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SYNTHESIS OF FERROCENYLACETYLENES

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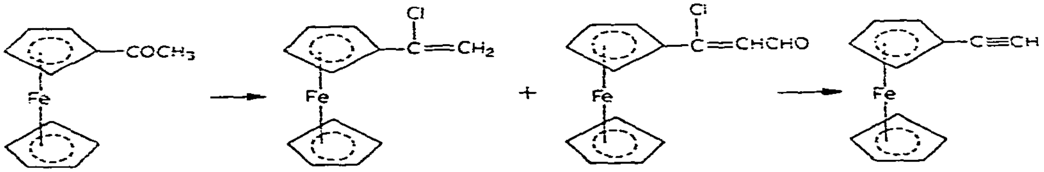
Ferrocenylacetylenes constitute an interesting class of ferrocene derivatives since they may serve as starting materials for the construction of more complex organometallics.

Ethynylferrocene, the simplest member of this class of compound, was first prepared in 1961 by Benkeser and Fitzgerald[1] from vinylferrocene by the classical method of bromination and dehydrobromination. Subsequently, Schlögl and Egger[2] described an improved four-step procedure, utilizing (chloroacetyl)ferrocene as an intermediate, by which the ethynyl derivative was obtained in 15 % overall yield from ferrocene.

We are prompted by the very recent publication of Schögl and Streyrer[3] to describe experiments paralleling theirs by which this acetylene may be conveniently prepared, and furthermore to illustrate its use in the synthesis of other ferrocenylacetylenes.

When acetylferrocene is treated with phosphorus oxychloride in dimethylformamide, following the procedure of Arnold and Žemliča[4], it is smoothly transformed to the β-chloroaldehyde (I). A second, rather unstable, crystalline material, which contains halogen, could be isolated from these reactions, but apart from its infrared spectrum its high reactivity prevented further characterization. This substance, m.p. 43°, is assigned the structure of (1-chlorovinyl)ferrocene (II) on the basis of a comparison of its infrared spectrum with that of the heteroannularly disubstituted ferrocene (V), and from its conversion in aqueous ethanol solution to acetylferrocene. That it is very likely an intermediate in the conversion of acetylferrocene to the chloroaldehyde (I) may be shown by its transformation, in high yield, to the latter derivative on treatment with phosphorus oxychloride in dimethylformamide[*]. The formation of undesired (1-chlorovinyl)ferrocene in these reactions may be obviated by employing an excess of phosphorus oxychloride, in which case the chloroaldehyde (I) is the sole product and is obtained in 87 % yield.



(II) (I) (III)

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[*] The substance is apparently the same as that reported by Schlögl and Streyrer[3] which they also could not fully characterize.

When the chloroaldehyde (I) is heated briefly in a basic aqueous dioxan solution, following a procedure recently reported by Bodendorf and Kloss[5], it is transformed to ethynylferrocene (III) in 88% yield. Since acetylferrocene may be obtained in essentially quantitative yield from ferrocene, this route constitutes a relatively simple and expeditious method for the preparation of ethynylferrocene. (The use of potassium amide in liquid ammonia has also been used to effect this transformation[3].)

As with acetylferrocene, treatment of 1,1′-diacetylferrocene with phosphorus oxychloride in dimethylformamide gave 1,1′-bis-(2-formyl-1-chlorovinyl)ferrocene (IV) in 85% yield. When these reactions were carried out in the presence of a smaller proportion of phosphorus oxychloride, the chlorovinyl derivative (V) was isolated with (IV). The structure of this substance follows from its analysis, its infrared spectrum which exhibits absorption at 6.22 and 10.95 μ, and its NMR spectrum which, in addition to a pair of doublets characteristic of the formyl and vinyl protons, also exhibits an AB quartet typical of the methylene group (Table 1).

TABLE 1

NMR DATA OF FERROCENE DERIVATIVES

Unless otherwise noted, all spectra were determined in $CDCl_3$ using tetramethylsilane as internal standard. Chemical shifts are given in τ. Fc = $C_5H_5FeC_5H_4$– or –$C_5H_4FeC_5H_4$–; s = singlet, d = doublet; t = triplet, m = multiplet.

Compound	*Chemical shifts of C_5H_4 protons*			*Other chemical shifts with assignments*
	H_α	H_β	J	
FcCCl=CHCHO	5.28 (t)	5.47 (t)	1.8	3.64 (d) C=CH, −0.06 (d) CHO, J 7.4; 5.79 (s) C_5H_5
Fc(CCl=CHCHO)$_2$	5.25 (t)	5.43 (t)	1.6	3.70 (d) C = CH, −0.01 (d) CHO, J 7.1
CH_2=CClFcCCl=CHCHO	5.69 (t)	5.48 (t)	1.8	4.62 (d) 4.70 (d) ClC=CH_2, J 0.9; 3.67 (d) C=CH, −0.06 (d) CHO, J 7.5
	5.30 (t)	5.46 (t)	1.8	
HC≡CFcCCl=CHCHO	5.52 (t)	5.72 (t)	1.7	3.62 (d) C=CH, −0.18 (d) CHO, J 7.4; 7.20 (s) C≡CH
	5.25 (t)	5.40 (t)	2.0	
FcC≡CH	5.52 (t)	5.80 (t)	1.9	7.28 (s) C≡CH; 5.79 (s) C_5H_5
FcC≡CPh	5.50 (t)	5.80 (t)	1.8	5.78 (s) C_5H_5; 2.56 (m) Ph
Fc(C≡CPh)$_2$	5.46 (t)	5.69 (t)	1.8	2.70 (m) Ph
FcC≡CFc	5.54 (t)	5.76 (t)	1.8	5.76 (s) 5.98 (s)[a] C_5H_5
	5.63 (t)[a]	6.12 (t)[a]		
Fc(C≡CFc)$_2$	5.53 (m)	5.76 (m)[b]	1.8	5.76 (s) C_5H_5
FcC≡CC≡CFc	5.50 (t)	5.78 (t)	1.8	5.76 (s) C_5H_5
FcCCl=CHCH=CHCO	5.53 (t)	5.72 (t)	1.7	Complex multiplet between 3.3 and 4.3
	5.13 (t)	5.47 (t)	1.7	

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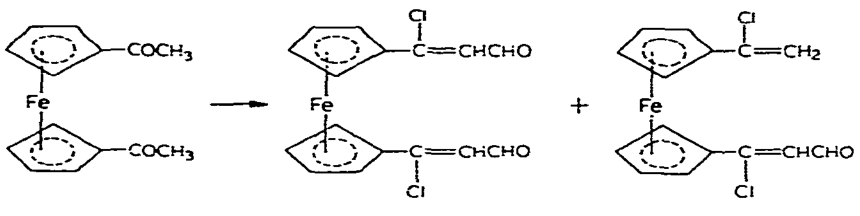
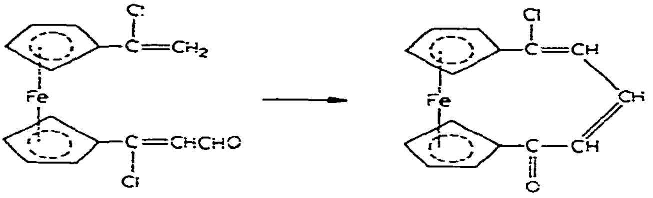
[a] Taken in dimethyl sulfoxide-d_6. [b] H_α absorption in the disubstituted and in the monosubstituted ferrocene nuclei overlap, while the corresponding H_β resonances overlap with that of the unsubstituted ring protons.



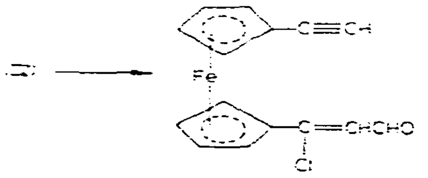
(IV) (V)

When this substance was treated with phosphorus oxychloride in dimethylformamide, it was transformed not to (IV) as was anticipated, but instead lost the elements of HCl and gave a substance $C_{15}H_{11}ClFeO$. This orange-red crystalline material exhibits carbonyl absorption at 6.08 μ, and on the basis of its NMR spectrum is tentatively assigned the bridged structure (VI).



(V) (VI)

Attempts to convert the bis-chloroaldehyde derivative (IV) into diethynylferrocene have thus far been without success*. Although the ethynyl derivative (VII) can be isolated from the base treatment of (IV), the reaction of this substance with base has yielded only decomposition products.



(VII)

Ethynylferrocene (III) serves as a very useful starting material for the synthesis of other acetylenic derivatives, following the recently published method of Stephens and Castro[6]. Thus, ethynylferrocene is readily converted to a stable cuprous salt on treatment with cuprous iodide in ethanolic ammonia solution**. When this salt is heated in pyridine solution with iodo- or 1,1'-diiodoferrocene[7], it is converted in high yield to the corresponding disubstituted acetylenes (VIIIa) and (IXa). The synthesis of diferrocenylacetylene has recently been reported by Pauson and Watts[8], but it is

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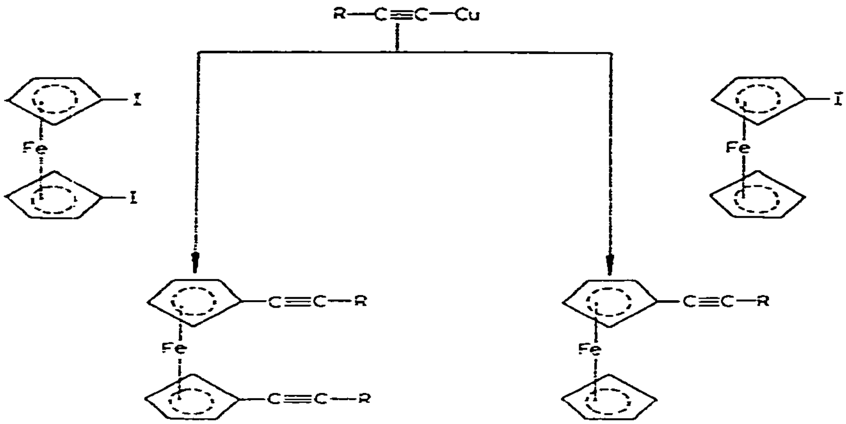
* Schlögl and Streyrer[3] have reported some spectral evidence for the presence of this substance in their crude reaction mixtures, but they too were unable to isolate any well-defined product.

** The cuprous salt must be washed only briefly with ethanol and ether, since continued washing in air leads to the formation of the coupling product.

clear that the present procedure offers distinct advantages in terms of simplicity and yield to the earlier procedure.



(IXa) R ferrocenyl
(IXb) R phenyl

(VIIIa) R ferrocenyl
(VIIIb) R phenyl

In similar fashion *iodo-* and 1,1'-diiodoferrocenes were coupled with cuprous phenylacetylide to give the derivatives (VIIIb) and (IXb). The preparation of the former compound by a similar coupling reaction has also been reported by Nesmeyanov and co-workers[9].

NMR spectral data for all compounds reported in this papers are summarized in Table 1.

EXPERIMENTAL

Conversion of acetylferrocene into (1-chlorovinyl)ferrocene (II) and to (2-formyl-1-chlorovinyl)ferrocene (I)

A solution of 5 ml of phosphorus oxychloride (55 mmoles) in 20 ml of dimethylformamide, prepared at 0°, was added dropwise to a stirred solution of 5.7 g of acetylferrocene (25 mmoles) in 20 ml of dimethylformamide, kept in a nitrogen atmosphere, and cooled to 0°. After 15 minutes the deep green solution became purple. The reaction was allowed to proceed at 0° for 2 h and then at room temperature for 1 h, after which time the solution was poured into 150 ml of 20 % sodium acetate solution and allowed to stir, in a nitrogen atmosphere for 1.5 h. This solution was extracted several times with methylene chloride, and the combined organic extract was, in turn, washed with water to remove dimethylformamide, dried over magnesium sulfate and concentrated to a red oil. This was immediately placed onto a chromatographic column prepared from 500 g of Fisher alumina (treated with ethyl acetate). Elution with Skellysolve B gave two major bands. The first afforded 3.5 g of (1-chlorovinyl)ferrocene (59 % yield). Rapid recrystallization from ether/pentane afforded the substance as yellow plates, m.p. 43–44.5°, which decomposed slowly at 0°, evolving HCl. The second band, on elution with 20 % ether in Skellysolve B, and recrystallization of the product from the same solvent mixture, gave 1.17 g of (2-formyl-1-chlorovinyl)ferrocene, m.p. 76–78°, as red prisms (17 % yield) (Lit.[3] m.p. 78–79°). UV λ_{max} in EtOH 272, 309, 380, 503 μ;

ε 8600, 8200, 1500, 1400. (Found: C, 56.8; H, 3.85; Cl, 12.70. $C_{13}H_{11}ClFeO$ calcd.: C, 56.9; H, 4.01; Cl, 12.92 %.)

Reaction of 4.56 g (20 mmoles) of acetylferrocene in 30 ml of dimethylformamide and 6.1 ml (60 mmoles) of phosphorus oxychloride in 20 ml of the same solvent gave 4.77 g (87 %) of the chloroaldehyde (I) as the sole product, when the reaction was allowed to proceed for 15 minutes at 0° and then for 2 h at room temperature, before workup.

Conversion of (1-chlorovinyl)ferrocene (II) into (2-formyl-1-chlorovinyl)ferrocene (I)

To 2.55 g (10.3 mmoles) of (III) in 15 ml of dimethylformamide, cooled to 0°, and in a nitrogen atmosphere, was added 5.0 ml (55 mmoles) of phosphorus oxychloride, dissolved in 15 ml of the same solvent. After addition was complete, the ice-bath was removed and the deep purple solution was stirred for 1 h. The reaction was then quenched by the addition of 50 ml of an aqueous 35 % solution of sodium acetate, and stirring was continued in a nitrogen atmosphere for 12 h. The aqueous solution was then extracted several times with methylene chloride and the combined organic extract was then washed with water and dried over magnesium sulfate. The organic solution was then filtered twice through alumina and solvent was allowed to evaporate leaving 2.05 g (73 %) of the chloroaldehyde (I).

Conversion of (1-chlorovinyl)ferrocene (II) into acetylferrocene

The vinyl chloride (430 mg) was dissolved in 40 ml of ethanol and 10 ml of 10 % hydrochloric acid was added. The yellow solution, which immediately turned red-orange in color, was allowed to stand for 25 h at room temperature. After work up, 400 mg of a crude material was isolated, which after chromatography on alumina afforded 250 mg (63 %) of acetylferrocene, m.p. 82–83°, identical with an authentic sample of this substance.

Ethynylferrocene (III)

(2-Formyl-1-chlorovinyl)ferrocene (476 mg, 1.73 mmoles) was dissolved in 15 ml of dioxan and the solution was heated in a nitrogen atmosphere to reflux. To this solution was added rapidly 10 ml of 0.5 N NaOH solution. Reaction was allowed to continue for 5 min and the solution was then poured into 50 ml of cold water. After acidification with HCl, the solution was extracted exhaustively with ether, and the combined ether extract was washed to neutrality and dried over magnesium sulfate. Solvent was removed and the residue was chromatographed on 25 g of ethyl acetate washed Fisher alumina (activity 2). Elution with Skellysolve B led to the development of two bands. The first yellow band afforded 305 mg (88 %) of ferrocenylacetylene, m.p. 51–53.5° (lit.[1–3] 55–56°). An analytical sample was recrystallized from ether/pentane as yellow platelets, m.p. 52–53.5°. UV λ_{max} in EtOH 265, 445 μ; ε 3300, 116. (Found: C, 68.55; H, 4.93. $C_{12}H_{10}Fe$ calcd.: C, 68.59; H, 4.76 %.)

The second red band gave 22 mg of starting material.

Conversion of diacetylferrocene into (IV) and (V)

Diacetylferrocene (4.4 g, 16 mmoles) was treated with 3.0 ml (32 mmoles) of phosphorus oxychloride in 70 ml of dimethylformamide, following the procedure employed in the reaction of acetylferrocene. After hydrolysis with sodium acetate, the reaction mixture was filtered and undissolved material was washed three times with ether. These ether washings were combined with the ether extracts of the filtrate. The remaining, undissolved solid was taken up in methylene chloride. The separate organic solutions were washed several times with water, dried over magnesium sulfate, and after concentration were each chromatographed on 200 g of Merck acid washed alumina. The column containing ether-soluble material gave, after elution with ether, 1.85 g of the partially converted product (V). The column containing methylene chloride-soluble material gave an additional 0.28 g of this substance on elution with ether. Recrystallization from ether/petroleum ether gave (V) as ruby red platelets, m.p. 81–83. UV λ_{max} in EtOH 230, 275, 310, 483 mμ; ε, 17,700, 9500, 6200, 920. (Found: C, 53.7; H, 3.5; Cl, 21.28. $C_{15}H_{12}Cl_2FeO$ calcd.: C, 53.8; H, 3.6; Cl, 21.17%.)

A second band, removed from this latter column with chloroform, gave 1.32 g of the bis-chloroaldehyde (IV) as black prisms, m.p. 198–198.5, after recrystallization from chloroform/cyclohexane. (Schlögl and Steyrer[3] report this substance as having m.p. 88–89°.) UV λ_{max} in EtOH 285, 313, 422, 490 μ; ε 20,700, 18,100, 2130, 1760. (Found: C, 53.25; H, 3.49; Cl, 1971. $C_{16}H_{12}Cl_2FeO_2$ calcd.: C, 52.93; H, 3.31; Cl, 19.53%.)

When this reaction was carried out on 5.4 g (20 mmoles) of 1,1′-diacetylferrocene employing 12 ml (128 mmoles) of phosphorus oxychloride and the reaction was worked up by extracting the aqueous-organic solution with methylene chloride directly, the yield of bis-chloroaldehyde, the sole product of the reaction, was 6.2 g (85%).

Conversion of (V) to (VI)

A cold solution of 1 ml (11 moles) of phosphorus oxychloride in 10 ml of dimethylformamide was added with stirring and in a nitrogen atmosphere, to 2.1 g (6.3 mmoles) of (V) dissolved in 20 ml of the same solvent, cooled in an ice-bath. After 15 min the ice-bath was removed and the reaction was allowed to continue for 2 h. The solution was then poured into 100 ml of a 20% sodium acetate solution, stirred for 1.5 h and then extracted exhaustively with methylene chloride. The combined organic extract was washed with water and then dried over magnesium sulfate. On concentration of this solution 1.08 g (57%) of (VI) were obtained as orange-red crystals, m.p. 153–155°. The product was recrystallized from chloroform/cyclohexane for analysis. UV λ_{max} in EtOH 230, 307, 475 μ; ε 11,800, 2100, 340. (Found: C, 60.55; H, 3.81; Cl, 11.76; Fe, 18.43. $C_{15}H_{11}ClFeO$ calcd.: C, 60.34; H, 3.71; Cl, 11.87; Fe, 18.71%.)

Preparation of cuprous ferrocenylacetylide

A solution of 2.0 g (10.5 mmoles) of cuprous iodide in 30 ml of 30% aqueous-ammonia was added to 1.47 g (7.0 mmoles) of ferrocenylacetylene in 40 ml of absolute ethanol. After stirring for 15 min at room temperature the yellow salt was filtered off and was quickly washed with small portions of water, then ethanol and finally ether. The salt was dried in an oven at 80° to give 1.39 g of product (73%).

The organic washings were combined, washed free of ammonia, dried over magnesium sulfate and concentrated. The resulting red oil was chromatographed on 25 g of basic Fisher Alumina. Elution with ether gave 360 mg of diferrocenyldiacetylene, m.p. 200–202° (lit.[2] 196–198°). UV λ_{max} in EtOH 224, 285, 453; ε 45,000, 21,400, 1560. (Found: C, 69.34; H, 4.68. $C_{24}H_{18}Fe_2$ calcd.: C, 68.95; H, 4.33%.)

Preparation of diferrocenylacetylene (VIIIa)

A solution of 413 mg (1.5 mmoles) of cuprous ferrocenylacetylide and 624 mg (2.0 mmoles) of iodoferrocene[7] in 16 ml of pyridine, which had been flushed with nitrogen, was heated at reflux for 30 min. The reaction mixture was then poured into 50 ml of ice and water and the crude product collected by filtration and washed repeatedly with warm benzene until the washings were colorless. The combined benzene extract was washed to neutrality, dried over magnesium sulfate, concentrated and chromatographed on basic Fisher alumina. The single band which developed was eluted with benzene and gave 435 mg (73 %) of diferrocenylacetylene. An analytical sample obtained as deep red needles from chloroform/cyclohexane solution melted at 244–246° (lit.[8] 244–246°). UV λ_{max} in EtOH 230, 265, 302, 453 mμ; ε 19,400, 11,500, 10,900, 820. (Found: C, 67.41; H, 4.78. $C_{22}H_{18}Fe_2$ calcd.: C, 67.06; H, 4.59 %.)

Preparation of 1,1′-bis(ferrocenylethynyl)ferrocene (IXa)

Treatment of 438 mg (1.0 mmoles) of 1,1′-diiodoferrocene with 591 mg (2.2 mmoles) of cuprous ferrocenylacetylide in 30 ml of pyridine, according to the above procedure, gave 332 mg (55 %) of (IX), m.p. 260–263°, after chromatography and repeated crystallization from chloroform/cyclohexane. UV λ_{max} in cyclohexane 264, 303, 447 mμ; ε 18,650, 16,470, 1,290. (Found: C, 67.62, H, 4.49. $C_{34}H_{26}Fe_3$ calcd.: C, 67.82; H, 4.35 %.)

Preparation of 1-ethynyl-1′-(2-formyl-1-chlorovinyl)ferrocene (VII)

To 726 mg (2.0 mmoles) of the bis-chloroaldehyde (IV) in 50 ml of dioxan was quickly added a solution of 570 mg (10 mmoles) of potassium hydroxide in 2 ml of water and 10 ml of dioxan. After refluxing for 1 h, the red solution had turned orange in color. It was then poured into water and extracted exhaustively with ether. The ether extracts were combined, washed with water to neutrality and dried over magnesium sulfate. Removal of solvent left a red oil which was chromatographed on 25 g of alumiumina employing ether as eluent. A small yellow band was discarded. A larger pink band, which followed, yielded, on evaporation of solvent and addition of pentane, 277 mg of the ethynyl derivative (VII), m.p. 110–111°. The column was then washed through with ether containing 2 % methanol. In this manner a dark purple band was eluted which yielded 166 mg of starting material. UV λ_{max} in EtOH 255, 313, 380, 497; ε 10,700, 14,500, 1860, 1770. (Found: C, 60.18; H, 3.97; Cl, 11.83. $C_{15}H_{11}ClFeO$ calcd.: C, 60.33; H, 3.71; Cl, 11.89 %.)

Preparation of ferrocenylphenylacetylene (VIIIb)

Cuprous phenylacetylide (9.05 g, 29 mmoles) and iodoferrocene (9.98 g, 60 mmoles) were refluxed in pyridine solution for 16 h. The solution was then poured into 100 ml of water and extracted several times with ether. The combined ethereal extract was washed with water, then 2 *N* hydrochloric acid and finally with water to neutrality. After drying over magnesium sulfate, the solution was concentrated and chromatographed on basic Fisher alumina employing Skellysolve B as eluent. The first, yellow band gave 1.37 g of iodoferrocene, while the second, orange band gave 6.17 g (88 %) of ferrocenylphenylacetylene, m.p. 126–128° (lit.[8] 121–123°). Recrystallization for analysis from ether/pentane gave this substance as orange needles, m.p. 127–127.5° UV λ_{max} in EtOH 252, 298, 453 μ; ε 18,900, 16,900, 500. (Found: C, 75.20; 75.33; H, 5.37, 5.42; Fe, 19.92. $C_{18}H_{14}Fe$ calcd.: C, 75.55; H, 4.93; Fe, 19.52 %.)

Preparation of 1,1′-bis(phenylethynyl)ferrocene (IXb)

Treatment of 500 mg (1.2 mmoles) of 1,1′-diiodoferrocene with 1.14 g (7.0 mmoles) of cuprous phenylacetylide in pyridine solution, following the procedure given above, gave 177 mg (40 %) of (IXb), m.p. 174–175.5, after chromatography and recrystallization of the product from petroleum ether. UV λ_{max} in EtOH 253, 304, 453 μ; ε 31,800, 26,100, 870. (Found: C, 80.71; H, 4.97. $C_{26}H_{18}Fe$ calcd.: C, 80.84; H, 4.69 %.)

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SUMMARY

The action of dimethylformamide and phosphorus oxychloride on acetylferrocene converts it, via (1-chlorovinyl)ferrocene, into (1-chloro-2-formylvinyl)-ferrocene. This substance is transformed by sodium hydroxide in aqueous dioxan to ethynylferrocene. The two-step sequence constitutes a convenient synthesis of this substance.

1,1′-Diacetylferrocene is similarly converted into a bis-chloroaldehyde, but on treatment with base this gives 1-ethynyl-1′-(1-chloro-2-formylvinylferrocene as the only characterizeable product.

Cuprous ferrocenylacetylide couples readily with mono- and 1,1′-diiodoferrocenes to give diferrocenylacetylene and 1,1′-bis(ferrocenylethynyl)ferrocene. Similar reactions may be effected with cuprous phenylacetylide.

NMR spectra of all substances described are given.

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