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Synthesis of triorganostannylferrocenes, diorganostannyldiferrocenes, diorganochlorostannylferrocenes, and 1,1′-bis(diorganochlorostannyl)ferrocenes

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Abstract

Treatment of bis-triorganotin sulfides $(R_3Sn)_2S$ or diorganotin sulfides R_2SnS with diferrocenylmercury gives triorganostannylferrocenes and diorganostannyldiferrocenes, respectively. Reaction of R_2SnS with chloromercuriferrocene and 1,1′-bis(chloromercuri)ferrocene gives diorganochlorostannylferrocenes and 1,1′-bis(diorganochlorostannyl)ferrocenes.

Introduction

An earlier report involving one of us described the preparation of organotin α-substituted ketones and esters by reaction of organotin sulfides with organomercury derivatives [1,2]. The present paper deals with extension of the reaction of organotin sulfides with organomercury compounds to the synthesis of organostannylferrocenes and organochlorostannylferrocenes.

Results and discussion

Triorganostannylferrocenes and diorganostannyldiferrocenes were respectively made by treating diferrocenylmercury with bis-triorganotin sulfides $(R_3Sn)_2S$ and diorganotin sulfides R_2SnS in dioxane under nitrogen.

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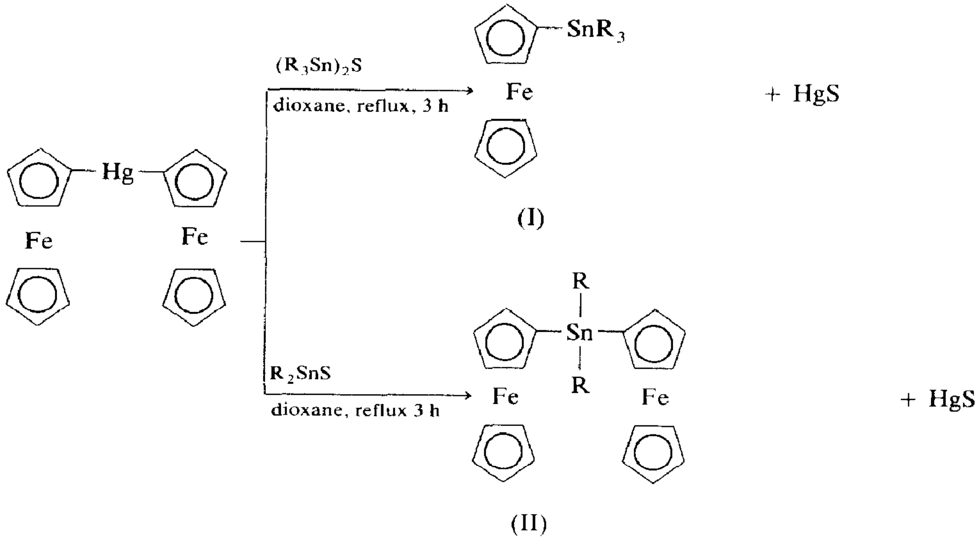
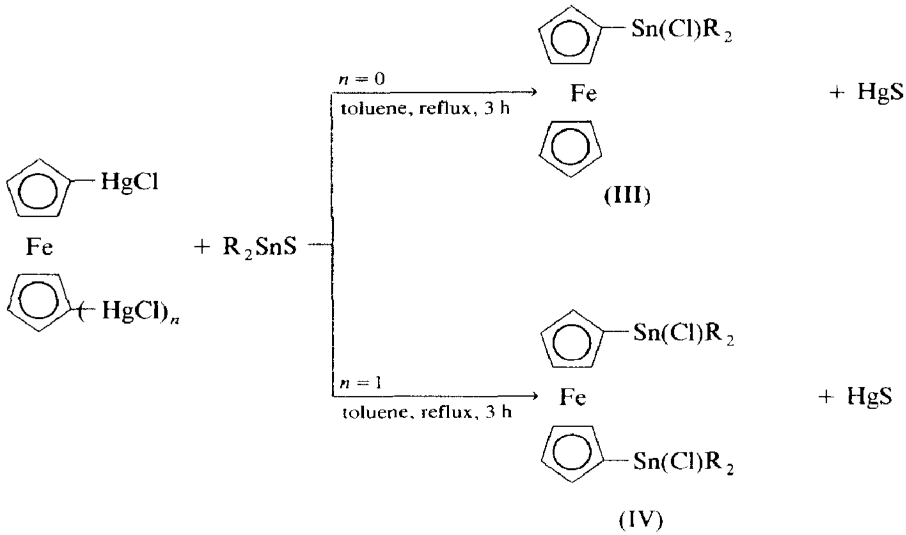


(I and II: a, R = CH_3; b, R = n-C_4H_9; c, R = C_6H_5)

Details of the procedure are given in the Experimental section, and yields and melting points are listed in Table 1.

Under analogous conditions but with toluene as solvent the reaction of diorganotin sulfides with chloromercuriferrocene and 1,1′-bis(chloromercuri)ferrocene gives diorganochlorostannylferrocenes and 1,1′-bis(diorganochlorostannyl)ferrocenes:



(n = 0, 1; III and IV; a, R = CH_3; b, R = n-C_4H_9; c, R = C_6H_5)

These products are of interest because they can serve as precursors of many organostannylferrocenes because of the reactivity of the Sn–Cl bond. Yields, melting points and mass spectroscopic data are listed in Table 2.

Table 1

Triorganostannylferrocenes and diorganostannyldiferrocenes

Product	Yield (%)	M.p. (°C) recrystallisation solvent	Reference
Ia	86	30–31 cyclohexane	9
Ib[a]	83		6
Ic	76	163–164 methanol	6
IIa	86	194–196 petroleum ether	7
IIb	82	161–162 benzene-ethanol	
IIc	76	185–186 cyclohexane	10

[a] A red-brown oil, b.p. 170–172°C/0.2 mmHg.

The IR spectra of triorganostannylferrocenes(I), diorganostannyldiferrocenes(II) and diorganochlorostannylferrocenes(III) show two strong bands at 1106 and 998 cm^{-1} which are absent in the spectra of 1,1′-bis(diorganochlorostannyl) ferrocenes(IV). Others [3,4, and 5] observed these two absorption bands in ferrocene itself and its monosubstituted derivatives, but not in 1,1′-disubstituted derivatives.

The ^1H NMR spectra of triorganostannylferrocenes(I), diorganostannyldiferrocenes(II), and diorganochlorostannylferrocenes(III) shows 4 signals; a singlet due to the H_γ protons of the unsubstituted ring, two peaks due to the H_α and H_β protons of the unsubstituted ring (C_5H_4Sn), and a peak due to the protons of the alkyl or phenyl groups. The singlet due to the H_γ protons is absent from the ^1H NMR spectra of 1,1′-bis(diorganochlorostannyl)ferrocenes(IV), which still show the two signals due to the protons H_α and H_β. Details are given in Table 3.

Table 2

Diorganochlorostannylferrocenes and 1,1′-bis(diorganochlorostannyl)ferrocenes

Product	Yield	M.p. (°C) recrystallisation solvent	Empirical formula MW	MS (70 eV) ion with highest value of m/e
IIIa	82	105–106 petroleum ether	$C_{12}H_{15}ClFeSn$ 369	369
IIIb	85	72–73 cyclohexane	$C_{18}H_{27}ClFeSn$ 453	453
IIIc	74	132–134 hexane	$C_{22}H_{19}ClFeSn$ 493	493
IVa	86	130–131 cyclohexane	$C_{14}H_{20}Cl_2FeSn_2$ 552	551
IVb	85	103–105 cyclohexane	$C_{26}H_{44}Cl_2FeSn_2$ 720	720
IVc	80	164–165 cyclohexane	$C_{34}H_{28}Cl_2FeSn_2$ 800	764[a]

[a] The ion *m/e* 764 arises from loss of a chlorine atom.

Table 3

^{1}H NMR data for triorganostannylferrocenes, diorganostannyldiferrocenes, diorganochlorostannylferrocenes and 1,1′-bis(diorganochlorostannyl)ferrocenes

Product	^{1}H NMR (δ ppm, $CDCl_3$, TMS)			
	H_α	H_γ	H_β	H_R
Ia	4.22(t,2)	4.00(s,5)	3.95(t,2)	0.25(s,9H,methyl) $J(^{119}Sn-CH_3)$ 56 Hz
Ib	4.22(t,2)	4.10(s,5)	3.91(t,2)	0.70–1.80(m, 27 H, Bu)
Ic [a]				7.10–7.80(m, 15 H, Ph)
IIa	4.51(t,4)	4.43(s,10)	4.18(t,4)	0.85(s,6 H, Me) $J(^{119}Sn-CH_3)$ 60 Hz
IIb	4.50(t,4)	4.42(s,10)	4.12(t,4)	0.67–1.76(m, 18H Bu)
IIc [b]				7.20–7.90(m, 10 H, Ph)
IIIa	4.45(t,2)	4.29(s,5)	3.96(t,2)	1.02 and 0.98 (2 × s, 6H, Me) $J(^{119}Sn-CH_3)$ 61 Hz
IIIb	4.10(s,2)	4.00(s,5)	3.90(s,2)	0.70–1.90(m, 18 H, Bu)
IIIc	4.22(s,2)	4.00(s,5)	3.95(s,2)	7.10–7.80(m, 10 H, Ph)
IVa	4.10(t,4)		3.98(t,4)	1.02 and 0.98 (2 × s, 12 H, Me) $J(^{119}Sn-CH_3)$ 57 Hz
IVb	4.00(s,4)		3.90(s,4)	0.75–2.00(m, 36 H, Ph)
IVc	4.00(s,4)		3.95(s,4)	7.10–7.90(m, 20 H, Ph)

[a] δ 4.16(m, 9, $H_{\alpha\beta\gamma}$). [b] δ 4.30(m, 18, $H_{\alpha\beta\gamma}$). H_α and H_β: protons of stannyl substituted cycles, H_γ: protons of unsubstituted cycles, H_R: protons of alkyl or phenyl groups s, singlet; d, doublet; t, triplet.

Organostannylferrocenes have some potential application in industry [6,7]. Synthesis of organostannylferrocenes has been the subject of several studies involving the reaction of lithioferrocenes [6,7,8,9], the Grignard reagents [10] or the reaction of diferrocenylmercury with hexaorganodistannanes [11]. Our method appears to be more convenient because it involves readily available starting materials and mild conditions and particularly because it gives a single product in good yield, and so avoids the necessity of separating of the triorganostannylferrocenes and 1,1′-bis(triorganostannyl)ferrocenes which are formed together in the procedures involving lithioferrocenes [6,7,8,9].

Experimental

Melting points were determined with an electrothermal apparatus. IR spectra were recorded for KBr pellets on a Perkin–Elmer 177 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP80SY spectrometer in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were determined with Nermag RI0-10C linked GLC-mass spectrometer.

Starting materials were prepared by the following methods: (1) chloromercuriferrocene and 1,1′-bis(chloromercuri)ferrocene by mercuration of ferrocene [12,13]; (2) diferrocenylmercury by symmetrisation of chloromercuriferrocene by treatment with sodium stannite [13]; (3) organotin sulfides by the reaction of alkaline or hydrogen sulfides with organotin chlorides [14,15] or oxides [16].

General procedure for synthesis of triorganostannylferrocenes and diorganostannyldiferrocenes

A stirred solution of diferrocenylmercury (0.005 mol) in 70 ml of dioxane under dry N_2 was heated under reflux, and a solution of 0.005 mol of organotin sulfide in

80 ml of hot dioxane was added dropwise. The mixture was refluxed for 3 h, and then cooled and filtered to remove the mercuric sulfide. The filtrate was evaporated to dryness in vacuo, and the residue recrystallised to give the orange, crystalline product in 76–86% yield (Table 1).

With toluene as solvent in place of dioxane, a similar procedure gave diorganochlorostannylferrocenes and 1,1′-bis(diorganochlorostannyl)ferrocenes in 74–86% yield (Table 2).

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