CHEMISTRY

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, and O. A. NESMEYANOVA

1958

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, and O. A. NESMEYANOVA

REACTIONS OF DIFERROCENYLMERCURY

The mercury derivatives of ferrocene obtained by us for the first time ([1]), as has already been shown, can be used for the synthesis of ferrocene derivatives. Thus, they react with halogens (iodine and bromine), giving the corresponding halogen compounds. By this method we obtained haloferrocenes ([2]).

In the present work we used the interaction of diferrocenylmercury with triphenylchloromethane, with halogen anhydrides of carboxylic and sulfonic acids, with rhodanogen (at the moment of its formation), and with tetrabromoselenium.

Diferrocenylmercury interacts with triphenylchloromethane under very mild conditions, giving ferrocenyltriphenylmethane in a yield of 18% of theory and a small amount of ferrocene:

$$(C_5H_5FeC_5H_4)_2Hg + 2(C_6H_5)_3CCl \rightarrow 2C_5H_5FeC_5H_4C(C_6H_5)_3 + HgCl_2.$$

With chlorides of sulfonic acids the reaction proceeds with greater difficulty. Thus, on heating in benzene solution diferrocenylmercury with the chlorides of ferrocene- and benzenesulfonic acids, diferrocenyl sulfone and phenylferrocenyl sulfone are obtained in yields of 5-6%. At the same time 35-38% of the diferrocenylmercury is converted into ferrocene.

$$\begin{array}{c} C_5H_5FeC_5H_4SO_2Cl \\ (C_5H_5FeC_5H_4)_2Hg \longrightarrow (C_5H_5FeC_5H_4)_2SO_2 \\ C_6H_5SO_2Cl \\ \longrightarrow C_5H_4FeC_5H_4SO_2C_6H_5 \end{array}$$

With acetyl chloride the reaction proceeds still more difficultly. Acetylferrocene is obtained in a yield of only 1%; at the same time a considerable part of the diferrocenylmercury is also converted into ferrocene. Diferrocenylmercury does not react with benzoyl chloride.

The reaction proceeds considerably better, as was to be expected, with sulfoiodides than with sulfochlorides. Thus, upon interaction of diferrocenylmercury with the iodoanhydride of benzenesulfonic acid, the yield of phenylferrocenyl sulfone is 22%.

Upon interaction of diferrocenylmercury with rhodanogen, taken in excess, a complex is formed; after treatment of this complex with an aqueous solution of sodium thiosulfate, diferrocenyl disulfide is obtained in a yield of 15%, calculated on the mercury compound that has entered into reaction (12% of the diferrocenylmercury was recovered unchanged):

$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow{(CNS)_2} [C_5H_5FeC_5H_4SCN] \xrightarrow{Na_2S_2O_3} C_5H_5FeC_5H_4{-}S{-}S{-}C_5H_4FeC_5H_5.$$

Apparently, the initially formed rhodanoferrocene is reduced by the action of thiosulfate to the disulfide; in addition, 25% of the diferrocenylmercury that entered into the reaction is converted into ferrocene.

When diferrocenylmercury is treated with $SeBr_4$, diferrocenyl selenide is obtained in 21% yield; in this process selenium is reduced to the divalent state, which may occur through oxidation of the iron in the ferrocenyl group or during the subsequent treatment of the reaction mixture with sodium thiosulfate:

$$(C_5H_5FeC_5H_4)_2Hg \xrightarrow[(Na_2S_2O_3)]{SeBr_4} (C_5H_5FeC_5H_4)_2Se.$$

It should be noted that in all cases the reaction product is isolated wholly or partly in an oxidized (ferricinium) form and is then reduced with sodium thiosulfate.

Thus, the high nucleophilic activity of the carbon atoms of ferrocene, manifested in the ease of electrophilic substitution of the hydrogens of the cyclopentadienyl rings, is also revealed in the properties of the mercury derivatives of ferrocene: diferrocenylmercury reacts with sulfur halides under milder conditions than diphenylmercury ([3,4]). The interaction of triphenylchloromethane with diphenylmercury has not been described.

It should be noted that in all the reactions studied (except the reaction with $SeBr_4$), ferrocene was isolated as a by-product. It is possible that the formation of ferrocene is due to the appearance of a ferrocenyl radical, which abstracts hydrogen from the solvent or from other ferrocenyl groups.

Experimental Part

Preparation of ferrocenyltriphenylmethane. To a suspension of 1.9 g (0.0033 mole) of diferrocenylmercury in benzene was added 1.9 g (0.0068 mole) of triphenylchloromethane. After several minutes the orange precipitate of diferrocenylmercury became pink, a color characteristic of complexes of ferrocene with sulfuric acid. The reaction mixture was boiled for 4 hr; during this time the color of the precipitate changed from pink to green. The benzene was distilled off. The residue was treated with a saturated aqueous solution of sodium

thiosulfate. The precipitate was filtered off and extracted with ether. The substances remaining after removal of the ether were dissolved in petroleum ether and separated on a chromatographic column packed with Al_2O_3. The column was eluted with petroleum ether. There were isolated 0.01 g of ferrocene (about 1% of the diferrocenylmercury was converted into ferrocene), a small amount of an unidentified oily substance, and 0.5 g of ferrocenyltriphenylmethane, melting after recrystallization from *n*-butyl alcohol at 179–181°. Yield 18% of theory (the percentages of theoretical yield in all cases were calculated with allowance for both ferrocenyl groups of diferrocenylmercury). Ferrocenyltriphenylmethane is readily soluble in benzene and somewhat less soluble in alcohol and ether.

$C_{29}H_{24}Fe$	Found	% :	C 81.08; 81.00; H 5.78; 5.82
	Calculated	% :	C 81.31; H 5.65

Preparation of phenyl ferrocenyl sulfone. To 4.8 g (0.0084 mole) of diferrocenylmercury was added a benzene solution of benzenesulfonyl iodide, taken in excess. The reaction mixture was left overnight and then treated with a saturated aqueous solution of sodium thiosulfate. The precipitate was filtered off and extracted with benzene. The benzene solutions were combined and chromatographed on Al_2O_3.

There were isolated 0.5 g of ferrocene, apparently contaminated with iodoferrocene, 0.9 g of phenyl ferrocenyl sulfone, and 1.3 g (27%) of the starting diferrocenylmercury.

Phenylferrocenyl sulfone was recrystallized from alcohol. M.p. 145–146°. Yield 22%, calculated on the diferrocenylmercury that entered into the reaction.

Found	% :	C 59.30; 59.16;	H 4.48; 4.44;	S 9.57; 9.48;	Fe 16.96; 17.08		
$C_{16}H_{14}SO_2Fe$	Calculated	% :	C 58.91;	H 4.32;	S 9.83;	Fe 17.12	

Preparation of diferrocenyl sulfone. 1.6 g (0.0028 mole) of diferrocenylmercury and 1.6 g (0.0056 mole) of ferrocenesulfonyl chloride were heated in absolute benzene to boiling for 18 hours. The reaction mixture was then worked up as described for phenylferrocenyl sulfone. 0.35 g of ferrocene was obtained (yield 35%), 0.48 g of the initial ferrocenesulfonyl chloride (30% of that taken into the reaction; in addition, part of the sulfonyl chloride on the chromatographic column was converted into the acid), 0.1 g of diferrocenyl sulfone, and 0.02 g of chloromercuriferrocene.

Diferrocenyl sulfone was recrystallized from butyl alcohol. Yield 6%, calculated on the ferrocenesulfonyl chloride that entered into the reaction. M.p. 270–275° with decomposition.

Found	% :	C 54.99; 55.20;	H 4.07; 4.24;	S 6.83; 6.71;	Fe 26.44; 26.45		
$C_{20}H_{18}SO_2Fe_2$	Calculated	% :	C 55.33;	H 4.18;	S 7.38;	Fe 25.73	

With benzenesulfonyl chloride the reaction was carried out on heating for 13 hours. The yield of phenylferrocenyl sulfone was 5% of theoretical. 38% of the diferrocenylmercury was converted into ferrocene.

Reaction of diferrocenylmercury with acetyl chloride. To a suspension of 1 g (0.0017 mole) of diferrocenylmercury in absolute benzene was added 0.25 ml (0.0035 mole) of acetyl chloride. The reaction mixture was boiled for 5 hours, after which the benzene was removed, and the solid dark residue was reduced with a saturated aqueous solution of sodium thiosulfate and then extracted with ether. The residue after removal of the ether was added to the benzene solution. The benzene solution was diluted twofold with petroleum ether, and ferrocene (1.05 g) and acetylferrocene were isolated from it by chromatographic adsorption on alumina.

94% of the initial diferrocenylmercury was converted into ferrocene. The yield of acetylferrocene was 0.01 g (1.1% of theoretical). M.p. and mixed-sample m.p. 82–84°.

Under analogous conditions it was not possible to obtain benzoylferrocene; in this case 80–95% of the diferrocenylmercury was recovered unchanged.

Preparation of diferrocenyl sulfide. 4 g (0.007 mole) of diferrocenylmercury was ground in a mortar with an alcoholic rhodan solution prepared by extracting with alcohol a mixture, ground in a mortar, of equivalent amounts of $CuSO_4$ and KSCN. Addition of the alcoholic rhodan solution and grinding were continued until the solution no longer became decolorized. Then the reaction mass was heated with stirring for 10–15 min; during this operation more alcoholic rhodan solution was added several times (approximately 20 ml), until the color of the solution no longer changed. The reaction mixture was poured into a saturated aqueous solution (150 ml) of sodium thiosulfate and after 3 hours was diluted with water until precipitation of the precipitate ceased (the volume of the solution reached 800–900 ml). The filtered precipitate was extracted with petroleum ether. The insoluble part (0.5 g) was the initial diferrocenylmercury (m.p. and mixed-sample m.p. 232–233°).

The substances that dissolved in petroleum ether were separated on a chromatographic column packed with Al_2O_3. Ferrocene (0.6 g) was washed from the column with petroleum ether. 25% of the diferrocenylmercury was converted into ferrocene.

Then washing was continued with a mixture of petroleum ether and benzene in a ratio of 2:1. After distillation of the solvent, a yellow crystalline substance remained, together with a small amount of an oily product, which was carefully washed off with ether and was not investigated further. The remaining crystalline substance (0.4 g) was diferrocenyldisulfide. Yield 15%, calculated on the diferrocenylmercury introduced into the reaction. After recrystallization from *n*-butyl or ethyl alcohol, m.p. 185–187°.

Diferrocenyldisulfide is readily soluble in benzene, less soluble in ether and

petroleum ether.

	Found %:	C	55.12;	55.09;	H	4.12;	4.12;	S 14.68;	14.50
$C_{20}H_{18}S_2Fe_2$	Calculated %:	C	55.32;		H	4.18;		S 14.76	

Preparation of diferrocenylselenium*. To a suspension of 5 g (0.0092 mole) of diferrocenylmercury in $CHCl_3$, a solution of 8.3 g (0.0415 mole) of $SeBr_4$ in 250 ml of $CHCl_3$ was added with stirring. The mixture was heated to boiling for 1 hour. Then the red chloroform solution was decanted. The dark residue was ground in a mortar and treated with a saturated aqueous solution of sodium thiosulfate. After several days, the aqueous layer and the dark precipitate were extracted repeatedly with ether. The diferrocenylselenium (1.4 g) remaining after distillation of the ether was recrystallized from isobutyl and ethyl alcohols. Yield 0.8 g, 21% of theoretical. M.p. 151–153°.

	Found %:	C	53.22;	53.63;	H	4.16;	4.40	
$C_{20}H_{18}SeFe_2$	Calculated %:	C	53.45;		H	4.01		

Moscow State University
named after M. V. Lomonosov

Received
25 XII 1957

CITED LITERATURE

[1] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, O. A. Nesmeyanova, DAN, **97**, 459 (1954).
[2] A. N. Nesmeyanov, E. G. Perevalova, O. A. Nesmeyanova, DAN, **100**, 1099 (1955).
[3] R. Otto, Ber., **18**, 246 (1885).
[4] F. C. Whitmore, N. Thurman, J. Am. Chem. Soc., **45**, 1068 (1923).

* Diferrocenylselenium was obtained by us jointly with Yu. I. Baukov.

Note: Figure translations are in progress. See original paper for figures.