Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SYNTHESIS OF [2.2]FERROCENOPHANE-1,13-DIYNE*

M. ROSENBLUM, N. M. BRAWN, D. CIAPPENELLI AND J. TANCREDE
Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154 (U.S.A.)

(Received March 20th, 1970)

SUMMARY

The synthesis of [2.2]ferrocenophane-1,13-diyne, the first member of this class of ferrocenes having bridging acetylenic elements is achieved by coupling of the cuprous salt of 1-ethynyl-1′-iodoferrocene. The physical properties of this substance are described.

INTRODUCTION

Although a considerable number of ferrocenophanes with one or more bridges joining the two rings of a ferrocene nucleus are known, members of this general class of compounds in which two ferrocene nuclei are joined through two or more bridges have, by comparison, been little examined**.

The simplest member of this class of ferrocenophanes, 1,1′-biferrocenylene ([0.0]ferrocenophane)*** has recently been described[3,4], as have several bridged homologues, which are either saturated or stereochemically unsuited for effecting further transformations, in particular those which might involve interactions between the bridging elements. The acetylene bridged [2.2]ferrocenophane (IV), reported here, seemed well suited to those purposes since the two acetylenic groups are held rigidly over one another and can in principal be brought into reaction either photochemically or through the agency of organometallic reagents.

RESULTS AND DISCUSSION

The most expeditious synthesis of (IV) appeared to be through the use of the cuprous acetylide coupling reaction (eqn. 1), which has previously been successfully applied to the synthesis of ferrocenylacetylenes[5-7], by extending it to a 1-ethynyl-1′-haloferrocene from which the desired diacetylene could be obtained in one step.

$$\mathrm{FcC{\equiv}CCu + ArX \rightarrow FcC{\equiv}CAr} \qquad (1)$$

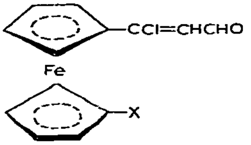
---

* Taken in part from a dissertation submitted by N. M. Brawn in partial fulfillment of the requirements for the Ph.D. degree, June 1968.

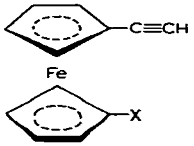
** A recent review of this area of metallocene chemistry has been provided by Watts[1].

*** The nomenclature system used is that proposed by Smith[2].

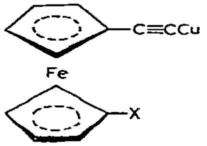
Bromoferrocene, prepared by treatment of (chloromercuri)ferrocene with *N*-bromosuccinimide[8] was converted to 1-acetyl-1'-bromoferrocene[9]. This substance was transformed to the aldehyde (Ia) by treatment with phosphorus oxychloride and dimethylformamide and this was in turn converted to 1-ethynyl-1'-bromoferrocene (IIa) by reaction of the aldehyde with sodium hydroxide in aqueous dioxane.



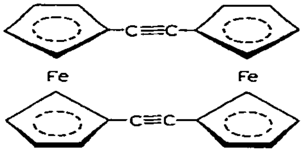
(I) a X = Br
b X = H
c X = HgCl
d X = I



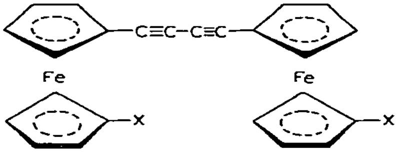
(II) a X = Br
b X = I



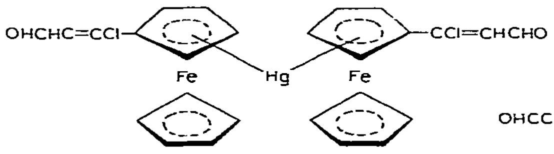
(III) a X = Br
b X = I



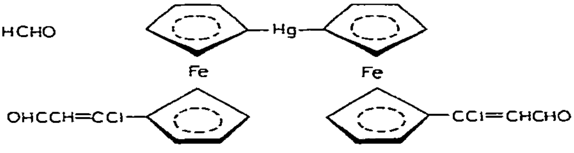
(IV)



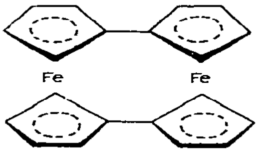
(V) a X = Br
b X = I



(VI)



(VII)



(VIII)

Several attempts to effect the desired coupling of the cuprous salt of this acetylene under a variety of conditions led to either undefined polymeric products or the halodiacetylene (Va), the product of oxidative coupling of (IIIa).

Since the desired coupling reaction was known to occur, with significantly greater ease when the halo component is an iodoferrocene and since it proved impossible to exclude the oxidative coupling reaction, we turned our attention to the synthesis of 1-ethynyl-1'-iodoferrocene.

The route employed for the synthesis of (IIa) could not, however, be applied for the preparation of the corresponding iodo derivative since it has been shown that acylation of iodoferrocene results in the loss of the iodide substituent[9]. Accordingly (2-formyl-1-chlorovinyl) ferrocene (Ib)[5–7] was transformed to the 1'-(chloromercuri) derivative (Ic) by treatment with mercuric acetate in aqueous acetic acid containing a small amount of perchloric acid, followed by addition of lithium chloride. Chloromercuration in neutral media (benzene/methanol) gave only very low yields of the desired product as well as the two mercurated products (VI) and (VII). The constitution of the former is evidenced by its IR and NMR spectral properties, and that of the latter by its conversion in good yield to (Id) on treatment with *N*-iodosuccinimide. The chloromercuri derivative (Ic) was likewise converted to (Id) with *N*-iodosuccinimide, and this in turn to the acetylene (IIb) with base. The preparation of the cuprous salt (IIIb) by reaction of (IIb) with cuprous iodide in aqueous ammonium hydroxide was accompanied by the formation of lesser amounts of the oxidative coupling product (Vb). When the cuprous salt was heated in benzene/pyridine solution for three hours the dimeric product (IV) was formed in moderate yield.

The diacetylene is a high melting orange substance which is very sparingly soluble in a wide range of organic solvents, closely resembling, in this respect, the properties of [0.0]ferrocenophane and bis(*as*-indacenyliron)[10] which are both reported to have melting points above 350° and to exhibit limited solubility in organic solvents. These properties reflect the high symmetry and relative rigidity of such substances.

In keeping with its structure and the previously observed fragmentation patterns of closely related ferrocenophanes such as [0.0]ferrocenophane[3,4] and bis(*as*-indacenyliron)[10], the mass spectrum of (IV) is unusually simple. At 70 eV the most intense peak is that due to the parent ion of *m/e* 416; the remaining two prominent peaks are at *m/e* 56 and 152, corresponding to Fe^+ and the fragment ion $[C_5H_4C_2C_5H_4]^+$. The abundance of this latter ion is unusual since normally fragmentation of the metal ring bond in metallocenes leaves the charge principally on metal bearing fragments rather than on the ligand. However no peak of significant intensity is observable at either *m/e* 264 or 132 corresponding to the residual fragment ion $[C_5H_4C_2C_5H_4Fe_2]^+$ or the doubly charged ion. A significant index of the stability of the parent ion is provided by the appearance of the doubly charged ion at *m/e* 208. The identity of this ion as the doubly charged ion (IV) rather than a fragment ion is evidenced by the presence of a peak at *m/e* 208.5. Its intensity relative to the peak at 208 is 0.30, corresponding to that calculated for the isotopic doubly charged parent ion $[C_{24}H_{16}{}^{56}Fe{}^{57}Fe]^{2+}$.

Less intense but significant peaks occur at *m/e* 360 and 304 which correspond to the loss of first one and then both of the iron atoms, a process which must therefore be either preceded by or simultaneous with fusion of the two hydrocarbon segments of the molecule. The peak at *m/e* 304 is accompanied by peaks at 303, 302, and 301 of comparable intensity and may possibly be derived from it by loss of hydrogen. The formation of hydrocarbon fragment ions by loss of the metal atom from substituted ferrocenes has normally been observed to occur with loss of a side chain, as for example, the formation of $(C_5H_5C_5H_4)^+$ from $(C_5H_4R)(C_5H_5)Fe$[11]. The peak at *m/e* 304 in the spectrum of (IV) would therefore appear to be unusual and may result from joining of the acetylenic groups in the molecule ion.

The NMR spectrum of (IV), taken in pyridine at 100°, exhibits two widely separated triplets at δ 5.09 and 4.02 which are assigned to α and β ring protons respectively*. Its spectrum closely resembles that of [0.0]ferrocenophane with respect to the

---

* In ethynylferrocene, the assignment of ring proton resonances at δ 4.48 and 4.20 ($CDCl_3$) to α and β ring protons respectively has been confirmed through specific deuteration[12]. In diferrocenylacetylene these resonances are at δ 4.46 and 4.24 ($CDCl_3$).

unusually large difference in shielding of α and β ring protons. This difference in shielding is primarily the consequence of a substantial decrease in shielding of α-protons in both substances, compared with the shielding of these protons in ferrocene itself. A lesser, but significant increase in shielding of β-protons in these substances is also apparent. Hedberg and Rosenberg[3] have suggested that this can be accounted for by a distortion of the ferrocene nuclei in which the iron atoms are forced away from one another along a line joining their centers [see structure (VIII)]. Similar distortions of the metal atom with respect to the rings have been invoked in α-ferrocenyl carbonium ions to account for anomalous shielding effects in these substances[13], but we have recently provided evidence against such an explanation[14]. Furthermore, whatever repulsive interactions may subsist in [0.0]ferrocenophane which would result in a molecular distortion such as is depicted in (VIII)*, these would clearly not apply to (IV). It would appear more reasonable to conclude that deshielding of α protons in (IV) and in [0.0]ferrocenophane is due to the magnetic anisotropy of each ferrocene nucleus and the molecular geometry which constrains the α-protons of one cyclopentadienyl ring in these substances to the deshielding volume of the other nucleus**. We have recently provided an example of these effects on shielding of arylferrocenes[18], and the same arguments have been advanced recently by Watts[19] (*cf.* also ref. 20) to account for the chemical shifts of protons in a [1.1]ferrocenophane. A comparison of the chemical shifts of ring protons in biferrocenyl, diferrocenylacetylene with the structurally related ferrocenophanes (IV) and [0.0]ferrocenophane provided in Table 1 puts these arguments in clear perspective. Doubtless other examples of this general phenomenon will come to light as other members of the general class of [*m.n*] ferrocenophanes are prepared and their NMR spectra are examined.

TABLE 1

CHEMICAL SHIFTS OF CYCLOPENTADIENYL PROTONS

Compound	H_α[a]	H_β[a]
(IV)[b]	5.09	4.02
Diferrocenylacetylene[c]	4.40	4.13
[0.0]Ferrocenophane[c]	5.27	3.77
Biferrocenyl[c]	4.26	4.06

[a] Chemical shifts given in ppm from internal TMS at 60 MHz. [b] Determined in pyridine solution. [c] Determined in benzene solution.

A study of the chemistry of (IV) is in progress and we hope to provide an account of this in the near future.

---

* It is doubtful in any event, if there is significant nonbonded interaction between the iron atoms of [0.0]-ferrocenophane. It may be estimated that the distance between the two iron atoms in an undistorted [0.0]-ferrocenophane is 3.86 Å, based on the distances in biferrocenyl[15]. The range for Fe–Fe bond distances is 2.4–2.9 Å, well within the distance separating metal atoms in [0.0] ferrocenophane[16].

** The molecular diamagnetic anisotropy of ferrocene has been determined by Mulay and Fox[17].

EXPERIMENTAL

Microchemical analyses were carried out by S. M. Nagy, Microchemical Laboratory, Belmont, Mass. and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. NMR spectra were determined using a Varian Model A 60-A spectrometer*. Mass spectra were recorded on an AEI MS-12 spectrometer**.

Preparation of 1-*bromo*-1′-(2-*formyl*-1-*chlorovinyl*)*ferrocene* (*Ia*)

A solution of 9.24 g (30 mmoles) of 1-acetyl-1′-bromoferrocene dissolved in 30 ml of dimethylformamide was added dropwise, under nitrogen, with stirring to a solution of 9.2 ml (90 mmoles) of phosphorus oxychloride in 20 ml of dimethylformamide cooled in an ice bath. After the initial green color had changed to purple, the ice bath was removed, and the reaction was allowed to continue for 2 h. The solution was then poured in 150 ml of cold 35% aqueous sodium acetate and stirred for 1 h. The blood red solution was extracted several times with methylene chloride, and the combined organic extract was washed to neutrality, dried over magnesium sulfate and evaporated to a red oil. Crystallization from ether/Skellysolve B afforded 8.7 g (82%) of aldehyde (Ia), m.p. 53–54°. Concentration of the mother liquor afforded an additional 1.8 g of somewhat cruder material.

Preparation of 1-*ethynyl*-1′-*bromoferrocene* (*IIa*)

The aldehyde (Ia) (8.5 g, 24 mmoles), was dissolved in 100 ml of dioxane and the solution was brought to reflux, at which point 70 ml of hot 3 *N* sodium hydroxide solution was added. After 30 min of reflux, the solution was allowed to cool to room temperature and 100 ml of water was then added. The solution was then extracted three times with ether, and the combined organic extracts were washed three times with water, dried over magnesium sulfate, and evaporated to a red oil. This material was chromatographed on 250 g of Camag alumina (act. 2) with Skellysolve B, and evaporation of the eluant afforded 6.23 g (90%) of the desired product. An analytical sample was recrystallized from an ether/pentane mixture, m.p. 33–34°. (Found: C, 49.97; H, 3.53. $C_{12}H_9BrFe$ calcd.: C, 49.88 H, 3.14%.)

Preparation of the cuprous salt of 1-*ethynyl*-1′-*bromoferrocene* (*IIIa*).

A solution of 2.86 g (15 mmoles) of cuprous iodide in 40 ml of 30% aqueous ammonium hydroxide was added to a stirred solution of 2.89 g (10 mmoles) of 1-ethynyl-1′-bromoferrocene in 60 ml of absolute ethanol. The lemon-yellow precipitate was carefully collected under nitrogen, washed 3 times with water, and three times each with ethanol and ether. Drying under vacuum at 80° gave 2.9 g (83%) of the desired salt.

The filtrate from the reaction mixture was extracted with ether, and the organic washings were combined with the ethanol and ether washings of the precipitate. After washing with water, the ether solution was dried over magnesium sulfate, and evaporated to a red oil. This material was chromatographed on 100 g of Camag alumina with Skellysolve B to give 30 mg of starting material, while an ether wash of

---

* Purchased on National Institutes of Health grant GM-13183-01.

** Purchased on National Science Foundation grant GP 3644.

the column gave 110 mg of bis(1'-bromoferrocenyl)diacetylene (Va). Recrystallization from benzene gave deep red prisms, m.p. 186–188°. (Found: C, 50.31; H, 2.98. $C_{24}H_{16}Br_2Fe_2$ calcd.: C, 50.04, H, 2.78%.)

Attempted dimerization of the cuprous salt (IIa)

The salt (IIIa) was dissolved in a mixture of 100 ml of benzene and 50 ml of pyridine both carefully dried. This solution was added dropwise to 250 ml of refluxing benzene in a high dilution apparatus. The addition was complete after 10 h but the solution was allowed to reflux for an additional 14 h. The reaction mixture was cooled, washed free of pyridine with water, dried, and evaporated to a red oil. This material was chromographed on 100 g of Camag alumina with benzene to give a single orange band. On evaporation of the eluant, 210 mg of bis(1'-bromoferrocenyl)diacetylene (Va) was isolated and identified by m.p. and by mixed m.p. with the material isolated above.

Preparation of 1-(*chloromercuri*)-1'-(2 *formyl*-1-*chlorovinyl*) *ferrocene* (*Ic*)

A solution of 7.01 g (22 mmoles) of mercuric acetate and 1.6 ml (11 mmoles) of 7 *M* perchloric acid in 40 ml of 80% aqueous acetic acid was added dropwise to a stirred solution of 5.48 g (20 mmoles) of (2-formyl-1-chlorovinyl)ferrocene (Ib) in 40 ml of 80% aqueous acetic acid, kept in a nitrogen atmosphere. After addition was completed, the solution was stirred for 1 h. The reaction mixture was then poured into 80 ml of an aqueous lithium chloride solution (5.09 g, 0.12 moles) and allowed to stir for 0.5 h. This solution was extracted several times with methylene chloride, and the combined organic extracts were, in turn, washed several times with water, dried over magnesium sulfate and concentrated to a red oil. The oil was taken up in benzene and cooled. Filtration yielded 2.4 g of crude product.

The filtrate was again concentrated and placed on a chromatographic column prepared from 100 g of Camag alumina (act. 3). Elution with benzene gave two major bands. The first afforded 2.06 g of starting material. The second band, on elution with methylene chloride, gave an additional 0.65 g of product, m.p. 184–186°, as a purple powder. Total yield, 48%. (Found: C, 30.77; H, 2.49. $C_{13}H_{10}Cl_2FeHgO$ calcd.: C, 30.64; H, 1.98%.)

Its NMR spectrum taken at 70° in $CDCl_3$ solution exhibited resonance absorption at δ 10.12 (d, 1 proton, J 7 Hz, CHO), 6.46 (d, 1 proton, J 7 Hz, C=CH), 4.83 (t, 2 protons, J 2 Hz, 2'-H), 4.60 (t, 2 protons, J 2 Hz, 3'-H), 4.48 (t, 2 protons, J 2 Hz, 2- or 3-H), 4.23 (t, 2 protons, J 2 Hz, 2- or 3-H). Its infrared spectrum taken in KBr showed split carbonyl absorption at 1645 cm^{-1}.

Preparation of 1-*iodo*-1'-(2-*formyl*-1-*chlorovinyl*)*ferrocene* (*Id*)

A solution prepared by dissolving *N*-iodosuccinimide (1.80 g, 8.0 mmoles) in 150 ml of dry methylene chloride, previously flushed with nitrogen, was added dropwise to a stirred solution of 1-mercurichloro-1'-(2-formyl-1-chlorovinyl)ferrocene (Ic) (3.06, 6.0 mmoles) in 150 ml of methylene chloride, maintained in a nitrogen atmosphere. After addition was complete, the solution was stirred for 15 min at room temperature, and then brought to reflux on a steam bath. The reaction was followed by TLC (silica/benzene) which showed only one spot after 2 h. The solution was then cooled to room temperature, filtered, and the filtrate was in turn washed several times with water, dried over magnesium sulfate and evaporated to a red oil. This was immediately placed on a chromatography column prepared from 50 g of Camag alumina (act. 2). Elution with ether gave one major band which yielded 2.45 g of 1-iodo-1'-(2-formyl-1-chlorovinyl)ferrocene (98% yield). Recrystallization from $CHCl_3$ gave red crystals, m.p. 90–91°. (Found: C, 38.50; H, 2.61; Fe, 14.01. $C_{13}H_{10}ClFeIO$ calcd.: C, 38.99; H, 2.52; Fe, 13.95%.)

The NMR spectrum of this substance in $CDCl_3$ solution exhibited resonance absorption at δ 10.15 (d, 1 proton, J 7 Hz, CHO), 6.43 (d, 1 proton, J 7 Hz, C=CH), 4.70 (t, 2 protons, J 2 Hz, 2'-H), 4.53 (t, 2 protons, J 2 Hz, 3'-H), 4.43 (t, 2 protons, J 2 Hz, 2-H), 4.21 (t, 2 protons, J 2 Hz, 3-H). Its infrared spectrum taken in KBr exhibited split carbonyl absorption at 1650 cm^{-1}.

Preparation of 1-*iodo*-1 -*ethynylferrocene* (*IIb*)

A solution of 1-iodo-1'-(2-formyl-1-chlorovinyl)ferrocene (6.9 g, 17.2 mmoles) in 150 ml of dioxane was heated in a nitrogen atmosphere to 85°. To this solution was added rapidly 150 ml of hot 0.8 *N* KOH solution. Reaction was allowed to continue for 20 min at 85°. After coding the solution was extracted with ether, washed to neutrality, and dried over magnesium sulfate. The solvent was removed and the residue was chromatographed on Camag alumina (act. 2). Elution with ether gave one major yellow band which gave 3.18 g of 1-iodo-1'-ethynylferrocene (66% yield), m.p. 27–27.5°.

Its NMR spectrum, recorded in $CDCl_3$ solution, had resonance at δ 4.41 (t, 4 protons, J 2 Hz, 2'- and 2-H), 4.21 (t, 4 protons, J 2 Hz, 3'- and 3-H) and 2.76 (s, 1 proton, C≡CH). Its infrared spectrum, recorded in KBr, showed acetylenic absorption at 2105 cm^{-1}.

Preparation of the cuprous salt of 1-*ethynyl*-1'-*iodoferrocene* (*IIIa*)

A solution of 3.86 g (15 mmoles) of cuprous iodide in 80 ml of 30% aqueous ammonium hydroxide was added to a stirred solution of 3.36 g (10 mmoles) of 1-ethynyl-1'-iodoferrocene in 100 ml of absolute ethanol. The resulting yellow precipitate was carefully collected under nitrogen, washed 5 times with water, and three times each with ethanol and ether. Drying under vacuum at 60° gave 2.5 g (62.5%) of desired salt.

The filtrate from the reaction mixture was extracted with ether, and the organic washings were combined with the ethanol and ether washings of the precipitate. After washing with water, the ether solution was dried over magnesium sulfate. On concentration, 0.5 g (0.75 mmoles) of bis(1'-iodoferrocenyl)diacetylene (Vb) crystallized out, m.p. 149–150°. The proton magnetic resonance of this substance ($CDCl_3$) exhibited triplet resonance at δ 4.45 due to ring protons α to the acetylene (2'-H) and iodo functions (2-H) and a second triplet at δ 4.21 due to ring protons β to these groups (3- and 3'-H). Both diferrocenyldiacetylene and iodoferrocene exhibit resonance with these chemical shifts. The IR spectrum of the compound shows acetylene absorption at 2150 cm^{-1} but no absorption at 1000 cm^{-1}. (Found: C, 43.23; H, 2.32. $C_{24}H_{16}I_2Fe_2$ calcd.: C, 43.01; H, 2.34%.)

Preparation of [2.2]*ferrocenophane*-1,13-*diyne* (*IV*)

The cuprous salt (800 mg, 2 mmoles) was suspended in 35 ml of dry benzene and heated to reflux, under a nitrogen atmosphere. Pyridine (degassed *in vacuo* and dried by distilling over barium oxide) was added dropwise until the solution cleared. An equal volume of pyridine was then added in excess (total of 30 ml). The reaction was refluxed for 3 h during which time benzene was allowed to distill, raising the temperature of the solution to 110°. After cooling by pouring into 300 ml of benzene, the solution was filtered, washed three times with water, then twice with 0.5 *N* HCl to remove the pyridine, and finally with water to neutrality. After drying over magnesium sulfate, this solution gave 148 mg of dimer on concentration, m.p. >380° d. UV λ_{max} 274 mμ; ε 1100 (cyclohexane). (Found: C, 68.77; H, 3.64. $C_{24}H_{16}Fe_2$ calcd.: C, 69.20; H, 3.89%.)

Mercuration of (2-formyl-1-chlorovinyl)ferrocene in neutral solution

A solution of 18.0 g of mercuric acetate (0.056 mole) in 200 ml of methanol was added quickly to a stirred solution of 13.7 g of (2-formyl-1-chlorovinyl)ferrocene (0.05 mole) in 200 ml of benzene. Reaction was followed by TLC (silica gel/benzene) on which the desired 1-chloromercuri-1'-(2-formyl-1-chlorovinyl)ferrocene (Ic) appeared as a purple spot, preceded by starting material and (VI). After 1 h, a fourth spot appeared which was assumed to be some polymercurated material. A solution of 4 g of lithium chloride (0.1 mole) in 20 ml of 50% aqueous ethanol was then added. This mixture was stirred for 30 min, concentrated, and the residue taken up in 300 ml of methylene chloride, followed by addition of 400 ml of water. The organic layer was filtered to remove the insoluble polymercurated material, washed 5 times with water, and evaporated to a red oil.

This oil was chromatographed on 1000 g of activity 3 Camag alumina. Elution with methylene chloride gave two major bands. The first was found to be a mixture of starting material and (VI). The second band yielded 1.3 g of 1-(chloromercuri)-1'-(2-formyl-chlorovinyl)ferrocene, m.p. 184–186°, identical with the product obtained from chloromercuration in acetic acid solution. The first band was rechromatographed on activity 2 Camag alumina and, on elution with benzene, gave 3.4 g of starting material, and 336 mg of (VI). (Found: C, 42.22; H, 3.08; Fe, 15.36. $C_{26}H_{20}Cl_2Fe_2HgO_2$ calcd.: C, 41.76; H, 2.70; Fe, 14.94%.) The IR spectrum of this substance exhibited bands at 1642 and 1565 cm^{-1} as well as two bands at 1000 and 1100 cm^{-1} characteristic of an unsubstituted ferrocene ring. Its NMR spectrum exhibited singlet absorption at δ 4.33 equivalent to 10 protons in an unsubstituted cyclopentadienyl ring. In addition to these materials 496 mg of a third product was eluted with benzene which is assigned structure (VII). Its IR spectrum had no bands indicative of an unsubstituted cyclopentadienyl ring and its NMR spectrum exhibited no singlet resonances typical of these protons. Treatment of 400 mg of this substance with *N*-iodosuccinimide, under conditions similar to these employed to effect the conversion of (Ic) to (Id), gave 326 mg of (Id), identical with (Id) by mixed m.p.

ACKNOWLEDGEMENT

We are indebted to the National Institutes of Health and the National Science Foundation for support under grants GM 5978, GM 16395 and GP 8714.

REFERENCES

1 W. E. WATTS, *Organometal. Chem. Rev.*, 2 (1967) 231.
2 B. H. SMITH, *Bridged Aromatic Compounds*, Academic Press, New York, 1964.
3 F. L. HEDBERG AND H. ROSENBERG, *J. Amer. Chem. Soc.*, 91 (1969) 1258.
4 M. D. RAUSCH, R. F. KOVAR AND C. S. KRAIHANZEL, *J. Amer. Chem. Soc.*, 91 (1969) 1259.
5 K. SCHLÖGL AND W. STREYRER, *Monatsh Chem.*, 96 (1965) 1520.
6 M. ROSENBLUM, N. BRAWN, J. PAPENMEIER AND M. APPLEBAUM, *J. Organometal. Chem.*, 6 (1966) 173.
7 M. O. RAUSCH, A. SIEGEL AND L. P. KLEMANN, *J. Org. Chem.*, 31 (1966) 2703.
8 R. W. FISH AND M. ROSENBLUM, *J. Org. Chem.*, 30 (1965) 1253.
9 D. W. HALL AND J. H. RICHARDS, *J. Org. Chem.*, 28 (1963) 1549.
10 T. J. KATZ, V. BALOGH AND J. SCHULMAN, *J. Amer. Chem. Soc.*, 90 (1968) 734.
11 A. MANDELBAUM AND M. CAIS, *Tetrahedron Lett.*, (1964) 3847.
12 M. D. RAUSCH AND A. SIEGEL, *J. Organometal. Chem.*, 17 (1969) 117.
13 M. CAIS, J. J. DANNENBERG, A. EISENSTADT, M. I. LEVENBERG AND J. H. RICHARDS, *Tetrahedron Lett.*, (1966) 1695.
14 J. FEINBERG AND M. ROSENBLUM, *J. Amer. Chem. Soc.*, 91 (1969) 509.
15 A. C. MACDONALD AND J. TROTTER, *Acta Crystallogr.*, 17 (1964) 872.
16 M. R. CHURCHILL, *Inorg. Chem.*, 6 (1967) 190.
17 L. N. MULAY AND M. E. FOX, *J. Amer. Chem. Soc.*, 84 (1962) 1308.
18 M. ROSENBLUM, *Chemistry of The Iron Group Metallocenes*, Interscience, New York, 1965, p. 217.
19 W. E. WATTS, *J. Amer. Chem. Soc.*, 88 (1966) 855.
20 J. S. MCKECHNIE, B. BERSTED, I. C. PAUL AND W. E. WATTS, *J. Organometal. Chem.*, 8 (1967) P29.