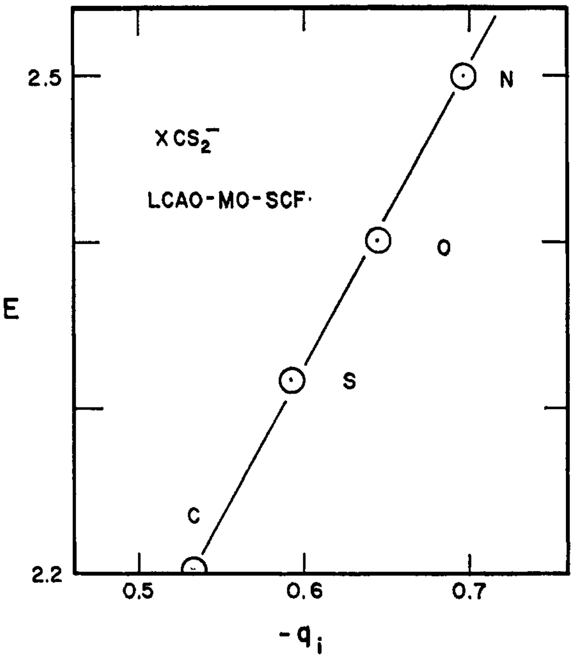

Figure 1.—Plot of kinetic E values in volts *vs.* the charge density, q_i, on the sulfur atom in dithioacetate, ethyl trithiocarbonate, ethyl xanthate, and diethyl dithiocarbamate. E is the oxidative dimerization potential plus 2.60 v for $2RS^- \rightleftharpoons RSSR + 2e^-$ in water at 25°.

Table II

Oxibase Scale Parameters of Thio Anions in Water at 25°

Nucleophile	E, v[a]	H	H/E
$H_2NCH_2CH_2S^-$ [b]	3.08	12.5	4.06
S^{2-} [c]	3.08	14.6	4.74
$H_3\overset{+}{N}CH_2CH_2S^-$ [b]	2.88	10.3	3.58
HS^- [c]	2.60	8.70	3.35
SO_3^{2-} [c]	2.57	9.00	3.50
O_3SS^{2-} [c]	2.52	3.6	1.43
$Et_2NCS_2^-$ [a]	2.49	5.74	2.29
CS_3^{2-} [a]	2.45	10.47	4.27
$EtOCS_2^-$ [a]	2.40	3.44	1.43
$EtSCS_2^-$ [a]	2.32	3.29	1.42
$CH_3CS_2^-$ [a]	2.18	4.29	1.97
NCS^- [c]	1.83	(1)	0.55

[a] This study. All are experimental values. Average σ ±0.03 v. [b] See ref 1. [c] Values reported by J. O. Edwards [ref 6, p 1540].

XCS_2^- ions ($X = C, S, O, N$) yields interesting results.[11] In particular the amount of charge density on the thio atom (as measured by $-q_i$) is related to the oxibase constant, E. The data are presented in Figure 1.

The basic ideas behind the oxibase scale[6,7] are simple and easy to use. Realistic model systems[12] are used to construct the linear free energy equations.[13]

Acknowledgment.—This work was supported by grants from the National Institutes of Health (GN-07655 and RH-00279) and from the Walter Reed Army Institute of Research (MD-2107).

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[11] M. J. Janssen, *Rec. Trav. Chim.*, **79**, 1066 (1960).

[12] J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 128–146, 251–254.

[13] R. E. Davis, *J. Am. Chem. Soc.*, **87**, 3010 (1965). The substrate parameters (α and β) for these materials used in obtaining the kinetic E values reported in Table II are reported in this reference. An estimate of all σ values, the standard deviations, of α and β are also given.

A Facile Route to Ferrocenyl- and 2-Thienylarylacetylenes[1a]

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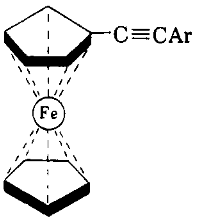
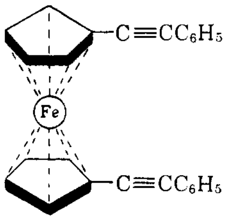
Stephens and Castro have recently described a useful new synthesis for tolane (diphenylacetylene) and substituted tolanes utilizing aryl iodides and cuprous phenylacetylide in refluxing pyridine.[2] It was of interest to us to determine if this procedure could be employed for the formation of ferrocenyl and certain heterocyclic arylacetylenes, and to study the chemistry of these substances. Our preliminary studies have been successful, and are reported herein.

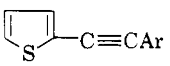
In a typical reaction, approximately equimolar amounts of iodoferrocene and cuprous phenylacetylide were refluxed in pyridine for 8 hr under nitrogen. Subsequent work-up afforded an 84% yield of ferrocenylphenylacetylene (**1a**).[3] In an analogous manner, the reaction between iodoferrocene and cuprous ferrocenylacetylide produced diferrocenylacetylene (**1b**) in 85% yield. Further, while the studies of Stephens and Castro were limited to monoiodobenzene derivatives, we have found that treatment of 1,1′-diiodoferrocene with an excess of cuprous phenylacetylide under similar conditions produces the diacetylene 1,1′-bis(phenylethynyl)ferrocene (2) in approximately 60% yield.



1a, Ar = C_6H_5
b, Ar = $FeC_{10}H_9$



2



3a, Ar = C_6H_5
b, Ar = $FeC_{10}H_9$

The iodoferrocenes used in these reactions are obtained in reasonably good yields from the readily available chloromercuriferrocenes,[4–7] or from the reaction of lithioferrocenes with iodine at low temperatures.[8] Ferrocenylacetylene has very recently become readily available by means of the reaction of acetylferrocene with the Vilsmeier complex from dimethyl-

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[1] (a) Part XI of a series "Organometallic π-Complexes." Part X: V. Mark and M. D. Rausch, *Inorg. Chem.*, **3**, 1067 (1964). Part IX: M. D. Rausch, *J. Org. Chem.*, **29**, 1257 (1964). Part VIII: M. D. Rausch and V. Mark, *ibid.*, **28**, 3225 (1963). (b) National Science Foundation Undergraduate Research Fellow, 1964.

[2] R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

[3] The preparation of **1a** in 48% yield using a similar reaction between bromoferrocene and cuprous phenylacetylide in dimethylformamide has recently been briefly described [A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Dokl. Akad. Nauk SSSR*, **154**, 158 (1964)].

[4] A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *ibid.*, **100**, 1099 (1955).

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

[6] M. Rosenblum and R. W. Fish, *ibid.*, **30**, 1253 (1965).

[7] M. D. Rausch, R. F. Kovar, A. Siegel, T. H. Mladineo, and L. P. Klemann, "Organometallic Syntheses," Academic Press Inc., New York, N. Y. in press.

[8] M. D. Rausch and R. F. Kovar, to be published.

formamide and $POCl_3$, followed by dehydrochlorination,[9] or by the more laborious earlier procedure of Benkeser and Fitzgerald.[10] Both ferrocenylacetylene and phenylacetylene are readily converted to their cuprous salts using the method of Stephens and Castro.[2] The present route would thus appear to be a distinct improvement in terms of over-all yield and simplicity compared to the previously available route to ferrocenylacetylenes such as **1a** and **1b**, and should make these acetylenes available for general study.[11,12]

We have also found that the method of Stephen and Castro can be readily employed for the synthesis of various ferrocenyl- and aryl-2-thienylacetylenes.[13] Thus, the reaction of 2-iodothiophene and cuprous phenylacetylide in refluxing pyridine afforded a 74% yield of phenyl-2-thienylacetylene (**3a**). This route to **3a** also offers distinct advantages over an earlier available method.[14] Ferrocenyl-2-thienylacetylene (**3b**) was likewise readily prepared from a reaction involving 2-iodothiophene and cuprous ferrocenylacetylide. The proton nmr spectra of the various acetylenes prepared in the present study are summarized in Table I.

TABLE I

PROTON NMR SPECTRA OF FERROCENYL- AND 2-THIENYLARYLACETYLENES[a]

	Chemical shifts (τ) and multiplicity[b]			
Acetylene	α	β	C_5H_5 ring	C_6H_5 ring
1a	5.53 (t)	5.82 (t)	5.80 (s)	2.62 (m)
1b	5.56 (t)	5.81 (t)	5.78 (s)	
2	5.48 (t)	5.70 (t)		2.62 (m)
3a				2.57 (m)[c]
3b[d]	5.53 (t)	5.79 (t)	5.78 (s)	

[a] All spectra were determined on a Varian A-60 spectrometer as *ca.* 10% (w/v) solutions in $CDCl_3$, and using tetramethylsilane as internal standard. Integration of various resonances in each spectra was consistent with each proposed structure. [b] s = singlet, t = apparent triplet, m = multiplet; *J* (apparent) for ferrocenyl protons in **1a**, **1b**, **2**, and **3b** = 1.8 cps. [c] Resonances for phenyl protons as well as 3 and 5 protons in the 2-thienyl ring occur as a broad multiplet between τ 2.32 and 2.82. The 4 proton on the 2-thienyl ring occurs as an apparent quartet at τ 3.02. The latter assignment is based upon similar assignments for other 2-thienyl derivatives (N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectra 49 and 94; see also L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 65). [d] Resonances for the thienyl protons occur as two multiplets centered at τ 2.80 and 3.08, respectively.

Detailed studies of these and related acetylenes are in progress in our laboratory, and results will be reported in forthcoming publications.

Experimental Section

General.—Phenylacetylene was purchased from Aldrich Chemicals Co. and ferrocenylacetylene was prepared by published procedures.[9,10] Cuprous phenylacetylide and cuprous ferrocenylacetylide were prepared by the method of Stephens and Castro.[2] It should be mentioned that prolonged washing of the cuprous salts in air leads in part to oxidative coupling and the formation of undesirable by-products. The cuprous salts were dried to constant weight at 50° in a vacuum drying oven. The pyridine was reagent grade and was dried over potassium hydroxide and refluxed over barium oxide before use. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Chromatography was generally performed on columns wrapped with aluminum foil to protect the compounds from light.

Ferrocenylphenylacetylene (1a).—Iodoferrocene (10.0 g, 0.032 mole) and cuprous phenylacetylide (6.6 g, 0.04 mole) were refluxed in 250 ml of pyridine for 8 hr under nitrogen.[15] The reaction mixture was cooled to room temperature, diluted with water, and extracted with ether. The ether portion was washed with water, 5% hydrochloric acid, 5% sodium hydroxide solution, and water and dried. Evaporation of the solvent and chromatography of the residue on alumina using 2:1 hexane–benzene as eluent produced 7.7 g (84% yield) of **1a** as yellow-orange crystals, mp 123–125°. After recrystallization from ethanol, the melting point was 127–128° (lit.[11] mp 121–123°).

Anal. Calcd for $C_{18}H_{14}Fe$: C, 75.54; H, 4.92. Found: C, 75.75; H, 4.90.

Diferrocenylacetylene (1b).—Iodoferrocene (6.0 g, 0.019 mole) and cuprous ferrocenylacetylide (4.0 g, 0.015 mole) were refluxed in 150 ml of pyridine under nitrogen for 8 hr. The reaction was worked up as before to give 4.8 g (84% yield) of **1b**, mp 240–242°. A subsequent recrystallization from ethanol produced bronze needles, mp 244–245° (lit.[11] mp 244–245°).

Anal. Calcd for $C_{22}H_{18}Fe_2$: C, 67.05; H, 4.60. Found: C, 66.82; H, 4.80.

1,1′-Bis(phenylethynyl)ferrocene (**2**).—In an analogous manner, treatment of 1,1′-diiodoferrocene (1.0 g, 0.0023 mole) with an excess of cuprous phenylacetylide (5.6 g, 0.034 mole) in 100 ml of pyridine under nitrogen at reflux for 8 hr and subsequent work-up gave 0.50 g (57% yield) of crude **2**, mp 166–167°. An infrared spectrum of this product exhibited no absorptions at 9 and at 10 μ. This spectrum as well as the proton nmr spectrum of the product (Table I) is consistent with heteroannular disubstitution. A slightly purer sample was prepared by additional chromatography on alumina followed by recrystallization from hexane; the melting point was 173.5–174°.

Anal. Calcd for $C_{26}H_{18}Fe$: C, 80.84; H, 4.70. Found: C, 80.01; H, 4.89.[16]

Phenyl-2-thienylacetylene (3a).—A reaction between 2-iodothiophene[17] (5.0 g, 0.024 mole) and cuprous phenylacetylide (5.0 g, 0.03 mole) in 100 ml of pyridine under nitrogen was refluxed for 10 hr. After hydrolysis, washing, and drying as above, ether was removed and the resulting solid was sublimed at 60° under reduced pressure. There was obtained 3.3 g (75% yield) of **3a** in the form of small, white needles, mp 50–50.5°.

Anal. Calcd for $C_{12}H_8S$: C, 78.22; H, 4.38; S, 17.40. Found: C, 78.32; H, 4.53; S, 17.40.

Ferrocenyl-2-thienylacetylene (3b).—2-Iodothiophene (1.00 g, 0.0048 mole) and cuprous ferrocenylacetylide (0.957 g, 0.0035 mole) were refluxed under nitrogen for 12 hr in 50 ml of pyridine. After work-up in the usual manner, chromatography of the reaction product on alumina gave 0.823 g (80% yield) of **3b**. A slightly purer product, mp 106–107° (lit.[9] mp 108–110°), could be obtained by recrystallization from hexane.

Anal. Calcd for $C_{16}H_{12}FeS$: C, 65.79; H, 4.14; S, 10.95. Found: C, 66.01; H, 4.09; S, 11.14.

Acknowledgments.—The authors wish to thank the Petroleum Research Fund of the American Chemical Society and the University of Massachusetts Research Council for their generous support of this program. We are also indebted to Professor Karl Schlögl for making available to us a portion of this results prior to publication.

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(9) K. Schlögl and W. Streyer, *Monatsh.*, **96**, 1520 (1965).

(10) R. A. Benkeser and W. P. Fitzgerald, *J. Org. Chem.*, **26**, 4180 (1961).

(11) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 2990 (1963).

(12) Professor Myron Rosenblum has recently informed us of some similar studies involving the formation of ferrocenylacetylenes in his laboratory.

(13) Analogous substitutions have been effected in the bithienyl series [R. E. Atkinson, R. F. Curtis, and G. T. Phillips, *Tetrahedron Letters*, **No. 43**, 3159 (1964)].

(14) F. Bohlmann and P. Herbst, *Chem. Ber.*, **95**, 2945 (1962).

(15) The reaction is conducted under a nitrogen atmosphere to prevent oxidative coupling to the diacetylene.[2]

(16) Several attempts to prepare a sample of **2** of analytical purity were unsuccessful. A subsequent study of the reaction products indicated that a small amount of **1a** was invariably formed during the reaction, even though high purity 1,1,-diiodoferrocene was employed initially. The very similar adsorptivities of **1a** and **2** on alumina or silica gel precluded their complete separation by means of either column or preparative thin layer chromatography.

(17) W. Minnis, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p 357.