903. *Ferrocene Derivatives. Part XI.*[1] *Azoferrocenes.*[2]

By G. R. Knox and P. L. Pauson.

Successive treatment with methyl- or phenyl-lithium and ferrous chloride converts diazocyclopentadiene into 1,1′-dimethyl(or phenyl)azoferrocene, reducible to 1,1′-diaminoferrocene. Extension of this synthesis to monophenylazoferrocene is described.

Aminoferrocene has been prepared by two routes. Nesmeyanov *et al.*[3] obtained it by metallation of ferrocene with butyl-lithium followed by treatment with *O*-benzylhydroxylamine (Kochetkov reaction). Although the first step is known [4] to lead to a mixture of mono- and di-substitution products, only the monoamine has been reported as formed by this procedure. Arimoto and Haven [5] prepared the same amine by Curtius degradation of ferrocenecarboxylic acid. An earlier attempt [6] to employ this method for the preparation of 1,1′-diaminoferrocene (I; R = H) had yielded the intermediate urethanes (I; R = CO·OEt and CO·O·CH_2Ph), but attempts to convert them into the free amines caused complete destruction.

Aminoferrocene proved very sensitive to oxidation and was completely destroyed by nitrous acid, no diazonium salt being detectable.[3] Moreover, it was shown in Part II [7] that, unlike other aromatic systems of comparable reactivity, ferrocene fails to couple with diazonium salts but, instead, undergoes arylation by such salts.

Extension of the reactions described in the preceding paper [1] to diazocyclopentadiene [8] (II) has now provided a direct route to alkyl- and aryl-azoferrocenes, inaccessible by the more conventional methods referred to above; and reduction of these azo-derivatives then afforded both the mono- and the 1,1′-diamino-derivative.

Organometallic compounds are known to add to diazomethane, giving the corresponding metal salts of azo-compounds, $M^{+-}CH_2 \cdot N{:}NR$, which on hydrolysis commonly yield substituted hydrazones, $CH_2{:}N \cdot NHR$.[9]

As expected, phenyl-lithium added similarly to diazocyclopentadiene. The initial product, the phenylazocyclopentadienyl ion (cf. III; R = Ph), was treated with ferrous chloride, affording diphenylazoferrocene (IV; R = Ph). Use of methyl-lithium similarly afforded dimethylazoferrocene (IV; R = Me).

Use of a mixture of the lithium salt (III; R = Ph) with unsubstituted cyclopentadienyl-lithium afforded the monosubstituted derivative, phenylazoferrocene (V).

When this product (V) was hydrogenated over Adams catalyst in methanol uptake of hydrogen was only ~ 1 mol. The resultant orange solution rapidly reverted to the

[1] Part X, preceding paper.

[2] For a preliminary communication see Knox, *Proc. Chem. Soc.*, 1959, 56.

[3] Nesmeyanov, Perevalova, Golovnya, and Shilovtseva, *Doklady Akad. Nauk S.S.S.R.*, 1955, **102**, 535.

[4] Benkeser, Goggin, and Schroll, *J. Amer. Chem. Soc.*, 1954, **76**, 4025.

[5] Arimoto and Haven, *J. Amer. Chem. Soc.*, 1955, **77**, 6295.

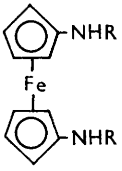
[6] Rosenblum, Thesis, Harvard, 1953.

[7] Broadhead and Pauson, *J.*, 1955, 367.

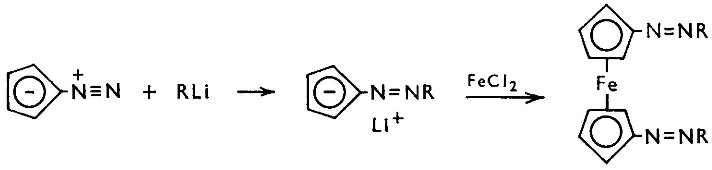
[8] Doering and De Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

[9] Kharasch and Reinmuth, "Grignard Reactions of Non-metallic Substances," Constable, London, 1954, p. 1223.

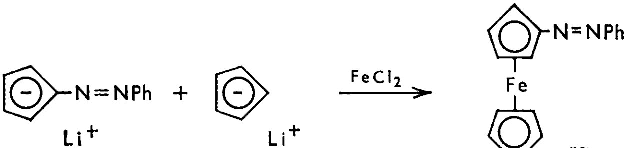
purple colour of the starting material (V) in air. On account of its extreme sensitivity to air, no attempt was made to isolate the phenylhydrazoferrocene which is undoubtedly present in these solutions. Use of acetic acid as solvent permitted hydrogenation of the azo-compound (V) to aminoferrocene. This was identified by its melting point and by conversion into the methoxycarbonylamino-derivative, identical with a sample kindly supplied by Dr. K. Schlögl.



(I)



(II) (III) (IV)



(V)

The behaviour of 1,1'-diphenylazoferrocene (IV) on hydrogenation in methanol and acetic acid was analogous. In the latter solvent, 1,1'-diaminoferrocene was undoubtedly obtained since treatment of the crude product with the appropriate alkyl chlorocarbonate yielded the urethanes (I; R = CO·OMe, CO·OEt, and CO·O·CH_2Ph), of which the last two agreed in m. p. with the samples previously reported.[6] In the first case, the presence of methyl carbanilate was also demonstrated and, together, these products provide good confirmation of the structure of the initial azo-compound (IV; R = Ph). The dimethylazo-compound (IV; R = Me) was reduced similarly and in this case complete evaporation of the filtered reaction mixture left the diamine as a yellow solid. Owing to its extreme sensitivity to air it has not been characterised.

EXPERIMENTAL

For general remarks see preceding paper.

1,1'-Diphenylazoferrocene.—Diazocyclopentadiene, prepared by the method of Doering and De Puy,[8] was distilled three times and used immediately. The yields after such purification varied between 20% and 40%. Diazocyclopentadiene (5·25 g., 0·06 mole) in ether (40 ml.) was added dropwise during 0·5 hr. to a solution of phenyl-lithium (0·06 mole) in ether (100 ml.), stirred at −30° under nitrogen. The resulting scarlet precipitate was treated with ferrous chloride [from ferric chloride (9·8 g., *ca.* 0·06 mole)] and tetrahydrofuran (45 ml.), producing an immediate change in colour to dark purple. After 14 hr. the temperature of the mixture had risen to 20°, and a black precipitate had been produced. The mixture was added to water (150 ml.), and the ether layer removed, washed with water (4 × 100 ml.), and dried (Na_2SO_4). The contents of the reaction vessel and the aqueous layer were extracted with benzene (5 × 150 ml.), and the deep red extracts washed, dried, evaporated, and combined with the residue from the evaporation of the ether extracts. The oily residue was dissolved in acetone, evaporated to about 200 ml., and cooled, yielding violet-black needles of *1,1'-diphenylazoferrocene* (6·8 g.), m. p. 170°. Concentration of the liquors to 20 ml. gave a further quantity (2·6 g.; total yield 80%) of crystalline material having a similar m. p. A sample for analysis was purified by chromatography on alumina in benzene, and by recrystallisation six times from pure acetone to a constant m. p. 183—185° (Found: C, 67·0; H, 4·9; N, 14·1. $C_{22}H_{18}FeN_4$ requires C, 67·0; H, 4·6; N, 14·2%).

Phenylazoferrocene.—Cyclopentadienyl-lithium was prepared in ether (250 ml.) from bromobenzene (43·2 g., 0·275 mole), lithium (4·07 g., 0·59 g.-atom), and cyclopentadiene (16·3 g., 0·25 mole). It was then added to phenylazocyclopentadienyl-lithium, prepared by stirring diazocyclopentadiene (7·65 g., 0·083 mole) and phenyl-lithium [from bromobenzene (14·4 g., 0·092 mole) and lithium (1·36 g., 0·195 g.-atom)] in ether (120 ml.) at −30° for 45 min. All operations were conducted under nitrogen. The mixture was left for 0·5 hr., and ferrous chloride [from ferric chloride (35 g., 0·215 mole)] in tetrahydrofuran (50 ml.) then added. Stirring was continued for 14 hr., while the temperature rose to 23°. The mixture was added to ice-water (500 ml.). The ether layer was removed and combined with ether extracts (5 × 250 ml.), dried (Na_2SO_4), and evaporated, and the sticky residual solid dissolved in ligroin (b. p. 40—60°). The solution was chromatographed on alumina (70 × 5·5 cm.), ligroin (b. p. 40—60°) developing a total of ten coloured bands, of which the very minute bands IV, V, VII, VIII, and IX were rejected. Band I yielded ferrocene (19·0 g., 82·8% based on cyclopentadiene). Band II, also yellow-orange, gave an oil (0·79 g.), which solidified after distillation at 88—90° (bath)/0·05 mm., giving azobenzene, m. p. 65° with previous softening (mixed m. p. 67—68°) (Found: C, 78·8; H, 5·7. Calc. for $C_{12}H_{10}N_2$: C, 79·1; H, 5·5%). A separate experiment suggested that this product arises from toluene-*p*-sulphonyl azide, present as a contaminant in the diazocyclopentadiene, by reaction with phenyl-lithium. Band III, a very pale yellow, yielded an orange oil (0·89 g.) from which biphenyl was sublimed. Band VI on elution, concentration, and cooling, gave violet needles of *phenylazoferrocene* (3·9 g., 5·5% based on cyclopentadiene) which, recrystallised from ligroin, had m. p. 109—110° (Found: C, 65·9; H, 5·1; N, 9·6. $C_{16}H_{14}FeN_2$ requires C, 66·2; H, 4·9; N, 9·7%). The last band was extruded from the top of the column and extracted from the alumina with acetone, from which 1,1′-diphenylazoferrocene (2·4 g., 14·65%), m. p. 172—180°, crystallised.

1,1′-Dimethylazoferrocene.—Diazocyclopentadiene (2·76 g., 0·03 mole) in ether (10 ml.) was added dropwise to methyl-lithium (0·03 mole) in ether (25 ml.), stirred at room temperature under nitrogen. Ferrous chloride [from ferric chloride (4·9 g., *ca.* 0·03 mole)] was added in tetrahydrofuran (50 ml.) after 0·25 hr. The mixture was stirred at room temperature for 14 hr., poured into water (50 ml.), and extracted with an additional 100 ml. of ether, and the combined ether extracts were washed with water (3 × 20 ml.) and dried (Na_2SO_4). The residue in the flask was treated with methanol (10 ml.) and water (50 ml.) and extracted with chloroform (2 × 50 ml.). The washed and dried chloroform extracts were evaporated, and the residues combined with the material from the ether extracts, giving a red oil (1·44 g.) which was passed in ligroin down a column of neutral alumina (30 × 3 cm.). The eluate yielded a red oil (1·05 g., 26%). *1,1′-Dimethylazoferrocene* was purified by recrystallisation from ligroin (b. p. 40—60°) and sublimation at 65°/0·005 mm., forming maroon-coloured needles, m. p. 101—103° (with previous softening) (Found: C, 53·5; H, 5·3; N, 21·0. $C_{12}H_{14}FeN_4$ requires C, 53·35; H, 5·2; N, 20·7%).

Hydrogenation of Phenylazoferrocene.—(a) *With Adams catalyst in glacial acetic acid.* Phenylazoferrocene (0·299 g.) in glacial acetic acid (20 ml.) was added to Adams catalyst (43·5 mg.; presaturated with hydrogen) in glacial acetic acid (5 ml.). Hydrogenation for 14 hr. at 21°/755 mm. resulted in the theoretical absorption (55 ml.). The orange solution was filtered and then evaporated under a reduced pressure of nitrogen, benzene (25 ml.) added, the brown benzene solution shaken with sodium hydrogen carbonate solution (4 × 50 ml.), then water (2 × 50 ml.), dried (Na_2SO_4), and evaporated to an orange oil (0·2 g.) which solidified on cooling. A fraction of the crude material (0·15 g.) was sublimed at 80°/0·0003 mm., yielding orange-yellow aminoferrocene (0·075 g.), m. p. 151—153° (lit.,[3] m. p. 153—155°).

(b) *With Adams catalyst in anhydrous methanol.* Phenylazoferrocene (0·295 g.) in methanol (35 ml.) was added to Adams catalyst (12·0 mg.; presaturated with hydrogen) in anhydrous methanol (4 ml.), and the flask surrounded by aluminium foil to keep out light. Hydrogen absorption had ceased after 40 hr. (40 ml. at 21°/760 mm.) and the solution had changed colour from violet to orange. On filtration the solution became violet at once, but could be re-hydrogenated without difficulty. Exposure to air for less than 5 sec. was sufficient to cause partial oxidation. A specimen of the hydrogenation mixture, when kept under hydrogen, was unchanged after 3 months and had deposited orange crystals of, presumably, phenylhydrazoferrocene.

Methoxycarbonylaminoferrocene.—Phenylazoferrocene (0·275 g.) in presence of Adams catalyst (12 mg. of known activity) was hydrogenated in acetic acid (10 ml.) overnight, resulting in the absorption of 45 ml. of gas (21°/750 mm.). The solution was filtered rapidly and evaporated *in vacuo* on a steam bath, the residue dissolved in dry benzene (10 ml.), and the solution saturated with nitrogen. Methyl chloroformate (1 ml.) was added, immediately producing a black precipitate. Sodium hydrogen carbonate solution (3 × 5 ml.) was added after 0·5 hr., and the benzene layer was separated, washed with sodium hydrogen carbonate solution (6 × 20 ml.) and water (4 × 50 ml.), dried, and evaporated. The residual yellow oil (0·325 g.) crystallised from water–methanol (0·5 : 2 ml.) at 0° as fine yellow needles (0·2 g., 80%), m. p. 126—138°. Further recrystallisation gave a sample, m. p. 138—142°, mixed m. p. with an authentic sample of methoxycarbonylaminoferrocene [10] 142—144°.

Hydrogenation of 1,1′-*Diphenylazoferrocene*.—(a) *With Adams catalyst in glacial acetic acid.* 1,1′-Diphenylazoferrocene (0·197 g.) in glacial acetic acid (5 ml.) and Adams catalyst (16·1 mg.) in acetic acid (5 ml.; pre-saturated with hydrogen) were stirred with hydrogen in the absence of light. Absorption was rapid (48 ml. at 21·3°/760 mm. in 2 hr.) (theor., 48·5 ml.). The solution had become orange, and yielded an orange oil on evaporation of the solvent at a reduced pressure of nitrogen. Air-free sodium hydrogen carbonate solution (5 ml.) and ether (20 ml.) were added to the residue, and the ether phase was removed, dried (Na_2SO_4) in the dark, and evaporated under a nitrogen atmosphere. The residual oil decomposed completely before crystallisation or sublimation could be effected.

(b) *With Adams catalyst in anhydrous methanol.* A suspension of Adams catalyst (*ca.* 10 mg.) in methanol (5 ml.) was saturated with hydrogen. 1,1′-Diphenylazoferrocene (0·197 g.), suspended in methanol (20 ml.), was added, and the mixture hydrogenated. Gas absorption was very slow and irregular. After 108 hr. the clear orange solution, presumably containing 1,1′-diphenylhydrazoferrocene was filtered by suction (with an immediate change in colour from orange to deep red) and evaporated to dryness (with an air leak), and the residual oil was passed in benzene down a column of alumina (30 × 3 cm.). A single pink-violet band yielded black crystals (0·0727 g.), m. p. 178—181° (from acetone), mixed m. p. with the starting material 180—182° (37% recovery).

Derivatives of 1,1′-*Diaminoferrocene*.—(a) 1,1′-*Di*(*benzyloxycarbonylamino*)*ferrocene*. The crude oily diamine obtained by hydrogenation of 1,1′-diphenylazoferrocene (0·788 g., 0·002 mole) in acetic acid, was dissolved in pyridine (30 ml.), and the apparatus and solution purged with nitrogen during 12 min., while benzyloxycarbonyl chloride (2·73 g., 0·016 mole, 100% excess) was added. The pyridine was removed by distillation after 12 hr., and benzene (20 ml.), ethanol (5 ml.), and water (20 ml.) were added to the residue. The organic phase was washed with 2N-hydrochloric acid (6 × 50 ml.), dried, and evaporated. The residual oil, on chromatography on neutral alumina (20 × 2·5 cm.) in benzene, afforded yellow needles (0·022 g., crystallised from ether at −78°) of 1,1′-di(benzyloxycarbonylamino)ferrocene, m. p. 107—108° (lit.,[6] m. p. 107·5—108·5°).

(b) 1,1′-*Di*(*ethoxycarbonylamino*)*ferrocene*. Crude 1,1′-diaminoferrocene (0·002 mole) was dissolved in tetrahydrofuran (10 ml.) and pyridine (5·5 ml.), and ethyl chloroformate (10 × 1 ml.) was added during 1·5 hr. The mixture was left under a nitrogen atmosphere for 5 hr., sodium hydrogen carbonate solution (20 ml.) added, and the benzene layer removed, neutralised, washed, dried, and evaporated. The residue was chromatographed in benzene on neutral alumina, the main yellow band yielding 1,1′-di(ethoxycarbonylamino)ferrocene (0·1 g., 14%), m. p. 118—120°. A single recrystallisation from methanol raised the m. p. to 121—123° (lit.,[6] m. p. 122—123°).

(c) 1,1′-*Di*(*methoxycarbonylamino*)*ferrocene*. 1,1′-Diphenylazoferrocene (0·792 g.) was hydrogenated in acetic acid (7 ml.) as above, the solution evaporated, and the resultant mixture of the acetates of aniline and 1,1′-diaminoferrocene was treated in benzene with methyl chloroformate (4 × 1 ml. added at 10 min. intervals). After 5 hr., sodium hydrogen carbonate solution (20 ml.) was added, and the organic phase separated, washed, dried, and evaporated to a total volume of about 20 ml. This concentrate was placed on neutral alumina (35 × 2 cm.) and eluted with benzene. The first 750 ml. of eluate were evaporated, to yield a slightly yellow oil (0·54 g., 90%), b. p. 95° (bath)/0·05 mm., which solidified to white needles, m. p. 43°. Methyl carbanilate has m. p. 47°. The main yellow band was eluted with 1 : 1 chloroform–benzene (500 ml.) and evaporated to a yellow oil (0·4 g.) which crystallised from methanol as yellow-brown rods of 1,1′-*di*(*methoxycarbonylamino*)*ferrocene* (0·33 g., 50%), m. p. 173—176°. Three recrystallisations from methanol yielded a sample of m. p. 177—178° (Found: C, 50·75; H, 5·0; N, 8·4. $C_{14}H_{16}FeN_2O_4$ requires C, 50·6; H, 5·0; N, 8·4%).

The authors thank the D.S.I.R. for a maintenance grant (to G. R. K.), and Dr. Schlögl for help.

THE UNIVERSITY, SHEFFIELD, 10.
[*Received, April* 10*th*, 1961.]

---

[10] Schlögl and Seiler, *Naturwiss.*, 1958, **45**, 337.