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Abstract

Full Text

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Reactions of Triferrocenylphosphine Oxide

Recently we reported the synthesis of triferrocenylphosphine oxide (1) by the reaction of direct phosphorylation of ferrocene with phosphorus trichloride in the presence of aluminum chloride in methylene chloride solution. The availability of triferrocenylphosphine oxide, obtained by our method in 97% yield, made it possible to use it for studying the behavior of the hydrogens of the ferrocene system in electrophilic substitution reactions.

It was found that triferrocenylphosphine oxide is capable of undergoing an isotope-exchange reaction of hydrogen on treatment with deuterotrifluoroacetic acid and of being sulfonated on treatment with sulfuric acid. It turned out that, under the action of conc. sulfuric acid, depending on the reaction conditions, triferrocenylphosphine oxide behaves differently. Under the action of equimolecular amounts of conc. sulfuric acid in the presence of acetic anhydride, this compound is readily sulfonated (2, 3).

Sulfonation of triferrocenylphosphine oxide proceeds at room temperature over 17-20 hr with a yield of 79-80%, forming a sulfonic acid containing three sulfo groups for each molecule of substituted triferrocenylphosphine oxide:

$$(C_{10}H_9Fe)_3PO + 3H_2SO_4 \xrightarrow{(CH_3CO)_2O} (HO_3SC_{10}H_8Fe)_3PO.$$

The tris-(1-sulfoferrocenylene-1′)-phosphine oxide obtained is a yellow substance, hygroscopic; on treatment with carbonates of the metals Na, Ba, Pb, and Mn it readily forms salts.

Tris-(1-sulfoferrocenylene-1′)-phosphine oxide and its salts are extremely readily soluble in water, readily soluble in alcohol, and insoluble in absolute ether and benzene. By reaction of the acid with an ethereal solution of diazomethane, tris-(1-sulfomethoxyferrocenylene-1′)-phosphine oxide with a melting point of 117° was obtained. In the IR spectra of the acid itself and of its methyl ester, bands in the region of 1000 and 1100 cm^{-1} are absent. Consequently, all three sulfo groups are located in three different ferrocene residues, namely in the previously unsubstituted cyclopentadienyl rings of ferrocene. It was not possible to determine the dissociation constants of tris-(1-sulfoferrocenylene-1′)-phosphine oxide because of the extreme instability of aqueous solutions of this compound.

Under the action of an excess of conc. or dil. H_2SO_4 in the absence of acetic anhydride at room temperature, and even in the cold, cleavage of the triferrocenylphosphine oxide molecule occurs with the formation of diferrocenylphosphinic acid. The easy cleavage of the triferrocenylphosphine oxide molecule under the action of acid has no analogy in the chemistry of organophosphorus derivatives of benzene (4), but recalls cleavages of ferrocene compounds with δ^+ in the α-position, described in the works of one of us, V. A. Sazonova, and coworkers (5–8). Only in our new case does the elimination of only one ferrocenyl residue readily occur.

It is known that triphenylphosphine oxide is nitrated ([4,9]) by a nitrating mixture at room temperature and gives tri-(n-nitrophenyl)-phosphine oxide in 70% yield. Conversely, decomposition of the triphenylphosphine oxide system proceeds under the action of alkali under severe conditions ([10]). In our case, no decomposition was observed upon prolonged boiling of triferrocenylphosphine oxide with 50% alkali.

The reaction of isotopic hydrogen exchange of triferrocenylphosphine oxide was carried out in trifluoroacetic acid containing 51.4 atom % deuterium. The kinetics of isotopic hydrogen exchange were studied at temperatures of 25, 35, and 45°. The rate constants of hydrogen exchange ($K_{\text{h.e.}}$) were $1.6 \cdot 10^{-7}$, $4.4 \cdot 10^{-7}$, and $12.8 \cdot 10^{-7}$ sec^{-1}, respectively. (All 27 hydrogen atoms of triferrocenylphosphine oxide were included in the calculation.)

It should be noted that the rate constants of hydrogen exchange of ferrocene under similar conditions are 3–4 orders of magnitude higher, which indicates the strong electron-acceptor properties of the phosphine oxide group.

The IR spectra of triferrocenylphosphine oxide isolated after the hydrogen-exchange reaction and containing about 50 atom % deuterium showed that the bulk of the deuterium is contained in the unsubstituted cyclopentadienyl rings.

Thus, we have been able to show that electrophilic substitution reactions—sulfonation and hydrogen exchange—take place predominantly in the unsubstituted cyclopentadienyl rings of triferrocenylphosphine oxide.

Experimental Part

I. Sulfonation of triferrocenylphosphine oxide.

To a mixture of 3 g (0.0046 mole) of triferrocenylphosphine oxide and 20 ml of acetic anhydride, 1.5 ml (0.028 mole) of sulfuric acid (0–5°) was slowly added, and the whole was left for 17–20 h at room temperature. The crystalline product that separated from the solution was isolated, washed with acetic anhydride and absolute ether, and then transferred under absolute ether into a dish and placed in a vacuum desiccator. The solvent was removed in the vacuum of a water-jet pump, and the residue was dried at 20 mm Hg. Weight 2.62 g. An additional 0.69 g of product was isolated from the filtrate by precipitation with absolute ether. Total yield 3.31 g (79% of theory).

Found, %:	C 40.50, 40.37;	H 3.32, 3.38;	Fe 19.18, 17.71;
	S 10.19, 9.83		
$C_{30}H_{33}Fe_3S_3PO_{13}$. Calculated, %:	C 40.201;	H 3.68;	Fe 18.71;
	S 10.72;		

The trisulfonic acid contains $3H_2O$. Isolated in air, it is hygroscopic, insoluble in benzene and ether, extremely readily soluble in water, alcohol, and alkali solutions. From alkaline solutions it is poorly precipitated by hydrochloric acid.

Interaction of tris-(1-sulfoferrocenylene-1′)-phosphine oxide with diazomethane.

To a suspension of 0.8 g of trisulfonic acid in 30 ml of absolute ether, an ethereal solution of diazomethane, prepared from 10 g of nitrosomethylurea, was added gradually. Yield 0.7 g (87% of theory), m.p. 118–120°. The ether contains two moles of water of crystallization.

Found, %:	C 43.04, 42.95;	H 4.03, 4.08;	S 9.79, 9.77
$C_{33}H_{35}Fe_3PO_{11}S_3$. Calculated, %:	C 43.07;	H 4.03;	S 10.04

Decomposition of triferrocenylphosphine oxide with sulfuric acid.

To 3 g (0.0046 mole) of triferrocenylphosphine oxide in the cold, 9 ml (0.168 mole) of conc. sulfuric acid was slowly added with stirring, and the mixture was left for 10–12 h at room temperature and then poured onto ice. The precipitate (A) that separated was isolated, washed with water and dried. A yellow product was extracted with benzene. Weight 1.4 g. The portion of the substance that did not dissolve in benzene was recrystallized from methanol. 0.1 g of a solid product of composition $C_{20}H_{19}Fe_2PO_5S \cdot 1.5H_2O$ was isolated.

Found, %:	C 43.74, 44.03;	H 4.06, 3.86;	S 5.98, 6.04
$C_{20}H_{19}Fe_2PO_5S \cdot 1.5H_2O$. Calculated, %:	C 44.36;	H 4.06;	S 5.91

The aqueous solution after separation of precipitate (A) and the wash water were reduced with ascorbic acid. The precipitate that formed was separated and treated analogously to that described above. 0.05 g was extracted with benzene, and 0.05 g was isolated from methanol. The aqueous filtrate was extracted with chloroform. After evaporation of the solvent, 0.21 g of a powdery product was isolated (hygroscopic, readily soluble in water), representing a mixture of substances containing up to 10% sulfur.

Table 1

Temp., °C	Time, h	E.w.d.*, ‰	E.w.d.*, ‰	$K_{\text{v.o}} \cdot 10^{-7}$, sec^{-1}
Temp., °C	Time, h	calculated for exchange of all H	found	$K_{\text{v.o}} \cdot 10^{-7}$, sec^{-1}
25	41.5	39100	1000	1.7
25	158.5	39100	3500	1.6
25	202.0	39100	4200	1.6
35	19.5	39100	1100	4.2
35	38.0	39100	2400	4.6
35	86.5	39100	4800	4.2
35	158.0	39100	9000	4.5
45	19.2	39100	3500	13.1
45	39.2	39100	6500	12.8
45	85.0	39100	13000	12.8
45	336	39100	29400	10.9

* E.w.d. –excess density of the combustion water.

The products isolated from the benzene extracts were combined, thoroughly washed with hot water, and again recrystallized from benzene. Thus, 1.5 g (71% of theory) of diferrocenylphosphinic acid was obtained.

Found, %: C 53.15, 53.06; H 4.64, 4.75; Fe 24.8

$C_{20}H_{19}Fe_2P \cdot H_2O$. Calculated, %: C 53.14; H 4.68; Fe 24.71

II. Isotopic exchange of hydrogen in triferrocenylphosphine oxide. 5.3 g (0.0088 mole) of triferrocenylphosphine oxide was dissolved, under a nitrogen atmosphere, in 89.8 g (0.78 mole) of trifluoroacetic acid containing 51.4 at.% deuterium ($H_0 = -3.01$). The solution was divided among 11 ampoules and placed in a thermostat. Kinetic studies were carried out at 25, 35, and 45° (\$±\$0.1°). To interrupt the reaction, the reaction mixture was poured into ice water; the precipitate that formed was washed with 10 portions of boiling water, 70 ml each, dried in vacuum over P_2O_5, and then treated with petroleum ether to remove traces of ferrocene (the absence of ferrocene was monitored by thin-layer chromatography on aluminum oxide). The precipitate was then dried in vacuum at 98° for 2 h. The triferrocenylphosphine oxide isolated in this way, according to elemental analysis, contained no impurities.

The deuterium content was determined from the excess density of the combustion water by the drop method.

The results of the isotopic analysis of triferrocenylphosphine oxide are given in Table 1.

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