Friedel–Crafts Reaction of Ferrocene with Arsenic Trichloride. Some Monoferrocenyl Derivatives of Arsenic(III)[1]

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The reaction of ferrocene with arsenic trichloride under Friedel–Crafts conditions has been found to give only monosubstitution on arsenic. Results of efforts to optimize the yield of arsenosoferrocene thus obtained are presented. Arsenosoferrocene, formulated as a dimer, is readily converted to ferrocenyldichloroarsine, oxybis(ferrocenylchloroarsine), a polymeric arsenosoferrocene, and arsenoferrocene. The compounds described are the first known arsenic-containing ferrocene derivatives. The bis(chloroarsine) appears to be the first example of a new class of compounds of the type $(RAsCl)_2O$. Varied behavior encountered when dimeric arsenosoferrocene is converted to the polymeric species in aqueous alkali is explained in terms of hydrolysis of the ferrocenearsonite anion. Conversion of the dimer to the polymer in various solvents is attributed to solvolysis of the arsenic–oxygen linkage. Absorptions shown by ferrocene and benzene derivatives in the region, 750–700 cm.$^{-1}$, are associated with As–O–As bridges. Ferrocene is less reactive than benzene in Friedel–Crafts reactions with acid chlorides of As^{III}, although more reactive with acid chlorides of P^{III}. A possible explanation for this anomalous behavior is suggested.

Ferrocene undergoes trisubstitution on phosphorus in reactions with phosphorus trichloride, phenylphosphonous dichloride, and diphenylphosphinous chloride under Friedel–Crafts conditions.[2,3] This behavior is a result of the highly nucleophilic character of ferrocene, and prompted us to investigate the applicability of Friedel–Crafts reactions in the preparation of arsenic-containing ferrocene derivatives. Such compounds have not been previously reported.

We have found that the reaction of ferrocene with arsenic trichloride in the presence of anhydrous aluminum halide leads to monosubstitution on arsenic under a variety of experimental conditions, and have found no evidence that disubstitution occurs under the conditions investigated. Arsenosoferrocene (I), the anhydride of ferrocenylarsonous acid (Ia), was the only product obtained after hydrolysis of the reaction solids, and arose from ferrocenyldichloroarsine (II) as precursor. Table I summarizes the results. Employing ferrocene, arsenic trichloride, and aluminum chloride in a 3:1:1 molar ratio in refluxing *n*-heptane for 20 hr. gave the arsenoso compound in optimum although moderate yield. Under identical conditions except that aluminum bromide was used in place of aluminum chloride, an increase in yield of nearly 50% was realized. Benzene was less satisfactory than heptane as solvent for the reaction in the presence of aluminum chloride. When carbon disulfide or methylene chloride was used as solvent, little or no product was isolated. With excess arsenic trichloride as solvent, the product could be isolated after heating the reaction mixture at 75–80° (Table I), but only intractable black solids were obtained after refluxing (*ca.* 130°). In the latter case extensive decomposition of ferrocene was noted, as reflected in a low recovery of ferrocene (Table I). In the former case, in which the reflux time was 5 hr., the conditions paralleled those previously employed[2] in the reaction of ferrocene with phosphorus trichloride, which led to trisubstitution on phosphorus.

TABLE I

FRIEDEL–CRAFTS REACTION OF FERROCENE WITH ARSENIC TRICHLORIDE

Molar ratio, ferrocene: ACsl$_3$:AlCl$_3$	Solvent	Reflux time, hr.	Recovered ferrocene,[a] %	Yield of arsenosoferrocene (I),[b] %
1:1:1	*n*-Heptane	20	77 (22)	2
5:1:1	*n*-Heptane	20	91 (6)	4
3:1:1	*n*-Heptane	20	76 (8)	22
3:1:1	*n*-Heptane	10	86 (6)	5
3:1:1	*n*-Heptane	30	62 (6)	16
3:1:3	*n*-Heptane	20	88 (18)	6
3:1:1.5	*n*-Heptane	20	76 (12)	15
3:1:0.5	*n*-Heptane	20	85 (3)	10
3:1:1[c]	*n*-Heptane	20	68 (9)	32
3:1:1	Benzene	20	84 (10)	8
3:1:1	CS_2	20	90 (14)	<1
3:1:1	CH_2Cl_2	20	77 (13)	0
1:3:0.75	$AsCl_3$	5	28 (8)	0
1:3:0.75	$AsCl_3$	5[d]	82 (33)	5[e]
1:3:0.75	$AsCl_3$	20[d]	86 (30)	8[e]

[a] Includes ferrocenium ion converted to ferrocene, recorded in parentheses. [b] Based on arsenic trichloride unless otherwise indicated. [c] Aluminum bromide was used in place of aluminum chloride. [d] The reaction mixture was heated at 75–80°. [e] Based on ferrocene.

Starting with arsenosoferrocene (I), chemical transformations were performed giving ferrocenyldichloroarsine (II), oxybis(ferrocenylchloroarsine) (III), a polymeric arsenosoferrocene (IV), and arsenoferrocene (V), as indicated in the diagram below. Arsenosoferrocene (I) was converted nearly quantitatively to the dichloroarsine (II) by trituration with concentrated hydrochloric acid. Oxybis(ferrocenylchloroarsine) (III) was obtained in 34% yield from ferrocenyldichloroarsine (II) merely by evaporation of a benzene solution of the latter. The structure of III was supported by results of molecular weight determinations in benzene and camphor. Compound III appears to be the first example of a new class of compounds of the type $(RAsCl)_2O$. The phenyl analog could not be produced by evaporation of a benzene solution of phenyldichloroarsine. Like compound I, III was converted in nearly quantitative yield to the dichloroarsine (II) by trituration with concentrated hydrochloric acid. Both chloro compounds (II and III) were readily hy-

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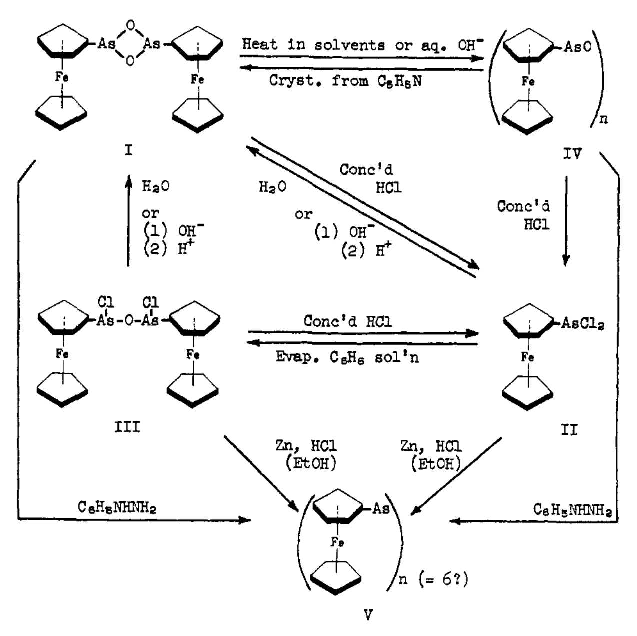
[1] Presented before the Organic Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964; Abstracts, p. 4S.

[2] G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, **27**, 4034 (1962).

[3] G. P. Sollott, H. E. Mertwoy, S. Portnoy, and J. Snead, *ibid.*, **28**, 1090 (1963).

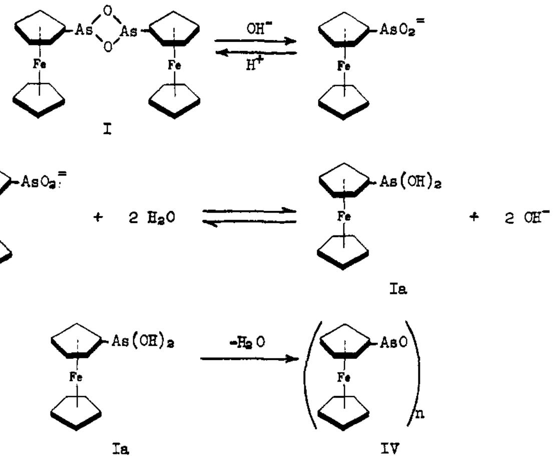


drolyzed either by alkali or water alone to arsenosoferrocene (I).

Generally, the structure of arsenoso compounds has not been established,[4–6] although it is now recognized that they are not monomeric as previously believed.[7] Arsenosobenzene, -toluene, and -anisole have been reported to be tetrameric in such solvents as benzene and camphor; the latter two arsenoso compounds, trimeric and dimeric, respectively, in chloroform.[8] Arsenosoferrocene in the solid state is formulated as a cyclic dimer (I) as opposed to a tetramer on the basis of its formation on trituration of III with water in the absence of solvent. The molecular weight determined by vapor pressure osmometry in pyridine, moreover, has been found to approach that of the dimer. Infrared spectral evidence supporting the existence of an As–O–As bridge in solid arsenosoferrocene and arsenosobenzene is presented later. It should be mentioned, in view of the variability of molecular weights of arsenosobenzenes in different solvents,[8] that arsenosobenzene itself might not be tetrameric in the solid state.

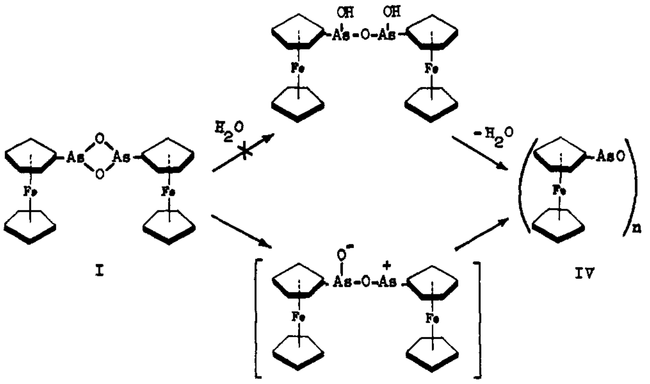
Arsenosoferrocene (I) is dissolved by 2 *N* aqueous alkali, like anhydrides of arsonous acids in general,[4] and is regenerated on acidification. Prolonged heating of the alkaline solution causes separation of a second arsenosoferrocene (IV), which is generally insoluble in organic solvents except pyridine (mentioned below), and is presumed to be polymeric.[9] Heating the dimer (I) in 0.1 *N* aqueous alkali also produces the polymer (IV), but with little apparent dissolution of the dimer.

This behavior of the dimer (I) in aqueous alkali is understandable in terms of the ferrocenearsonite anion first formed,[10] undergoing hydrolysis to the arsonous acid (Ia) which spontaneously dehydrates forming the polymer. Thus, hydroxide ion in high concentration (2 *N*) suppresses the tendency of the acid to form. As the arsonous acid forms during prolonged heating, it dehydrates to IV which separates from the solution, shifting the equilibrium in the direction of Ia. On the other hand, a low concentration of hydroxide ion (0.1 *N*) favors a comparatively rapid hydrolysis of the arsonite anion to the arsonous acid (Ia), hence the rapid formation of the polymer (IV).



Although the polymeric arsenosoferrocene (IV) is not dissolved by aqueous alkali, it is dissolved by sodium ethoxide or alcoholic sodium hydroxide. The dimer (I) was obtained from these solutions, or similar solutions of the dimer itself, after dilution with water or acidification with hydrochloric acid. The polymer could not be isolated from these solutions.

Attempts to crystallize I from chloroform, benzene, or ethyl alcohol caused conversion to IV. The same conversion was obtained using dry benzene, establishing that the formation of IV from I in benzene at least does not occur by addition of water across the oxide bridge of I followed by intermolecular dehydration. It is probable that the polymer (IV) is produced by solvolysis of the arsenic–oxygen linkage *via* a solvated ionic transition state. It is suggested that transient ionization of the As–O linkage due to solvolysis gives



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[4] For a recent review of the chemistry of arsenic compounds, see G. O. Doak, L. D. Freedman, and G. G. Long in "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 2, H. Mark, chairman of editorial board, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 718-733.

[5] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 207.

[6] C. K. Banks, J. Controulis, D. F. Walker, and J. A. Sultzaberger, *J. Am. Chem. Soc.*, **69**, 5 (1947).

[7] The naming of these compounds (alternately arsenoxides) derives from an earlier concept that the AsO group is formally analogous to the nitroso group: *cf.* C. R. Noller in "Textbook of Organic Chemistry," W. B. Saunders Co., Philadelphia, Pa., 1951, p. 590; *cf.* ref. 4 and 28.

[8] F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **52**, 2946 (1930).

[9] Two forms of arsenosobenzene, one of them "polymeric" and insoluble in benzene, have been reported: *cf.* W. Steinkopf, S. Schmidt, and H. Penz, *J. prakt. Chem.*, **141**, 301 (1934); *Chem. Abstr.*, **29**, 1401⁷ (1935).

[10] A hydrolytically unstable sodium salt was obtained impure from the 2 *N* alkaline solution by crystallization. Acid titration of an aqueous solution of the impure compound indicated it to be the monosodium salt of ferrocenylarsonous acid, but it seems likely that the disodium salt was formed initially.

rise to the differences in molecular weights observed[8] for arsenosobenzenes dissolved in various solvents (*vide supra*). Infrared spectral evidence supporting the existence of the oxide bridge in arsenosobenzene is presented later. In passing, it appears that benzene-insoluble, polymeric arsenosobenzene[9] is not formed by taking up the soluble arsenosobenzene in solvents.[8]

The dimer (I) could be crystallized unchanged from pyridine. Attempted crystallization of the polymer (IV) from the same solvent caused conversion to the dimer (I). After freezing of a solution of I or IV in pyridine, however, IV crystallized on thawing. This behavior of I and IV in pyridine indicated that the polymer (IV) is not present during determination of the molecular weight of the dimer (I) by vapor pressure lowering in pyridine (mentioned above). The interconversion of I and IV occurs in dried, redistilled pyridine as well as ordinary pyridine, while neither I nor IV is dissolved by relatively strong bases such as diethylamine or piperidine. These observations rule out the existence of a hydroxyarsine or an arsonite or pyridine salt species as an intermediate in the interconversion of I and IV in pyridine. It seems likely that this interconversion also occurs, as in the case of the conversion of I to IV by solvents mentioned above, *via* solvolysis of the arsenic–oxygen linkage.

Polymeric arsenosoferrocene (IV), like the dimer (I) and the bis(chloroarsine) (III), could be converted almost quantitatively to ferrocenyldichloroarsine (II) by trituration with concentrated hydrochloric acid. Treatment of a solution of II in 95% ethyl alcohol with zinc dust and hydrochloric acid gave a quantitative yield of arsenoferrocene (V) instead of the expected ferrocenylarsine ($RAsH_2$).[11] Oxide I could also be reduced to V in this manner, but much less satisfactorily because of its tendency to convert to the insoluble oxide, IV. The same product (V) was obtained quantitatively by a similar reduction of the bis(chloroarsine) (III), and could also be prepared in lower yield by reduction of oxide I or IV with phenylhydrazine. Formation of V unequivocally by the quantitative reduction of oxide I with hypophosphorous acid established that the product obtained by reduction of the dichloroarsine (II) with zinc and hydrochloric acid was not ferrocenylarsine. The arsine, moreover, would be subject to air oxidation; the arseno compound (V) is stable in air. Arsenoferrocene shows little tendency to dissolve in organic solvents, but can be crystallized from pyridine in which it has rather limited solubility. It is a new member of a class of compounds formerly regarded as analogous in structure to azobenzene, but which now appear to be polymeric, probably consisting of a six-membered arsenic ring.[4] Arsenobenzene and its derivatives are soluble in benzene and chloroform.[8] The almost total lack of solubility of arsenoferrocene in these solvents, however, may indicate that the substance is actually a higher polymer than a hexamer. It is significant that insoluble, presumably polymeric phenylphosphines have been reported in addition to soluble cyclotetramers, and that the dimeric phosphorus analog of azobenzene appears not to exist.[12]

The infrared spectra of compounds I–V,[13] like the spectra of phosphorus-containing ferrocene derivatives,[2,3,14] show the usual absorptions near 1110 and 1005 cm.$^{-1}$ characteristic of monosubstituted ferrocenes and typical ferrocene bands in the regions, 3060–3100, 1410–1420, and 810–840 cm.$^{-1}$. Bands appear in all spectra in the regions, 1305–1320 and 1015–1045 cm.$^{-1}$, previously associated with the ferrocenyl–phosphorus group,[2,3,14] and are tentatively attributed to the ferrocenyl–arsenic group. All compounds show two bands, one near 1195 (medium intensity) and one near 1155 cm.$^{-1}$ (strong intensity), which also appear to be characteristic of phosphorus^{III}-containing ferrocene derivatives,[3,14] and which are due possibly to ferrocene in-plane C–H bending.

The spectrum of polymeric arsenosoferrocene (IV) differs from that of the dimeric species (I) by the presence of a band at 1036 and peaks at 839 and 827 in place of a shoulder near 830 cm.$^{-1}$. The other difference is seen in Table II, which summarizes bands appearing below 750 cm.$^{-1}$ in the spectra of compounds I–V. These bands, of strong intensity, are absent from the spectra of ferrocenyldichloroarsine (II) and arsenoferrocene (V), and are attributed to As–O–As absorptions.[15,16]

TABLE II

ABSORPTION BANDS[a] IN THE REGION, 750–680 CM.$^{-1}$

Compd.[b]	As-O-As stretching[c]	Phenyl
$(FcAsO)_2$ (I)	725	. . .
$(FcAsO)_n$ (IV)	740, 720(sh), 707	. . .
$(FcAsCl)_2O$ (III)	720	. . .
$FcAsCl_2$ (II)	. . .	. . .
$(FcAs)_n$ (V)	. . .	. . .
$(C_6H_5AsO)_{4?}$[d]	748, 742, 721	731, 692
$[(C_6H_5)_2As]_2O$	749, 743, 724	737, 694
$C_6H_5AsCl_2$	. . .	737, 687
$(C_6H_5)_2AsCl$	. . .	738, 688
$(C_6H_5)_3As$	. . .	735, 693
$(C_6H_5)_3AsO$[e]	. . .	738, 693

[a] See footnote 13. [b] Fc = ferrocenyl. [c] See footnote 16. [d] Might not be tetrameric in the solid state. [e] Shows As=O stretching at 880 cm.$^{-1}$.[17,18]

Examination of the spectra of the soluble form of arsenosobenzene[9] and oxybis(diphenylarsine) reveals, in addition to phenyl bands, other strong bands in the region, 750–680 cm.$^{-1}$ (Table II), and these are also attributed to As–O–As absorptions.[16] This implies that, while solid arsenosobenzene might not be tetrameric (*vide supra*), it is *not* monomeric in that form.[5] The spectra of phenyldichloroarsine, diphenylchloroarsine, and triphenylarsine and its oxide[17] show no comparable absorptions in this region other than phenyl bands (Table II). Triphenylarsine oxide shows As=O stretching at 880 cm.$^{-1}$.[17,18] No band appears in the spectrum of arsenosobenzene attributable to

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(11) See ref. 5, p. 203.

(12) W. A. Henderson, Jr., M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963), and references cited therein.

(13) Infrared spectra were obtained from Nujol mulls employing a Perkin-Elmer Model 21 spectrophotometer.

(14) G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, **29**, 2451 (1964).

(15) P-O-P absorptions occur in the region, 900–980 cm.$^{-1}$; *cf.* L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961).

(16) Multiple absorptions are possibly manifestations of asymmetric and symmetric stretching modes of the As-O-As group. A doublet near 1262 and 1378 cm.$^{-1}$ appears to be characteristic of the B-O-B group: *cf.* W. Gerrard, "The Organic Chemistry of Boron," Academic Press Inc., London, 1961, p. 225.

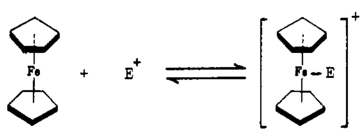
(17) Spectrum reported by J. Bernstein, M. Halmann, S. Pinchas, and D. Samuel [*J. Chem. Soc.*, 821 (1964)].

(18) D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

As=O. It is significant that a suggestion has recently been made that Sb=O does not exist in certain organic compounds of pentavalent antimony, and that broad areas of absorption between 800 and 400 cm.$^{-1}$ are associated with Sb–O–Sb bridges which link the compounds polymerically.[19]

That ferrocene has been found to undergo only monosubstitution on arsenic in its reaction with arsenic trichloride under Friedel–Crafts conditions is significant in view of the report[20] that benzene gives mono-, di-, and trisubstitution on arsenic in a similar reaction. This behavior of benzene, plus the reported formation of tertiary arsines by Friedel–Crafts reactions of benzene and several of its derivatives with a monochloroarsine,[21] indicates a stepwise electrophilic process analogous to the case of ferrocene and acid chlorides of phosphorus.[2,3] This is evident despite the report by Lyon and Mann[22] that diphenylchloroarsine can arise by disproportionation from phenyldichloroarsine under the influence of aluminum chloride, and then give rise to the tetraphenylarsonium ion by thermal decomposition. Ferrocene is thus less reactive than benzene towards arsenic trichloride, although more reactive towards acid chlorides of trivalent phosphorus in electrophilic substitution reactions. This anomalous behavior of ferrocene cannot be attributed to a reluctance of ferrocenyldichloroarsine to interact with aluminum chloride to generate an electrophile. This was apparent when, in the light of the reactivity of benzene with arsenic trichloride, attempted reactions of ferrocene with phenyldichloroarsine and diphenylchloroarsine under Friedel–Crafts conditions did not produce the ferrocenylphenylarsines.

A general mechanism for electrophilic substitution reactions of ferrocene has been suggested in which the metal atom, rather than the cyclopentadienyl ring, is the primary site for electrophilic attack.[23] Thus,



the decreased reactivity of ferrocene towards Friedel–Crafts alkylations relative to acylations was attributed to the planar alkyl carbonium ion experiencing greater steric hindrance than the linear acylonium ion on interacting with the metal orbitals. The anomalous behavior encountered in the present work is readily explained if the steric requirement of the arsenic electrophile unable to produce the secondary ferrocenylchloroarsine is appreciably greater than that of the phosphorus electrophile which produces the corresponding phosphinous chloride.[2] The following represent the possible formation of a bulky arsenic electrophile[24] and of a relatively small phosphorus electrophile.

$$C_6H_5AsCl_2 \xrightarrow{AlCl_3} (C_6H_5AsCl_2)_3AlCl_3$$

$$\xrightarrow{AlCl_3} [(C_6H_5AsCl_2)_2(C_6H_5\overset{+}{As}Cl)AlCl_3]AlCl_4^-$$

$$C_6H_5PCl_2 \xrightarrow{AlCl_3} [C_6H_5\overset{+}{P}Cl]AlCl_4^-$$

Lyon and Mann[22] have isolated the complex, $(C_6H_5AsCl_2)_3AlCl_3$, in which aluminum has a coordination number of six. That an analogous complex of phosphorus is formed has not been established.[25] Clearly, information is needed concerning composition, size, and configuration of the arsenic and phosphorus electrophiles before a completely satisfactory explanation of the anomalous behavior based on steric hindrance may be formulated. Moreover, it remains to be established that arsenic- and phosphorus-containing ferrocene derivatives are formed under Friedel–Crafts conditions by initial electrophilic attack on the iron atom.

Experimental[26]

Arsenosoferrocene (I) *via* the Friedel–Crafts Reaction.—A mixture of 55.8 g. (0.3 mole) of ferrocene and 13.3 g. (0.1 mole) of anhydrous aluminum chloride in 400 ml. of *n*-heptane was stirred under nitrogen. A solution of 18.1 g. (0.1 mole) of arsenic trichloride in 200 ml. of *n*-heptane was added dropwise over a period of 30 min. after which the mixture was refluxed 20 hr. with stirring.

The orange heptane phase was decanted through a filter, and the blue-black solids were treated cautiously with 300 ml. of water and filtered. The orange-brown filter cake was washed free of the blue aqueous solution with fresh water, and the combined inky blue solutions were set aside for further treatment. The solids on the filter were extracted twice with 150 ml. of hot benzene and some dark brown, insoluble solids were discarded. The dark brown benzene solution was dried over anhydrous sodium sulfate, filtered, and combined with the heptane phase above. The solvent was removed in a rotary evaporator, and the remaining orange-brown solids were triturated with 2 *N* aqueous sodium hydroxide. Additional 2 *N* aqueous alkali (400 ml.) was added; the mixture was boiled gently for 10 min., and the undissolved orange solids were removed by filtration. These were boiled gently with fresh 2 *N* aqueous alkali (200 ml.) and the undissolved orange solids (A) were collected on a filter. The combined orange, alkaline filtrates were cooled to 5° and acidified dropwise with concentrated hydrochloric acid. The precipitated pale yellow product was collected on a filter and dried *in vacuo* at 110°; weight 3.5 g. Solids A were extracted with 600–800 ml. of boiling heptane, and the insoluble solids (impure polymeric IV, as determined by infrared spectrum) were dissolved in either alcoholic sodium hydroxide or sodium ethoxide. The solution was filtered and acidification with concentrated hydrochloric acid caused 2.6 g. of product (I) to precipitate; combined yield 6.1 g. (22%). For analysis the product was purified by crystallization from pyridine at −10°; pale yellow crystals, m.p. 261–262° (with gradual darkening above 250°), instantaneous m.p. 275.5–276.0°.

Anal. Calcd. for $(C_{10}H_9AsFeO)_2$: C, 43.53; H, 3.28; As, 27.14; Fe, 20.24; mol. wt., 552. Found: C, 43.17; H, 3.52; As, 27.44; Fe, 19.97; mol. wt., 484 (vapor pressure lowering in pyridine).

The product was dissolved by sodium ethoxide or alcoholic or 2 *N* aqueous sodium hydroxide with warming. It precipitated on acidification with concentrated hydrochloric acid, except in

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[19] G. O. Doak, G. G. Long, and L. S. P. Madamba, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 36O.

[20] H. Wieland and A. Kulenkampff, *Ann.*, **431**, 30 (1923); W. La Coste and A. Michaelis, *ibid.*, **201**, 184 (1880); *cf. Chem. Abstr.*, **17**, 1783 (1923), and C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 171.

[21] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, **119**, 426 (1921); A. F. Hunt and E. E. Turner, *ibid.*, 2667 (1925).

[22] D. R. Lyon and G. D. Mann, *ibid.*, 666 (1942).

[23] M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963), and references cited therein.

[24] Steric considerations indicate that there would be no undue hindrance in the case where the arsenic-containing electrophile is simply $C_6H_5As^+Cl$ or $C_5H_5FeC_5H_4As^+Cl$.

[25] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 44.

[26] All melting points are uncorrected. The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

the case of alcoholic solutions which additionally required boiling to reduce the volume.

Evaporation of solvent from the heptane extract of solids A produced 38 g. (68%) of unchanged ferrocene. From the inky blue aqueous solution (above) was obtained 4.2 g. (8%) of ferrocene after reduction with powdered zinc, and extraction with benzene.

Ferrocenyldichloroarsine (II).—Arsenosoferrocene (I) (3.0 g., 5.4 mmoles) was triturated with concentrated hydrochloric acid. More acid (15 ml.) was added to the dark red paste, and the mixture was transferred through a filter under suction. The red-brown solids were then extracted with 250 ml. of hot heptane, in portions, and a small quantity of insoluble solids was discarded. The combined heptane extracts were evaporated to dryness under an air stream giving 3.4 g. (95%) of golden yellow leaflets. The product was purified by crystallization from dry heptane; yellow powder, m.p. 63.5–64°.

Anal. Calcd. for $C_{10}H_9AsCl_2Fe$: C, 36.30; H, 2.74; As, 22.64; Cl, 21.43; Fe, 16.88; mol. wt., 330.8. Found: C, 36.95; H, 3.02; As, 22.33; Cl, 21.43; Fe, 17.15; mol. wt., 323 (camphor).

Ferrocenyldichloroarsine was obtained by a procedure similar to that described above, and in comparable yield from oxybis(ferrocenylchloroarsine) (III) and from polymeric arsenosoferrocene (IV). The compound (II) gradually hydrolyzed over a period of 1 month in air, or rapidly on trituration with water, to arsenosoferrocene (I). Dissolution of II in aqueous alkali followed by acidification with hydrochloric acid also produced I. On standing under nitrogen for extended periods (2 weeks–1 month), the dichloroarsine darkened and heptane-insoluble, dark brown solids formed. These were not characterized.

Oxybis(ferrocenylchloroarsine) (III).—Ferrocenyldichloroarsine (II) (1.8 g., 5.5 mmoles) was dissolved in hot benzene, and the solvent was evaporated under an air stream. The red oil (or occasionally solid) was taken up in a minimum quantity of hot petroleum ether, and the solution was filtered and cooled in a Dry Ice–acetone bath for 10 min. The mixture was then allowed to warm to room temperature with occasional stirring to hold unconverted dichloroarsine in solution. The powdery yellow solids were then collected on a filter; yield 0.6 g. (34%). The yield was subject to large variation and ranged as low as 18%. Crystallization from dry heptane afforded a yellow powder, m.p. 118.5–120°.

Anal. Calcd. for $C_{20}H_{18}As_2Cl_2Fe_2O$: C, 39.59; H, 2.99; As, 24.69; Cl, 11.69; Fe, 18.41; mol. wt., 606.8. Found: C, 40.37; H, 3.33; As, 24.01; Cl, 11.06; Fe, 18.10; mol. wt., 585 (camphor), 594 (vapor pressure lowering in benzene).

Evaporation of a solution of II in petroleum ether (35–75°) instead of benzene, also gave the product but in lower yield (12%). No product was obtained by evaporation of a solution of II in *n*-heptane. The product was moisture sensitive but to a lesser degree than the dichloroarsine (II), and was stable for longer periods under nitrogen. Trituration with water and with concentrated hydrochloric acid converted the product to the arsenoso (I) and dichloroarsine (II) derivatives, respectively. Dissolution of the product (III) in aqueous alkali followed by acidification with hydrochloric acid also produced I.

A benzene solution of phenyldichloroarsine was evaporated to dryness. However, work-up of the residue as above did not produce the phenyl analog of III.

Polymeric Arsenosoferrocene (IV).—Boiling of arsenosoferrocene (I) in chloroform, benzene, or ethyl alcohol caused quantitative conversions to the insoluble polymeric product. The polymer was obtained analytically pure by freezing of a solution of dimeric arsenosoferrocene (I) or the polymer (IV) in pyridine, then allowing to thaw and stand at 0°. The product, a fine, pale yellow powder, was collected on a filter; infusible under normal melting procedure (with darkening above 260°), instantaneous m.p. 266–267°.

Anal. Calcd. for $(C_{10}H_9AsFeO)_n$: C, 43.53; H, 3.28; As, 27.14; Fe, 20.24. Found: C, 43.61; H, 3.21; As, 27.25; Fe, 19.91.

Boiling of a solution of dimeric arsenosoferrocene (I) in 2 *N* aqueous sodium hydroxide for at least 1 hr. resulted in formation of the insoluble polymeric form in appreciable quantity. In 0.1 *N* aqueous sodium hydroxide, in which compound I appeared to be insoluble, conversion to the polymeric form was completed in a matter of minutes.

Dissolution of the polymer in sodium ethoxide or alcoholic sodium hydroxide, followed either by dilution with water or acidification with hydrochloric acid, then boiling to reduce the volume, gave the dimer (I). The polymer was converted to the dimer by crystallization at −10° from dried, redistilled pyridine. Several recrystallizations from ordinary (unpurified) pyridine were necessary for complete conversion of the polymer to the dimer. The polymeric product was distinguishable from the dimeric species (II) by its infrared spectrum (*vide supra*).

Arsenoferrocene (V). A. By Reduction of Ferrocenyldichloroarsine (II) or Oxybis(ferrocenylchloroarsine) (III) with Zinc and Hydrochloric Acid.—Both chloro derivatives (II and III) were reduced quantitatively in 95% ethyl alcohol at room temperature by granular or powdered zinc and sufficient concentrated hydrochloric acid to cause a visible evolution of hydrogen. The insoluble, orange, powdery product was removed by filtration, washed with alcohol, and shown *via* infrared spectra to be identical with the product obtained by reduction with hypophosphorous acid and with phenylhydrazine (below).

B. By Reduction of Dimeric Arsenosoferrocene (I) with Hypophosphorous Acid.—Arsenosoferrocene (I) was reduced quantitatively on heating 2.5 hr. (steam bath) in excess 50% hypophosphorous acid dissolved 1:1 by volume in 95% ethyl alcohol. The cottony, yellow-orange product was collected on a filter, washed with alcohol, and shown by infrared spectra to be identical with the product obtained by reduction with zinc and hydrochloric acid (above) and with phenylhydrazine (below).

C. By Reduction of Dimeric Arsenosoferrocene (I) or Polymeric Arsenosoferrocene (IV) with Phenylhydrazine.—Arsenosoferrocene (I or IV) was dissolved in a minimum quantity of hot phenylhydrazine, heated almost to boiling, and allowed to stand at room temperature for 30 min. Heating and cooling were repeated, after which the product, in the form of orange needles, was collected on a filter and washed free of phenylhydrazine with acetone; yield 10–15%. Crystallization from pyridine gave a bright yellow powder, m.p. 328–331° (with darkening above 290°).

Anal. Calcd. for $(C_{10}H_9As)_n$: C, 46.20; H, 3.49; As, 28.82; Fe, 21.49. Found: C, 46.39; H, 3.52; As, 28.87. Fe, 21.03.

Attempted Reaction of Ferrocene with Phenyldichloroarsine under Friedel–Crafts Conditions.—Phenyldichloroarsine was prepared by reduction of benzenearsonic acid with sulfur dioxide in concentrated hydrochloric acid by the method of Barker, *et al.*[27] Ferrocene, phenyldichloroarsine, and anhydrous aluminum chloride in a 2:1:1 molar ratio were refluxed for 20 hr. in *n*-heptane. Work-up of the blue-black reaction mixture was analogous to that employed for the reaction of arsenic trichloride, above. Extraction of the water-washed reaction solids with 2 *N* aqueous sodium hydroxide followed by dropwise acidification at 0° with concentrated hydrochloric acid, produced arsenosobenzene (white, crystalline solid from acetone, m.p. 142–144°; lit. m.p. 142–145°,[9] 144–146°[28]). No arsenic-containing ferrocene derivative was isolated. The alkali-insoluble solids were largely intractable after removal of unchanged ferrocene (83%) by steam distillation. Reduction of the inky blue aqueous solutions with zinc gave an additional quantity of ferrocene (12%).

Attempted Reaction of Ferrocene with Diphenylchloroarsine under Friedel–Crafts Conditions.—Diphenylchloroarsine was prepared by oxidation of phenylhydrazine with arsenic acid in the presence of copper powder as catalyst, and subsequent treatment with concentrated hydrochloric acid, according to the method of Barker, *et al.*[29] Ferrocene, diphenylchloroarsine, and anhydrous aluminum chloride in a 1:1:1 molar ratio were refluxed for 20 hr. in *n*-heptane. After treatment of the blue-black reaction mixture with water, the remaining solids were steam distilled, removing unchanged ferrocene (50%). The residue, a brown oil consisting mainly of diphenylchloroarsine, was warmed with 2 *N* aqueous sodium hydroxide producing oxybis(diphenylarsine) (white, crystalline solid from *n*-heptane, m.p. 93–94.5°; lit.[30] m.p. 92.5–93.5°). No arsenic-containing ferrocene derivative was isolated. Reduction of the inky blue aqueous solutions with zinc produced more ferrocene (46%).

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