Russian Journal of General Chemistry, Vol. 72, No. 3, 2002, pp. 390–391. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 3, 2002, pp. 419–420.
Original Russian Text Copyright © 2002 by Sharutin, Sharutina, Bondar', Pakusina, Adonin, Starichenko.

Synthesis of Tetra- and Triarylantimony Fluorobenzoates

V. V. Sharutin, O. K. Sharutina, E. V. Bondar',
A. P. Pakusina, N. Yu. Adonin, and V. F. Starichenko

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

Received August 3, 2000

Abstract—Pentaarylantimonies Ar_5Sb (Ar = Ph, *p*-Tol) was reacted with triarylantimony bis(perfluorobenzoate) and bis(3,4,5-trifluorobenzoate) in toluene at elevated temperature to obtain tetraarylantimony fluorobenzoates in 90% yield. Triarylantimony bis(fluorobenzoates) were prepared in an yield of up to 98% from triarylstibine and fluorobenzoic acid by oxidative addition in ether in the presence of hydrogen peroxide.

It is known that pentaarylantimonies react with antimony derivatives of the general formula Ar_3SbX_2, where X are oxygen-containing ligands, to form pentavalent antimony derivatives Ar_4SbX [1–4]. It was shown that functional substituents in an acylate substituent X prevent this disproportionation reaction. Thus, the reaction of triphenylantimony disalicylate with pentaphenylantimony does not lead to tetraphenylantimony salicylate [3]. The problem of a more wide use of the above reaction for preparing Ar_4SbX derivatives might be solved only by having studied reaction of pentaarylantimonies with symmetrical antimony derivatives of the general formula Ar_3SbX_2 with X containing other functional groups.

We have studied reactions of pentaarylantimonies **I** with triarylantimony bis(fluorobenzoates) **II**. It was shown that the reactions proceed already at 20°C in aromatic hydrocarbons and result in formation of tetraarylantimony fluorobenzoates **III** as coarse crystals.

$$\underset{\textbf{I}}{Ar_5Sb} + \underset{\textbf{II}}{Ar_3Sb[OC(O)R]_2} \longrightarrow \underset{\textbf{III}}{2Ar_4SbOC(O)R},$$

Ar = C_6H_5, R = C_6F_5 (**a**); Ar = $C_6H_4CH_3$-4; R = C_6F_5 (**b**); Ar = C_6H_5, R = $C_6H_2F_3$-3,4,5 (**c**); Ar = $C_6H_4CH_3$-4; R = $C_6H_2F_3$-3,4,5 (**d**).

For the reactions to compete requires heating (1h, 90°C). The IR spectra and melting points of the resulting tetraarylantimony fluorobenzoates agree with analogous physicochemical characteristics of compounds prepared from pentaarylantimony and fluorobenzoic acid.

$$Ar_5Sb + HOC(O)R \longrightarrow Ar_4SbOC(O)R.$$

The starting triarylantimony bis(fluorobenzoates) were prepared according to Thepe [5] from triphenylstibine, fluorobenzoic acid, and hydrogen peroxide in ether solution at room temperature.

$$Ar_3Sb + 2HOC(O)R + H_2O_2 \rightarrow Ar_3Sb[OC(O)R]_2 + 2H_2O.$$

Triarylantimony bis(fluorobenzoates) crystallized as the ether slowly evaporated (12–24 h).

The yields, melting points, and elemental analyses of the products are listed in the table.

Hence, the disproportionation of aryl derivatives of pentavalent antimony, involving pentaaryl antimony and symmetrical aryl antimony derivatives, is of a greater utility than had been considered.

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer for suspensions in Vaseline oil between NaCl plates.

Triphenylantimony bis(pentafluorobenzoate) (IIa). To a solution of 1.12 g of triphenylstibine in 10 ml of ether, 1.35 g of pentafluorobenzoic acid and 0.36 ml of 30% aqueous hydrogen peroxide were added. The resulting mixture was kept for 12 h at 20°C. Crystals formed and were filtered off and dried to obtain 2.38 g (97%) of triphenylantimony bis(pentafluorobenzoate), mp 173°C (decomp.). IR spectrum, ν, cm^{-1}: 1672 v.s, 1340 v.s, 1260 v.s, 1100 s, 1065 m, 990 v.s, 920 s.

Tetraphenylantimony pentafluorobenzoate (IIIa). *a.* A mixture of 0.91 g of pentaphenylantimony, 1.40 g of triphenylantimony bis(pentafluorobenzoate), and 15 ml of toluene were heated for 1 h at 90°C. The solvent was removed, and the dry residue was crystallized from toluene–heptane, 1:1, to give 2.00 g (86%) of tetraphenylantimony pentafluorobenzoate,

1070-3632/02/7203-0390 $27.00 © 2002 MAIK "Nauka/Interperiodica"

Yields and elemental analyses of tetra- and triarylantimony fluorobenzoates

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	F		C	H	F
IIa	97	173 (decomp.)	50.13	1.65	24.22	$C_{32}H_{15}F_{10}O_4Sb$	49.55	1.93	24.52
IIb	98	147 (decomp.)	51.11	2.75	23.02	$C_{35}H_{21}F_{10}O_4Sb$	51.41	2.57	23.26
IIc	99	236	54.19	2.83	16.08	$C_{32}H_{19}F_6O_4Sb$	54.62	2.70	16.22
IId	99	171	56.12	3.49	15.14	$C_{35}H_{25}F_6O_4Sb$	56.38	3.36	15.30
IIIa	69	161 (decomp.)	57.83	3.47	14.43	$C_{31}H_{20}F_5O_2Sb$	58.03	3.12	14.82
IIIb	78	150	60.06	3.84	13.29	$C_{35}H_{28}F_5O_2Sb$	60.26	4.02	13.63
IIIc	97	161	61.06	3.87	9.05	$C_{31}H_{22}F_3O_2Sb$	61.49	3.64	9.42
IIId	96	173	63.48	4.87	8.34	$C_{35}H_{30}F_3O_2Sb$	63.54	4.54	8.62

mp 161°C (decomp.). IR spectrum, ν, cm^{-1}: 1655 v.s, 1335 v.s, 1275 v.s, 1098 s, 1060 m, 980 v.s.

b. A mixture of 1.00 g of pentaphenylantimony, 0.42 g of pentafluorobenzoic acid, and 10 ml of toluene was heated for 1 h at 90°C. The solvent was removed, and the dry residue was crystallized from toluene–heptane, 1 : 1, to obtain 1.23 g (98%) of tetraphenylantimony pentafluorobenzoate, mp 161°C (decomp.).

REERENCES

1. Sharutin, V.V., Senchurin, V.S., Sharutina, O.K., Pakusina, A.P., and Panova, L.P., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 10, pp. 1755–1756.
2. Sharutin, V.V., Sharutina, O.K., Panova, L.P., and Bel’skii, V.K., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 9, pp. 1531–1535.
3. Sharutin, V.V., Sharutina, O.K., Pakusina, A.P., and Bel’skii, V.K., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 9, pp. 1536–1541.
4. Sharutin, V.V., Sharutina, O.K., Tarasova, T.A., Kharsika, A.N., and Bel’skii, V.K., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 12, pp. 1979–1981.
5. Thepe, T.C., Garascia, R.J., Selovski, M.A., and Patel, A.N., *Ohio J. Sci.*, 1977, vol. 77, no. 3, pp. 134–135.