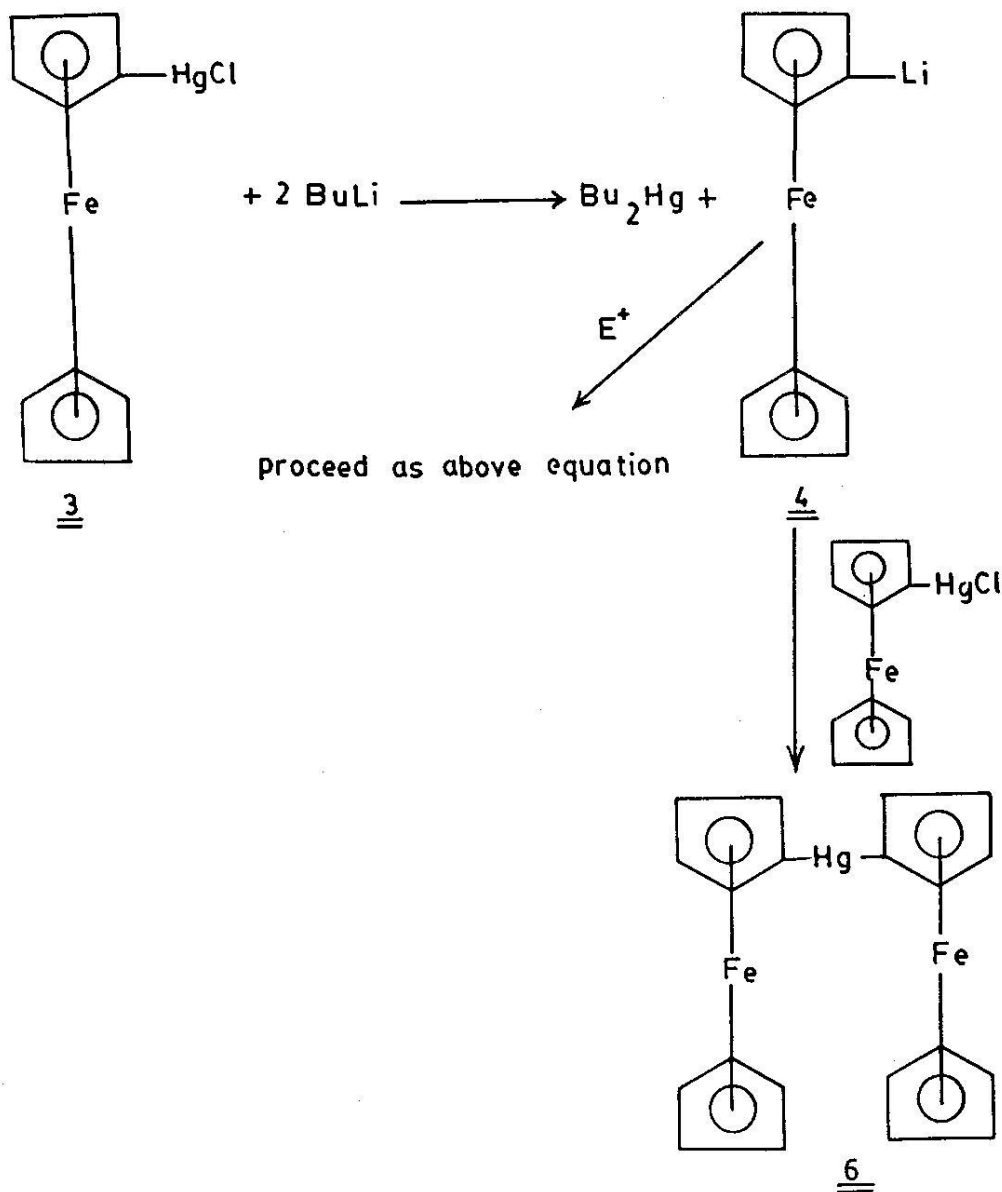
Rausch [7] reported that polyferrocene was produced in the thermal decomposition of mercury-bridge ferrocenes. Nemureyanov and co-workers [8] obtained some polyferrocene in an Ullmann coupling where bromo and 1,1'-dibromoferrocene were used. Now we report the preparation of some biferrocene derivatives from lithioferrocene. The ferrocenyl mercury chloride (3) was treated with *n*-butyl lithium at room temperature for two hours under nitrogen atmosphere to give lithioferrocene (4). The lithioferrocene was condensed with phthalic anhydride or methyl benzoate to give 60% ferrocene, 15% biferrocene (5) and 10% biferrocenyl mercury (6). On the other hand treatment of lithioferrocene



which was obtained from lithiation of ferrocene with *n*-butyl lithium with phthalic anhydride or methyl benzoate gave 63% ferrocene and 20% biferrocene (5).

The formation of biferrocene from lithiated ferrocene in the presence of electrophiles (phthalic anhydride or methyl benzoate) to displace all lithium of lithiated ferrocene, may be accounted for by an initial formation of ferrocene adduct, decomposed to give ferrocenyl radicals and coupled to form biferrocene as in equations.

Ferrocenyl radical coupling was proposed earlier [4,5,9,10] they obtained biferrocene by adding cobaltous chloride to metalation of ferrocene. When ferrocenyl lithium was obtained from ferrocenyl mercury chloride and treated with phthalic anhydride or methyl benzoate, there was obtained in addition of 60% ferrocene, 15% biferrocene (5) and 10% biferrocenyl mercury (6). Although this reaction could be explained by metal halogen interconversion [11] to give lithioferrocene followed by Wurtz-



Fitting reaction to give observed products.

Ferrocenyl coupling by the addition of organic halides to lithioferrocene was first indicated when biferrocene was isolated in very small amounts of lithioferrocenes and tri-alkyl halosilane reaction products [2,3]. We have found that coupling ferrocenyl group in the reactions of lithioferrocene and organic halides is general. Thus from the reaction products of lithioferrocenes with phenyl iodide we could separate 24.8% ferrocene, 10.36% 1-phenyl ferrocene (7), 2.5% 1,1'-diphenyl ferrocene (8),

1.6% 1-phenyl ferrocenyl-1-ferrocene (9) and 2% bis[1(1'-phenyl ferrocenyl)] (10).

The structures of compounds (7-10) were inferred from their IR and PMR spectra as shown in Table 1.

Experimental

The infrared absorption spectra were determined using Perkin Elmer spectrophotometer Model 577 using KBr pallet technique. The PMR spectra were determined using a Varian VN 1009 (S-60T) instrument, using CDCl_3

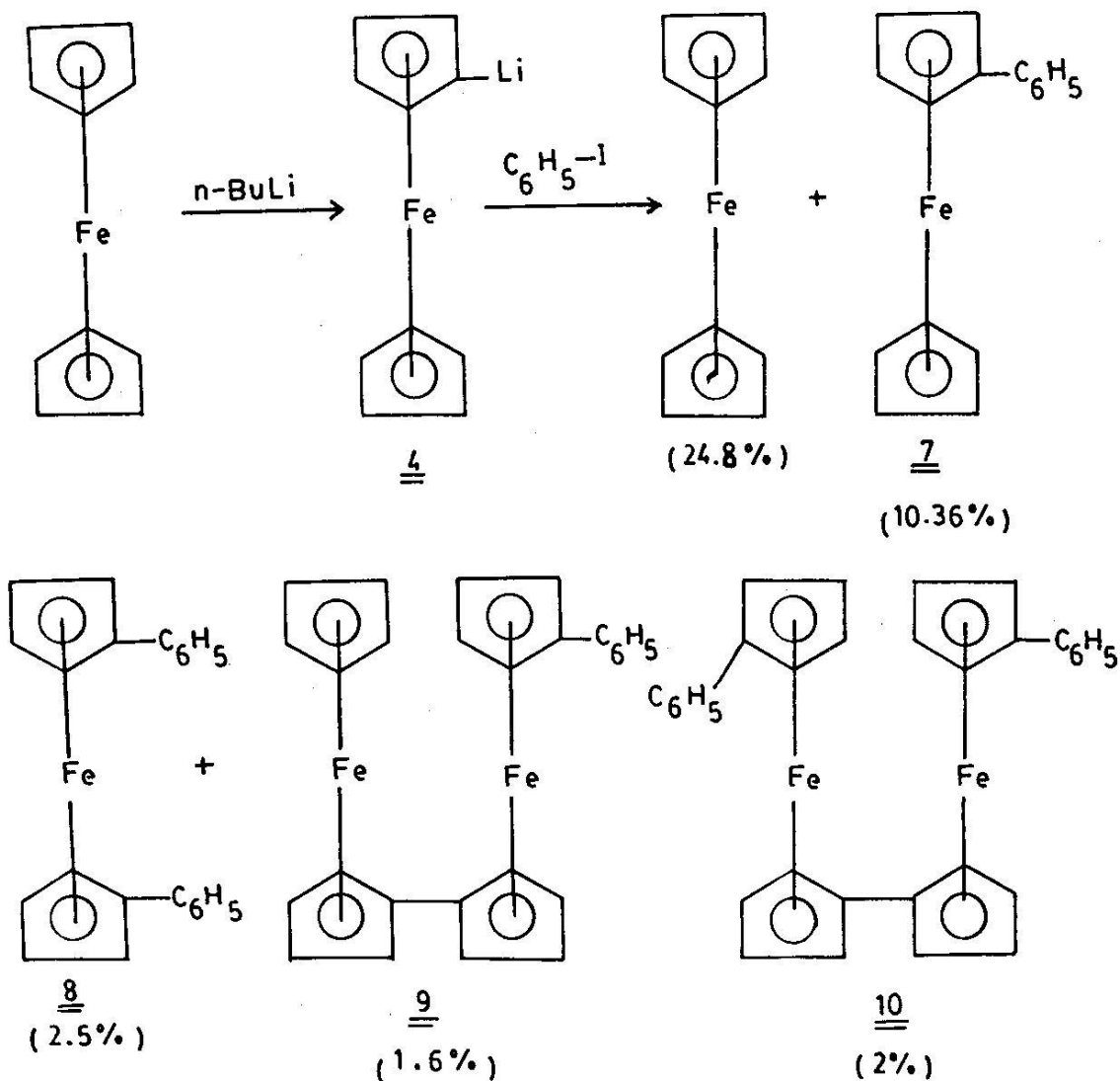


Table-1: Physical and Spectral data of adducts

Compd.	M.P. °C (colour)	Mol. Formula (M.Wt.)	Analysis % Calc. Found	I.R.	PMR
(1a)	85 (red)	C ₁₄ H ₁₄ 0Fe (254)	C: 66.14 H: 5.51	66.16 5.72 νC=O at 1645 cm ⁻¹ νC=C at 1610, 1605 cm ⁻¹ and CH of ferrocene at 1085- 1120 cm ⁻¹	δ 2.3 (<u>s</u> for 3H of -C-CH ₃) δ 3.96-4.12 (<u>m</u> for 5H of unsub. ferrocene ring), δ 4.17-4.51 (<u>m</u> for 4H of sub. ferrocene ring) and 6.16, 6.45 & 7.27, 7.56 (two <u>d</u> for 4H of two -CH=CH-)
(1b)	105 (red)	C ₁₅ H ₁₆ 0Fe (268)	C: 67.16 H: 5.97	67.10 6.04 νC=O at 1640 cm ⁻¹ , νC=C at 1610 cm ⁻¹ and CH of ferro- cene at 1110-1120 cm ⁻¹	δ 1.08-1.34 (<u>t</u> for 3H of -CH ₂ -CH ₃), 2.46-2.89 (<u>q</u> for for 2H of -CH ₂ -CH ₃), 3.96- 4.21 (<u>m</u> for 5H of unsub. ferrocene ring), 4.34-4.65 (<u>m</u> for 4H of sub. ferrocene ring) and 6.26, 6.34 & 7.29, 7.38 (two <u>d</u> for 2H or -CH=CH-)
(1c)	72 (red)	C ₁₆ H ₁₈ 0Fe (282)	C: 68.08 H: 6.38	68.12 6.22 νC=O at 1635 cm ⁻¹ , νC=C at 1610 cm ⁻¹ , and CH of ferro- cene at 1085-1115 cm ⁻¹	δ 1.08-1.20 (<u>t</u> for 3H of -CH ₂ -CH ₃), 2.04 (<u>s</u> for 3H of -CH ₃), 2.63-3.00 (<u>q</u> for 2H of -CH ₂ -CH ₃), δ 3.96-4.17 (<u>m</u> for 5H of unsub. ferrocene ring), δ 4.46-4.55 (<u>m</u> for 4H of sub. ferrocene ring) and δ 7.34 (<u>S.B.</u> for 1H of -CH=C).
(2a)	202 (red)	C ₂₅ H ₂₂ 0Fe ₂ (450)	C: 66.66 H: 4.88	66.34 5.02 C=O at 1630 cm ⁻¹ , C=C at 1600-1590 cm ⁻¹ and CH of ferrocene at 1090- 1120 cm ⁻¹	3.85-4.12 (<u>m</u> for 10H of unsub. ferrocene ring), 4.27-4.51 (<u>m</u> for 8H of sub. ferrocene ring) and 6.34, 6.59 & 7.27, 7.46 (two <u>d</u> for 4H of two -CH=CH-)
(2b)	205 (red)	C ₂₆ H ₂₄ 0Fe ₂ (464)	C: 67.24 H: 5.17	67.32 5.23 νC=O at 1635 cm ⁻¹ , νC=C at 1610-1590 and νCH of ferro- cene at 1085-1120	δ 2.03 (<u>s</u> for 3H of -CH ₃), δ 3.9-4.12 (<u>m</u> for 10 H of unsub. ferrocene ring), δ 4.21-4.34 (<u>m</u> for 8H of

Table-1: cont..

Compd.	M.P. °C (colour)	Mol. Formula (M.Wt.)	Analysis % Calc. Found		I.R.	PMR
					cm^{-1}	ferrocene ring), 6.34-6.59 (\underline{d} for 2H of $-\underline{\text{CH}}=\underline{\text{CH}}-$) and δ 7.1 ($\underline{\text{S-B}}$ for 1H of CH_3 C= $\underline{\text{CH}}-$)
(7)	110-111 (orange)	$\text{C}_{16}\text{H}_{14}\text{Fe}$ (262)	C: 73.28 H: 5.34	73.50 5.26	$\nu\text{C}=\text{C}$ at 1610-1600 cm^{-1} cm^{-1} and νCH of ferrocene at 1080-1120 cm^{-1}	δ 3.85-3.96 (\underline{m} for 5H of unsub. ferrocene ring), δ 4.31-4.5 (\underline{m} for 4H of sub. ferrocene ring) and 7.09-7.42 (\underline{m} for 5H of aromatic protons)
(8)	150-151 (orange)	$\text{C}_{22}\text{H}_{18}\text{Fe}$ (338)	C: 78.10 H: 5.34	78.34 5.22	$\nu\text{C}=\text{C}$ at 1610-1585 cm^{-1} and νCH of ferrocene at 1085-1115 cm^{-1}	δ 4.21-4.6 (\underline{m} for 8H of ferrocene ring) and 7.3-7.4 (\underline{m} for 10 H of aromatic protons).
(9)	85-88 (brown)	$\text{C}_{26}\text{H}_{22}\text{Fe}_2$ (446)	C: 69.95 H: 4.93	70.13 5.02	$\nu\text{C}=\text{C}$ at 1610-1590 cm^{-1} and νCH of ferrocene at 1080-1115 cm^{-1}	δ 3.80-3.96 (\underline{m} for 5H of unsub. ferrocene ring) 4.01-4.12 (\underline{m} for 12H of sub. ferrocene ring) and 7.20-7.40 ($\underline{m-b}$ for 5H of aromatic protons).
(10)	98-103 (brown)	$\text{C}_{32}\text{H}_{26}\text{Fe}_2$ (522)	C: 73.56 H: 4.98	73.72 4.63	$\nu\text{C}=\text{C}$ at 1610-1585 cm^{-1} and νCH of ferrocene at 1080-1120 cm^{-1}	δ 4.0-4.35 (\underline{m} for 16H of ferrocene ring) and 7.22-7.48 (\underline{m} for 10 H of aromatic protons).

as a solvent and TMS as internal standard.

General procedure for the formation of ferrocylidene ketones (1) and biferrocylidene ketones (2)

To a stirred solution of 2.14 gm (0.01 mol.) formyl ferrocene in 20 ml of 95% ethanol, cooled to 5°, (0.01

mole) of ketone namely acetone, ethyl methyl ketone and/or diethyl ketone was added. A solution of sodium hydroxide (1 gm, 0.015 mol. in 6 ml of water) was added dropwise over a period of one-half hour. After stirring for 10 hours at 5°, the reaction mixture was diluted with cold 100 ml hydrochloric acid (1% aqueous solution).

The mixture was extracted three times with 50 ml ether. The extract was washed three times with 200 ml water then dried over anhydrous magnesium sulphate; slow evaporation of the ether left residue. The organic residue was chromatographed on silica gel. Elution with hexane (300ml) gave monoferrocylidene ketones (1a-c), yield (70-74%) which recrystallized from hexane and showed single spot on thin-layer chromatography. Elution with hexane-benzene mixture (3:1, 500 ml) yielded biferrocylidene ketones (2a,b), yield (10-20 %) which recrystallized from hexane and showed single spot on thin-layer chromatography. Further elution with chloroform (60 ml) yielded (10-30%) of unreacted formyl ferrocene.

Preparation of biferrocylidene (2a,b)

Heating at the boiling point of the mixture 2.14 gm (0.01 mol.) of formyl ferrocene in 20 ml of 95% ethanol, (0.02 mol.) of ketone namely acetone and/or ethyl methyl ketone in the presence of sodium hydroxide (1 gm, 0.015 mol in 6 ml of water) for 6 hours. The reaction mixture was worked up as described before and gave biferrocylidene ketone (2a,b) (yield 60-70%).

Conversion of ferrocylidene ketone (1a) into biferrocylidene ketone (2a)

A mixture of monoferrocylidene acetone(1a)(0.001 mol.) formyl ferrocene (0.001 mol.) sodium hydroxide (2 ml. 1% aqueous solution) and 5 ml ethanol was refluxed for two hours. The reaction mixture was worked up as described before and gave biferrocylidene ketone (2a) (0.369 gm; 82%).

Preparation of biferrocene (5) and biferrocenyl mercury (6)

To a solution of lithioferrocene (4) which was prepared as the following [stirring ferrocenyl mercury chloride

(0.421 gm, 0.001 mol.), n-butyl lithium 17 ml (0.025 mol., of 1.5 M solution) of n-butyl lithium in hexane and 10 ml dry ether for two hours at room temperature under an atmosphere of dry nitrogen free oxygen]. Phthalic anhydride or methyl benzoate (0.001 mol.) as suspension or solution in 10 ml dry ether was added dropwise through half an hour. The stirring was continued to ten hours, reflux for one hour, cooled, then 15 ml water was added. Extract three times with 50 ml ether, the extract was washed two times with 200 ml (10% aqueous sodium hydroxide solution), washed four times with 200 ml water, then dried over dry magnesium sulphate. The residue obtained after evaporation dissolved in hexane and the yellow undissolved part crystallized from chloromethylene and gave biferrocenyl mercury (6) (0.052 gm 10%) which decompose at 245-247° (lit [12] 248-249°). The hexane solution was concentrated and chromatographed on alumina. Elution with 150 ml hexane gave ferrocene which melted at 171-173° (0.11 gm 60%). Further elution with 200 ml hexane-benzene mixture (80/20) gave biferrocene (5) (0.05 gm, 15%) which melted at 238-240° (lit [13] 239-240°).

Preparation of biferrocene (5)

Lithioferrocene was obtained in 10 ml dry ether from 0.186 gm (0.001 mol.) of ferrocene, and 17 ml (0.025 mol. of 1.5 M solution) of n-butyl lithium, then phthalic anhydride or methyl benzoate (0.001 mol.) in 10 ml dry ether was added within 30 minutes. The mixture was stirred for ten hours and then poured into ice-water (5 gm of ice and 10 ml water). The reaction mixture worked up as described before, and gave ferrocene which melted at 171-172° (0.11 gm, 60-63%) and biferrocene (5) which melted at 238-240° (0.074 gm 20%).

Reaction of lithioferrocene with phenyl iodide

Lithioferrocene was prepared in ether-tetrahydrofuran 50 ml (1/1 V) from 26 ml (0.038 mol of 1.5 M solution) of n-butyl lithium and 3.33 gm of ferrocene (0.017 mol.). Then added 3.4 gm of phenyl iodide (0.016 mol.) in 30 ml tetrahydrofuran through 90 minutes. The reaction mixture was stirred for ten hours, keep overnight and then poured into ice and water (50 gm of ice and 100 ml water), extract two times with 200 ml ether-benzene mixture (1/1 V), washed with water and dried over anhydrous magnesium sulphate, solvent was removed with evaporation the residue extracted with boiling hexane several times. Both the residue and hexane solution were chromatographically separated over silica gel. Elution of the hexane solution after concentration by 300 ml hexane gave ferrocene (0.82 gm, 24.84% m.p. 173°), further elution by 100 ml hexane-benzene mixture (80/20 V) gave 1-phenyl ferrocene (7) (0.342 gm, 10.36%, crystallized from hexane) and 1',1-diphenyl ferrocene (8) (0.085 gm; 2.5%, crystallized from hexane). On the other hand elution of the residue by hexane-benzene mixture (1/1 V) gave 1'-phenyl-1-ferrocenyl ferrocene (9) (0.027 gm, 0.6%, crystallized from benzene-hexane mixture and bis[1(1'-phenyl ferrocenyl)] (10) (0.066 gm, 2%, crystallized from benzene-hexane mixture).

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