filtered off, the solution evaporated to dryness *in vacuo* and the residue crystallized from methanol-water to give 60 mg. of 17-desoxyrauwolscine, m.p. 210-212° $[\alpha]_D^{25}$ $-12.2°$ (pyridine). λ_{max}^{Nujol} 2.93 μ, 5.82 μ.

Anal. Calcd. for $C_{21}H_{26}O_2N_2$ (338.43): C, 74.52; H, 7.74. Found: C, 74.49; H, 7.74; N.E. ($HClO_4$) 337.

Hydrolysis of 17-desoxyrauwolscine to X and regeneration by esterification. A suspension of 89 mg. 17-desoxyrauwolscine in 15 ml. of 2*N* potassium hydroxide in 50% aqueous methanol was refluxed for 3 hr. during which time the alkaloid dissolved completely. After cooling, the solution was acidified with hydrochloric acid whereupon precipitation occurred. The precipitate was filtered and recrystallized from dilute hydrochloric acid to give 50 mg. of 17-desoxyrauwolscic acid hydrochloride (X), m.p. 300–302°, $[\alpha]_D^{24}$ $+39.3°$ (pyridine). λ_{max}^{Nujol} 3.20 μ, 5.82 μ.

Anal. Calcd. for $C_{20}H_{24}O_2N_2.HCl$ (360.88): C, 66.56; H, 6.98. Found: C, 66.51; H, 6.97.

Re-esterification of X with diazomethane converted it to 17-desoxyrauwolscine, identical in all respects with the starting material.

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Convenient Synthesis of Ferrocenyl Aryl Sulfides[1]

M. D. RAUSCH

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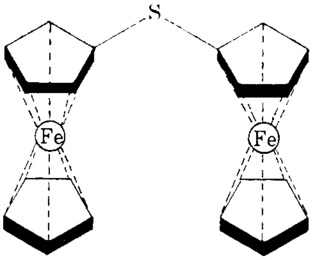
The discovery by three independent groups of investigators that ferrocene can readily be sulfonated has been followed by the preparation of a number of sulfur-containing ferrocene derivatives.[2–7] Knox and Pauson reported that ferrocenethiol can be formed by reduction of ferrocenesulfonyl chloride and have converted the sodium salt of ferrocenethiol to methyl and allyl ferrocenyl sulfides by reaction with dimethyl sulfate and allyl bromide, respectively.[7] Ferrocenyl methyl sulfide has also been subjected to the aminomethylation reaction.[8] Ferrocenyl aryl sulfides, however, have not previously been described in the literature.

In conjunction with our studies involving the haloferrocenes,[9,10] we wish to report a procedure by which ferrocenyl aryl sulfides can be readily prepared. Mauthner observed many years ago that aryl iodides reacted with various sodium arenethiolates in the presence of catalytic amounts of copper to yield diaryl sulfides.[11] We have found that iodoferrocene and sodium benzenethiolate react similarly to produce ferrocenyl phenyl sulfide in 76% yield. Phenyl-substituted sulfides such as ferrocenyl *p*-tolyl sulfide can likewise be readily prepared starting with the appropriate thiol. Of particular utility is the facile reaction of iodoferrocene and sodium ferrocenethiolate to produce diferrocenyl sulfide (I). Mauthner's procedure can therefore be used as a convenient and general synthesis of ferrocenyl aryl sulfides.



I

Several attempts to obtain diferrocenyl sulfide from diferrocenylmercury and sulfur were not successful. The only isolable products were ferrocene and a small amount of diferrocenyl disulfide.

EXPERIMENTAL[12]

Materials. Iodoferrocene was prepared in 60–70% yield by reaction of chloromercuriferrocene and iodine in xylene solution at 75–80°.[13] Copper bronze was obtained from B. F. Drakenfield and Co., Inc., New York, and was activated according to the procedure of Vogel.[14] Benzenethiol was obtained from Distillation Products Industries and *p*-toluenethiol from The Matheson Co., Inc. Ferrocenethiol was prepared according to the procedure of Knox and Pauson.[7] Diferrocenylmercury was obtained from chloromercuriferrocene according to published procedures.[15,16] Chromatographic alumina was obtained from Merck & Co., Inc. G.E. lamp-grade nitrogen was used throughout this investigation.

Diferrocenyl sulfide (I). To 5 ml. of absolute ethanol in a Schlenk tube under nitrogen was added 0.19 g. (0.0084 g.-atom) of sodium. Ferrocenethiol, prepared by the reduction of 2.40 g. (0.0084 mole) of ferrocenesulfonyl chloride by lithium aluminum hydride (1.28 g.) in 50 ml. of anhydrous

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[1] Part V of a series: "Ferrocene and Related Organometallic π-Complexes." Part IV, see Ref. 10.

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[12] All melting points are uncorrected. Elemental analyses and molecular weight determinations (cryoscopic in camphor) were performed by Mr. J. Edwards of this laboratory and by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

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ether,[7] was dissolved in a small amount of ethanol and combined with the sodium ethoxide solution. The mixture was heated on a steam bath for 15 min. and the excess ethanol was then removed by gentle heating at reduced pressure. A mixture of 2.62 g. (0.0084 mole) of iodoferrocene and 0.05 g. of freshly activated copper bronze was added and the reactants were mixed well. A 2-ft. air condenser was inserted and the tube was heated in a silicone bath at 150° (bath temperature) for 8 hr. The reaction residue and an orange sublimate that formed were combined and were extracted with 100 ml. of hot ethanol. The ethanol extracts were acidified with 100 ml. of 5% sulfuric acid solution and were subjected to steam distillation for approximately 1 hr. in the presence of several grams of powdered zinc.[17]

The distillate was collected, extracted with benzene, the benzene extracts were dried over Drierite, and the solvent was evaporated. The residue was dissolved in petroleum ether (b.p. 60–70°) and was chromatographed on alumina. A broad yellow foreband produced 0.55 g. of ferrocene, m.p. 170–173°. An orange trailing band produced 0.16 g. of crude diferrocenyl disulfide, m.p. 179–183°. One recrystallization from benzene–petroleum ether yielded orange crystals of the disulfide, m.p. 192–193° (reported m.p. 192°).[7] The infrared maxima (potassium bromide disk) of this product were identical to those published previously for diferrocenyl disulfide.[7]

The flask residue after cooling was extracted with benzene, the extracts were washed with water until the wash was neutral, the extracts were dried over Drierite, and the solvent was evaporated. There remained 2.50 g. of crude diferrocenyl sulfide, m.p. 152–153°. This product was dissolved in benzene–petroleum ether and chromatographed on alumina. A homogeneous band eluted, producing 2.14 g. of product, m.p. 155–156°. Recrystallization from *n*-heptane gave 2.00 g. (60% yield) of orange needles of diferrocenyl sulfide, m.p. 161.5–162°.

Anal. Calcd. for $C_{20}H_{18}Fe_2S$: C, 59.74; H, 4.51; Fe, 27.78; S, 7.97; mol. wt., 402. Found: C, 59.79; H, 4.59; Fe, 28.05; S, 8.22; mol. wt., 408.

The infrared spectrum of diferrocenyl sulfide (potassium bromide disk) exhibited bands at 3100, 1415, 1105, 1003, and 820 cm.$^{-1}$ characteristic of the ferrocenyl group, and other absorption bands at 1025 and 883 cm.$^{-1}$.

Ferrocenyl phenyl sulfide was prepared from 0.07 g. (0.003 g.-atom) of sodium, 0.35 g. (0.0032 mole) of benzenethiol, 0.936 g. (0.003 mole) of iodoferrocene, and 0.02 g. of copper bronze. The reaction mixture was heated at 158° for 2.5 hr. From the residue following steam distillation was obtained 0.67 g. (76% yield) of ferrocenyl phenyl sulfide, m.p. 110–111°. An analytical sample was prepared by chromatography of the product on alumina and subsequent recrystallization from petroleum ether; orange needles, m.p. 111.5–112°.

Anal. Calcd. for $C_{16}H_{14}FeS$: C, 65.31; H, 4.80; Fe, 18.98; S, 10.90; mol. wt., 294. Found: C, 65.12; H, 4.98; Fe, 18.90; S, 10.84; mol. wt., 288.

The infrared spectrum of ferrocenyl phenyl sulfide (potassium bromide disk) exhibited bands at 3100, 1418, 1108, 1002, and 820 cm.$^{-1}$ characteristic of the ferrocenyl group, bands at 1580, 1480, 745, and 690 cm.$^{-1}$ characteristic of the phenyl group, and other strong absorption bands at 1440, 1165, 1075, 890, and 830 cm.$^{-1}$

Ferrocenyl p-tolyl sulfide was prepared in 68% yield by a procedure identical to that described for ferrocenyl phenyl sulfide, except that *p*-toluenethiol was substituted for benzenethiol. The product was recrystallized from methanol, forming long yellow needles, m.p. 110.5–111°.

Anal. Calcd. for $C_{17}H_{16}FeS$: C, 66.25; H, 5.23; Fe, 18.12; S, 10.40; mol. wt., 308. Found: C, 66.23; H, 5.23; Fe, 18.28; S, 10.76; mol. wt., 315.

The infrared spectrum of ferrocenyl *p*-tolyl sulfide (potassium bromide disk) exhibited bands at 3100, 1411, 1103, 1006, and 816 cm.$^{-1}$ characteristic of the ferrocenyl group, bands at 1900, 1490, and 808 cm.$^{-1}$ characteristic of the *p*-tolyl group, and other strong absorption bands at 1182, 1165, 1083, 1023, 1018, 998, 890, 838, and 828 cm.$^{-1}$

Reaction of diferrocenylmercury and sulfur. A mixture of 1.14 g. (0.002 mole) of diferrocenylmercury and 0.16 g. of sulfur was thoroughly mixed and was added to a Schlenk tube under nitrogen. A loose-fitting plug of glass wool was inserted between the reactants and the upper portion of the tube. A 2-ft. air condenser was inserted and the tube was heated in a silicone bath at 160–180° for 18 hr. After cooling to room temperature, 0.20 g. of an orange sublimate was collected, m.p. 164–170°. The residue was extracted repeatedly with hot benzene, the solvent was evaporated, and the resulting residue plus the sublimate were chromatographed on alumina in benzene–petroleum ether solution. Elution with petroleum ether removed 0.16 g. of ferrocene, m.p. 173–174°. Continued elution with benzene produced 0.02 g. of an orange solid. This product was recrystallized from methanol, forming 0.01 g. of diferrocenyl disulfide, m.p. 185–187°. The infrared spectrum of this material (potassium bromide disk) was identical to the spectrum of diferrocenyl disulfide isolated above and with literature data.[7]

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(17) Under these conditions, any disulfide formed would be reduced to the thiol which in turn would distill with steam.[11] The diferrocenyl disulfide detected in the distillate probably resulted from distilled ferrocenethiol, since this thiol is known to oxidize readily in air to the disulfide.[7]

Indandiones. II. A Modified Dieckmann Reaction

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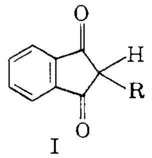
A new method affording excellent yields of arylindandiones (I) through the condensation of phthalide and aromatic aldehydes has been recently reported.[1] This reaction has now been recognized to proceed through the 3-(α-hydroxybenzyl)phthalide[1–3] *via* elimination of water to give the 2-arylindandione (I).[4]



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In the Dieckmann reaction, unlike other carbonyl methylene condensations,[5,6] formed water

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