

Preparation of mercapto compounds containing ferrocenyl group

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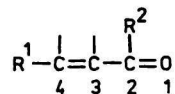
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Ten new mercapto-3-arylpropanoylferrocenes have been prepared by the addition of H₂S to substituted 3-arylacryloylferrocene. The principal products are adducts with the substituent at position 3, but small amounts of 2-substituted adducts were obtained, too.

Путем присоединения H₂S к замещенным 3-арилакрилоилферроценам получено десять новых меркапто-3-арилпропаноилферроценов. Основными продуктами являются аддукты с заместителем в положении 3, однако, получено также небольшое количество аддуктов с заместителем в положении 2.

It is known that the chalcones may undergo nucleophilic 1,2- or 1,4-addition.



The adducts depend on the steric factor. A smaller R¹ and a greater R² would mainly give a 4-substituted adduct, and conversely, a 2-substituted adduct is obtained principally. The nucleophile never attacks at position 3 [1—3]. But little attention has been paid to the addition of the nucleophiles to the chalcone analogues containing ferrocenyl group [4, 5].

In this paper, we report on some new 2- and 3-mercapto-3-arylpropanoylferrocenes formed by the nucleophilic addition of H₂S to cinnamoylferrocene and substituted cinnamoylferrocenes.

Experimental

3-(4-Methoxyphenyl)acryloylferrocene (*Ia*), 3-(4-nitrophenyl)acryloylferrocene (*Ib*), cinnamoylferrocene (*Ic*), 3-(4-chlorophenyl)acryloylferrocene (*Id*), 3-(2-chlorophenyl)-

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acryloylferrocene (*Ie*), 3-(3,4-dimethoxyphenyl)acryloylferrocene (*If*) have been prepared by the methods described in [6—8].

Specific rotations were taken on JASCO J-20C automatic recording spectropolarimeter. ^1H NMR spectra were recorded in CDCl_3 solution with TMS as internal standard on an FT-80A instrument. IR spectra were measured with FT-170SX spectrophotometer using KBr discs and sodium chloride optics.

3-Mercapto-3-(4-methoxyphenyl)propanoylferrocene (IIa)

The hydrogen sulfide was passed into a solution of *Ia* (2 g) in anhydrous ethanol (100 cm^3) at 25°C until it was saturated. 50 % aqueous KOH (1 cm^3) was added to this solution under stirring and again H_2S was passed into it for 8 h at room temperature. When a yellow precipitate appeared, H_2S was continuously passed into the solution for about 30 h until all *Ia* was almost completely reacted as shown by thin-layer chromatography. The precipitate of the product was collected by filtration using a Büchner funnel. The filtrate was concentrated under reduced pressure and another part of precipitate was obtained. The two parts of yellow precipitate were combined, washed with water to neutral and dried *in vacuo*. The crude product (2.05 g) thus obtained was separated on a chromatographic column packed with silica gel G, using the mixture petroleum ether—ether—chloroform ($\varphi_r = 3 : 1 : 1$) as eluant. 0.2 g of unreacted material and 1.85 g of the product *IIa* were obtained.

5.4 g of 3-mercapto-3-(4-nitrophenyl)propanoylferrocene (*I Ib*) were produced from 5.48 g of *Ib* by the method similar to that used in case of *IIa*.

3-Mercapto-3-phenylpropanoylferrocene (IIc) and 2-mercapto-3-phenylpropanoylferrocene (IIIc)

The hydrogen sulfide was passed into a solution of *Ic* (10 g) in anhydrous ethanol (1000 cm^3) at 25°C until it was saturated. 50 % aqueous KOH (2 cm^3) was added under stirring and H_2S was passed continuously into it for 20 h at room temperature. A part of yellow precipitate was collected on a Büchner funnel, the filtrate was concentrated under reduced pressure. Small amounts of water were added and again some portion of precipitate was obtained. The precipitates were combined, washed with water and dried *in vacuo*. 10.4 g of the mixture of *IIc* and *IIIc* was obtained. Yield = 95 %. 0.75 g of this mixture was separated on a silica gel column using petroleum ether—ether—chloroform ($\varphi_r = 3.5 : 1 : 1$) as eluant. At first 0.17 g of *IIIc*, then 0.58 g of *IIc* were released in turn from silica gel column.

I Id and *III d*, *I Ie* and *III e*, *I If* and *III f* were prepared by the method similar to that used in case of *IIc* and *IIIc*.

Results and discussion

The yields, physical properties, and elemental analyses of the above-mentioned adducts are listed in Table 1. The data of ^1H NMR and IR spectra are shown in Tables 2 and 3, respectively.

Table 1
Yields, physical properties, and elemental analyses of the adducts

Compound	Formula	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$				Yield %	M.p. °C	Colour
		C	H	S	Cl			
<i>Ila</i>	$\text{C}_{20}\text{H}_{20}\text{FeO}_2\text{S}$	63.17	5.30	8.43		94	98—99	Yellow
		62.85	5.23	8.36				
<i>Ilb</i>	$\text{C}_{19}\text{H}_{17}\text{FeNO}_3\text{S}$	57.73	4.33	8.11	3.54	90	180—181	Yellow
		57.82	4.22	8.24	3.72 ^a			
<i>Ilc</i>	$\text{C}_{19}\text{H}_{18}\text{FeOS}$	65.15	5.18	9.15		73	92.5	Yellow
		64.72	5.18	9.56				
<i>IIIc</i>	$\text{C}_{19}\text{H}_{18}\text{FeOS}$	65.15	5.18	9.15		22	119	Reddish orange
		65.08	5.22	9.43				
<i>IId</i>	$\text{C}_{19}\text{H}_{17}\text{ClFeOS}$	59.32	4.46	8.33	9.21	74	208—209	Yellow
		58.94	4.39	8.30	9.53			
<i>IIIId</i>	$\text{C}_{19}\text{H}_{17}\text{ClFeOS}$	59.32	4.46	8.33	9.21	13	132	Yellow
		58.93	4.50	7.99	9.47			
<i>Ile</i>	$\text{C}_{19}\text{H}_{17}\text{ClFeOS}$	59.32	4.46	8.33	9.21	50	196—197	Reddish orange
		59.68	4.37	8.40	8.89			
<i>IIIe</i>	$\text{C}_{19}\text{H}_{17}\text{ClFeOS}$	59.32	4.46	8.33	9.21	39	86—87	Yellow
		59.73	4.43	8.52	8.91			
<i>IIf</i>	$\text{C}_{21}\text{H}_{22}\text{FeO}_3\text{S}$	61.47	5.41	7.81		68	75—76	Orange
		59.97	5.46	7.60				
<i>IIIIf</i>	$\text{C}_{21}\text{H}_{22}\text{FeO}_3\text{S}$	61.47	5.41	7.81		16	86—87	Reddish orange
		61.56	5.44	7.95				

a) Nitrogen content.

The compounds *Ila*—*IIf* and *IIIc*—*IIIIf* are soluble in chloroform, methylene chloride, and ethyl acetate, sparingly soluble in ethanol, petroleum ether, and hexane. They easily remove H_2S and produce the original reactant and a precipitate of the black sulfides when refluxing in the presence of Al_2O_3 , CuCl_2 , CdCl_2 or NiCl_2 .

3-Arylacryloylferrocenes can undergo the addition of H_2S

Table 2

¹H NMR spectra (δ /ppm) of compounds *Ila*—*Ilf* and *IIIc*—*IIIf*

Compound	C ₅ H ₃ Fe	C ₅ H ₄ Fe	CH ₂	C—H	S—H	Aryl	OCH ₃
<i>Ila</i>	4.02 (5H, s)	4.42 (2H, t) 4.70 (2H, t)	3.40 (2H, m)	4.33 (1H, m)	1.66 (1H, m)	6.83 (2H, d) 7.20 (2H, d)	3.73 (3H, s)
<i>Ilb</i>	4.09 (5H, s)	4.56 (2H, t) 4.77 (2H, t)	3.36 (2H, m)	4.40 (1H, m)	1.50 (1H, m)	8.27 (2H, d) 7.67 (2H, d)	
<i>Ilc</i>	4.10 (5H, s)	4.53 (2H, t) 4.78 (2H, t)	3.43 (2H, m)	4.30 (1H, m)	1.60 (1H, m)	7.37 (5H, s, br)	
<i>IIIc</i>	4.07 (5H, s)	4.50 (2H, t) 4.80 (2H, t)	3.30 (2H, m)	4.60 (1H, m)	1.40 (1H, m)	7.30 (5H, m)	
<i>IId</i>	4.08 (5H, s)	4.51 (2H, t) 4.76 (2H, t)	3.34 (2H, m)	4.35 (1H, m)	1.63 (1H, m)	7.30 (4H, s, br)	
<i>IIIId</i>	4.05 (5H, s)	4.47 (2H, t) 4.68 (2H, t)	3.27 (2H, m)	4.15 (1H, m)	1.70 (1H, m)	7.29 (4H, m)	
<i>IIIe</i>	4.05 (5H, s)	4.42 (2H, t) 4.70 (2H, t)	3.38 (2H, m)	4.90 (1H, m)	1.53 (1H, m)	7.39 (4H, m)	
<i>IIIe</i>	4.15 (5H, s)	4.50 (2H, t) 4.73 (2H, t)	3.40 (2H, m)	5.00 (1H, m)	1.57 (1H, m)	7.33 (4H, m)	
<i>IIf</i>	4.08 (5H, s)	4.40 (2H, t) 4.70 (2H, t)	3.50 (2H, m)	4.50 (1H, m)	1.70 (1H, m)	6.75 (3H, m)	3.78 (3H, s) 3.82 (3H, s)
<i>IIIIf</i>	4.15 (5H, s)	4.43 (2H, t) 4.66 (2H, t)	3.33 (2H, m)	4.60 (1H, m)	1.62 (1H, m)	6.83 (3H, m)	3.80 (3H, s) 3.85 (3H, s)

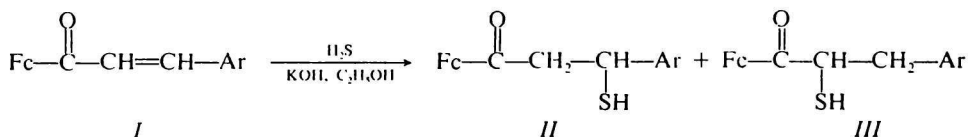
s — singlet, d — doublet, t — triplet, m — multiplet, br — broad.

Table 3

IR spectra ($\tilde{\nu}/\text{cm}^{-1}$) of compounds *IIa—IIf* and *IIIc—IIIf*

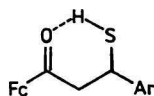
Com- pound	$\nu(\text{C—H})$	$\nu(\text{S—H})$	$\nu(\text{C=O})$	$\nu(\text{C}\cdots\text{C})$			$\delta(\text{C—H})$		$\gamma(\text{C—H})$	
<i>IIa</i>	3094 w 2998 w 2955 w	2551 w	1663 s	1609 m	1583 w	1410 w	1106 m	1079 m	893 m	826 s
	2933 w 2904 w 2835 w			1512 s	1453 s	1378 m	1030 m	1002 m	795 m	
<i>IIb</i>	3115 w 3079 w 2997 w	2540 w	1663 s	1603 m	1554 s	1379 w	1109 m	1079 m	894 m	857 m
	2933 w 2900 w 2854 w			1519 w	1413 w	1346 s	1028 m	1004 m	825 m	779 w
<i>IIc</i>	3087 w 3059 w 3028 w	2559 w	1662 s	1600 w	1580 w	1409 w	1106 w	1071 m	893 m	822 s
	2954 w 2918 w 2850 w			1493 w	1455 w	1378 m	1027 w	1003 w	754 m	699 s
<i>IIIc</i>	3104 w 3026 w 2953 w	2563 w	1662 s	1607 w	1582 w	1397 w	1105 w	1090 m	892 m	824 s
	2923 w 2881 w 2852 w			1494 w	1456 s	1379 m	1029 m	1002 w	765 m	742 m
<i>IIId</i>	3091 w 3060 w 3025 w	2592 w	1664 s	1593 w	1491 m	1414 m	1091 m	1080 m	895 m	825 s
	2953 w 2928 w 2882 w			1454 s	1379 m	1030 w	1009 w	796 m	754 m	
<i>IIIe</i>	3092 w 3020 w 2926 w	2574 w	1665 s	1594 w	1491 m	1410 m	1092 w	1078 w	894 m	825 s
	2903 w 2852 w 2834 w			1454 s	1378 m	1028 w	1014 w	783 m	720 w	
<i>IIe</i>	3095 w 3058 w 3026 w	2558 w	1666 s	1591 w	1569 w	1441 m	1107 w	1080 m	892 m	824 s
	3016 w 2903 w 2856 w			1473 m	1452 s	1378 m	1032 m	1002 w	757 s	730 m
<i>IIIe</i>	3096 w 3058 w 3027 w	2567 w	1665 s	1571 w	1514 w	1397 w	1105 w	1084 m	896 m	827 s
	2922 w 2900 w 2853 w			1477 m	1455 s	1380 m	1028 m	1003 w	763 s	730 w
<i>IIIf</i>	3090 w 2992 w 2954 w	2590 w	1664 s	1593 w	1589 w	1417 m	1106 w	1079 w	893 m	824 m
	2932 w 2907 w 2834 w			1514 s	1452 s	1377 m	1025 s	1003 m	783 w	764 w
<i>IIIIf</i>	3080 w 2998 w 2984 w	2579 w	1662 s	1592 w	1599 w	1416 m	1105 w	1082 w	893 w	852 w
	2919 w 2874 w 2840 w			1515 s	1456 m	1368 m	1024 s	1001 w	818 s	785 w

w — weak, s — strong, m — medium.



where Fc = $\eta\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4$; Ar = 4- $\text{CH}_3\text{OC}_6\text{H}_4$ (a), 4- $\text{NO}_2\text{C}_6\text{H}_4$ (b), C_6H_5 (c), 4- ClC_6H_4 (d), 2- ClC_6H_4 (e), 3,4- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$ (f).

The compounds *Ic—If* were released at first when separating the mixture of *Ic—If* and *IIIc—IIIf* by means of column chromatography. It is shown that their polarity is smaller than that of *IIIc—IIIf*, perhaps the molecules of *Ic—If* form easily intramolecular hydrogen bonding



It can be seen from the IR spectra of these compounds that the $\nu(\text{S—H})$ and $\nu(\text{C=O})$ appear at about $\tilde{\nu} = 2565$ and 1660 cm^{-1} , respectively. It is obvious that the 1,2-addition has not been realized, because the product which exhibits the characteristic vibrations of hydroxyl group and $\delta(\text{C—H})$ of carbon—carbon double bond has not been observed. In addition, the specific rotation of these compounds $[\alpha](\text{D}, 20^\circ\text{C}) = 0^\circ$, *i.e.* *Ic—If* are not enantiomers of the corresponding *IIIc—IIIf*. Everyone of them was a racemate.

It was also found from the ^1H NMR spectra that *IIIc—IIIf* have proton signals similar to those of *Ic—If*, thus they should have the same groups as described in [2, 3]. It is possible that the formation of small amounts of *IIIc—IIIf* is related to the great steric hindrance of ferrocenyl group and more electron density on cyclopentadienyl group due to electron transfer from the iron atom to cyclopentadienyl ring [9].

In conclusion we may state that the nucleophilic addition of H_2S to the chalcones containing ferrocenyl group differs from that of the general chalcones. The adduct with the substituent at position 2 has not been observed, but the additive 3-substituted product is undoubtedly produced besides the principal 4-substituted adduct.

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