NITRATION OF AROMATIC COMPOUNDS CATALYZED BY ZrO_2/SO_4^{2-}

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UDC 542.971.3:542.958.
1:547.546:547.673.1

Catalytic activity was demonstrated for zirconium dioxide, which is a solid acid, modified by sulfate ions in the nitration of inactive aromatic compounds.

Considerable attention has recently been given to solid acid catalysts for electrophilic substitution in aromatic compounds. Metal oxides such as ZrO_2, HfO_2, TiO_2, Fe_2O_3, and SnO_2 modified by sulfate ions occupy a special place among such catalysts. These oxides have superacid properties ($H_0 < -12$) [1, 2]. In particular, the ZrO_2/SO_4^{2-} and SnO_2/SO_4^{2-} systems are the strongest of the presently reported solid acids ($H_0 \leq -16.04$) [2,3,4]. Such catalysts display high activity in the alkylation and acylation of benzene and its derivatives [5-7].

In the present work, we studied the possibility of using sulfate-modified zirconium dioxide in the electrophilic nitration of aromatic compounds. There is virtually no information on the use of solid acid catalysts for the nitration of aromatic compounds, whose reactivity in electrophilic substitution reactions is less than for halobenzenes. We selected compounds whose aromatic ring is deactivated by electron-withdrawing substituents: nitrobenzene (I), N-methylphthalimide (II), and 9,10-anthraquinone (III). Mixtures of nitric acid with sulfuric acid or oleum are ordinarily used for the nitration of these compounds [8-10].

The nitration of (I)-(III) was carried out using concentrated nitric acid in the presence of a solid acid catalyst in CCl_4 solution at about 20°C. The data given in Table 1 indicate high catalytic activity of the ZrO_2/SO_4^{2-} system in the reactions studied. Without the addition of the catalyst, the nitration does not proceed to a significant extent. The observed isomer composition of the products is ordinary for a nitration reaction proceeding through an electrophilic substitution mechanism [8-10].

The catalyst activity depends to a significant extent on the temperature of its roasting prior to the reaction (see Fig. 1). Dependence curves similar to those observed in our work on the nitration reaction were noted for other reactions catalyzed by ZrO_2/SO_4^{2-} such as the acylation of benzene derivatives [6] and the isomerization of butane [3]. Apparently, this indicates that the same types of acid sites on the solid catalyst surface are involved in all these reactions.

The use of a solid acid ZrO_2/SO_4^{2-} catalyst significantly simplifies the isolation of the products in comparison with standard procedures since the catalyst, which is insoluble in the reaction mixture, is readily separated at the end of the reaction by filtration. The reuse of a treated portion of the catalyst is possible after regeneration by roasting in an air stream.

EXPERIMENTAL

The reaction mixtures were analyzed by gas–liquid chromatography on an LKhM-80 chromatograph with a flame ionization detector using a column packed with 15% SKTFT-50Kh on Chromaton N-AW-DMCS and helium as the gas carrier. The high-efficiency liquid chromatography was carried out on a Milichrom chromatograph using a silica gel adsorbent and 1:1 methylene chloride–hexane as the eluent.

The ZrO_2/SO_4^{2-} catalyst was prepared according to the procedure of Hino and Arata [3] from $ZrOCl_2$ or $ZrO(NO_3)_2$,* roasted immediately before use for 3 h in an air stream. The roasting temperatures of the catalysts are given in Table 1 and Fig. 1.

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*The efficiency of the catalyst depends only slightly on which precursor salt was used.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1650-1652, July, 1990. Original article submitted September 25, 1989.

0568-5230/90/3907-1500$12.50

TABLE 1. Nitration of Aromatic Compounds by Nitric Acid in the Presence of ZrO_2/SO_4^{2-} (the catalyst roasting temperature was 500°C)

Substrate	HNO_3/substrate mole ratio	Time, h	Composition of the reaction mixture	
			compound	content, %
Nitrobenzene	1,5	5	Nitrobenzene m-Dinitrobenzene o- and p-Dinitrobenzene	44 55 0,7
N-Methylphthalimide	5,0	17	N-Methylphthalimide N-Methyl-4-nitrophthalimide N-Methyl-3-nitrophthalimide	69 31 <0,1
9,10-Anthraquinone	1,5	0,5	9,10-Anthraquinone 1-Nitro-9,10-anthraquinone 2-Nitro-9,10-anthraquinone Other compounds	66 31 3 ~0,5

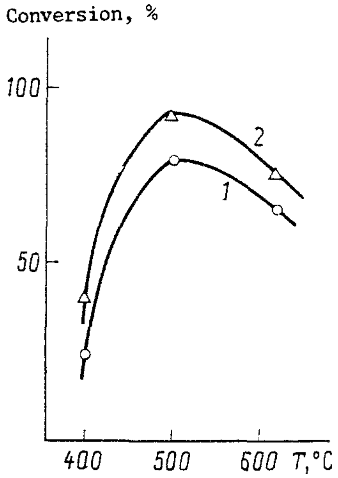

Fig. 1. Dependence of the conversion of 9,10-anthraquinone on the roasting temperature of the ZrO_2/SO_4^{2-} catalyst. The HNO_3/substrate mole ratio was 5.0. The catalyst/HNO_3 weight ratio was 13. The reaction time was 30 min (1) and 60 min (2).

General Nitration Procedure. A sample of concentrated nitric acid (d = 1.51) was added dropwise with strong stirring to a suspension of freshly roasted catalyst in CCl_4 (the catalyst/HNO_3 weight ratio was 13). After 5 min, the substrate was added and stirring was continued at -20°C for a given time (the reagent ratio and reaction times are given in Table 1). The catalyst was filtered off and washed with chloroform. The reaction mixtures in chloroform solution were analyzed by gas–liquid chromatography in the case of nitration of (I) and (II) and by high-efficiency liquid chromatography in the case of the nitration of (III).

LITERATURE CITED

1. K. Tanabe, Sekubai, 27, No. 3, 198 (1985).
2. H. Matsuhashi, M. Hino, and K. Arata, Chem. Lett., No. 6, 1027 (1988).
3. M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., No. 18, 851 (1980).
4. V. S. Komarov, M. F. Sinilo, and E. A. Stepanova, Dokl. Akad. Navuk BelorusSSR, 33, No. 5, 439 (1989).
5. Yu. I. Kozorezov and Yu. V. Ryabtseva, Zh. Prikl. Khim., 52, No. 10, 2191 (1979).
6. K. Tanabe, T. Yamaguchi, K. Akiyama, et al., Proceedings of the Eighth International Conference on Catalysts, Vol. 5, Verlag Chemie, Weinheim (1984), p. 601.
7. M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., No. 3, 112 (1985).

8. K. Schofield, Aromatic Nitration, Cambridge University Press, Cambridge, England (1980), p. 376.
9. M. V. Gorelik, The Chemistry of Anthraquinones and Their Derivatives [in Russian], Khimiya, Moscow (1983), p. 174.
10. F. J. Williams and P. E. Donahue, J. Org. Chem., 43, No. 8, 1608 (1978).

SELENIUM-CONTAINING ESTERS OF PENTAVALENT PHOSPHORUS ACIDS

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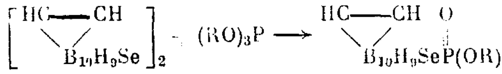
UDC 542.91:547.1'127'118+546.23

New carboranyl selenophosphates and selenophosphonates have been prepared. A series of S-β-carboranylselenoethyl esters of pentavalent phosphorus acids has been prepared. These compounds hold interest as potentially physiologically active compounds.

In previous work [1], we prepared the first representatives of carboranyl esters of O,O-dialkylselenophosphoric acid formed upon heating trialkyl phosphites and di(o-carboran-9-yl)diselenide in toluene at reflux .

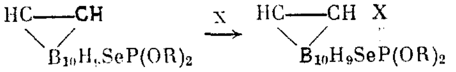


R = Me, Et.

In the present work, we have synthesized other selenium-containing carboranyl esters of pentavalent phosphorus acids holding interest as potentially physiologically active compounds.

In order to prepare carboranyl selenophosphates and selenophosphonates by the reaction of o-carboran-9-ylselenol with dialkyl chlorophosphites in the presence of triethylamine, we obtained O,O-dialkyl Se-(o-carboran-9-yl)selenophosphites ($\delta^{31}P$ 203-205 ppm), which were converted without isolation into pentavalent phosphorus derivatives.

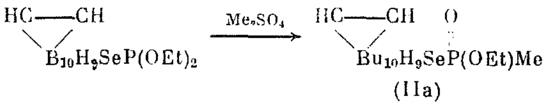
Esters of carborane-containing selenothio- and diselenophosphoric acids are readily formed by the addition of sulfur and selenium to the corresponding selenophosphites. On the other hand, oxidation by atmospheric oxygen leads to decomposition of carboranylselenophosphites. Furfural was used as a mild oxidizing agent to obtain O,O-diethyl Se-(o-carboran-9-yl)selenophosphate [2].



(Ia—b)

X = S, R = Et (Ia), Bu (Ib); X = Se, R = Et (Ic), Bu (Id); X = O, R = Et (Ie).

Attempts to perform the Arbuzov reaction with O,O-dialkyl Se-(o-carboran-9-yl)selenophosphites by heating with alkyl iodides at reflux were unsuccessful. The reaction featured decomposition of the starting selenophosphites with the formation of di(o-carboran-9-yl)diselenide and an unidentified mixture of phosphorus-containing products. This behavior is apparently related to the low thermal stability of the starting selenophosphites. The use of a stronger alkylating agent, namely, dimethyl sulfate, which permitted us to carry out the reaction at -20°C, led to the formation of O-ethyl Se-(o-carboran-9-yl)methylselenophosphonate (IIa). We also obtained (IIa) and selenothiophosphonate in the reaction of (o-carboran-9-yl)selenol [3] with O-ethyl methylchlorophosphonate and chlorothiophosphonate in the presence of triethylamine in ether.



(IIa)

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