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TRIPHENYLANTIMONY DIESTER PREPARATION

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Summary

A series of triphenylantimony diesters of monocarboxylic acids has been prepared in a simple way by reacting triphenylantimony oxide with the corresponding acids in methanol. The antimony content was determined in the obtained compounds and the ^{1}H NMR spectra were measured.

Compounds of the $Ph_3Sb(OCOR)_2$ type, as diesters formally derived from triphenylantimony oxide, have so far been prepared by various methods. Ph_3Sb oxidation with hydrogen peroxide was carried out by Schmidt [1] obtaining $Ph_3Sb(OCOCH_3)_2$ for the first time by subsequent reaction with acetic acid. By dissolving triphenylantimony dihydroxide in hot formic acid Doak [2] obtained triphenylantimony diformiate.

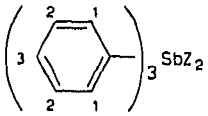
The preparation of derivatives from halogenized acetic acids by adding a benzene solution of triphenylantimony dihalogenide to the silver monoxide to the corresponding acid in aqueous solution is described by Goel [3]. Triphenylantimony dipropionate was prepared by Ladochnikova [4] by reacting triphenyl· antimony with plumbous (IV) propionate in chloroform. Challenger [5] obtained triphenylantimony dibenzoate by heating Ph_3Sb with dibenzoyl peroxide in petroleum ether. Musher demonstrates in his patent [6] the preparation of triphenylantimony diacrylate by reacting Ph_3SbO with acrylic acid. The preparation of diesters from substituted maleic and fumaric acids was dealt with by Chang [7].

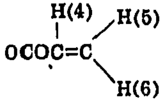
Triphenylantimony diester preparation was based on the direct reaction of triphenylantimony oxide with carboxylic acids according to the following principle:

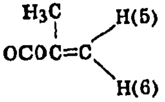
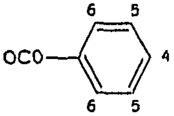
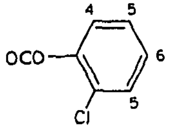
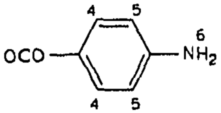
$$Ph_3SbO + 2\ RCOOH \rightarrow Ph_3Sb(OCOR)_2 + H_2O$$

(continued on p. 166)

TABLE 1

^{1}H-NMR DATA FOR THE COMPOUNDS OF TYPE 

Z	Yield (%)	M.p. (°C)	% Sb found (calcd.)	Chemical shift (δ)				
				(1)	(2,3)	(4)	(5)	(6)
$\mathrm{OCO\overset{(4)}{H}}$	61.2	159–60	27.30 (27.45)	7.90, q, 6H	7.45, m, 9-H	7.90, s, 2-H		
$\mathrm{OCO\overset{(4)}{CH_3}}$	37.5	213–15	26.17 (25.84)	7.90, q, 6-H	7.40, m, 9-H	1.90, s, 6-H		
$\mathrm{OCO\overset{(4)}{CH_2}Cl}$	75.3	149–50	22.51 (22.54)	7.90, q, 6-H	7.45, m, 9-H	3.80, s, 4-H		
$\mathrm{OCOCCl_3}$	75.7	152 dec.	18.48 (17.96)	7.95, q, 6-H	7.55, m, 9-H			
$\mathrm{OCO\overset{(4)}{CH_2}\overset{(5)}{CH_3}}$	33.0	134–5	24.55 (24.39)	7.90, q, 6-H	7.40, m, 9-H	2.10, q, 4-H	0.90, t, 6-H	
 $\mathrm{OCO\overset{H(4)}{C}{=}C\genfrac{}{}{0pt}{}{H(5)}{H(6)}}$	73.1	152–3	25.14 (24.59)	7.75, q, 6-H	7.25, m, 9-H	5.90, *A*, 2-H	5.50, *B*, 2-H	5.90 ^{b}, *C*, 2-H

(4) 	75.7	160—61	22.97 (23.27)	7.90, q, 6-H	7.35, m, 9-H	1.80 *X*, 6-H	6.30, *A*, 2-H	5.90[c], *B*, 2-H
	70.0	176—7	20.25 (20.45)	8.05, q, 6-H		7.35, m, 15-H		7.85, q, 4-H
	61.2	170—71	18.55 (18.33)	8.05, q, 6-H	7.40, m, 11-H		7.15, m, 6-H	
	51.4[a]	237—9	19.46 (19.47)	8.00, q, 6-H	7.40, m, 9-H	7.70, *AA'*, 4-H	6.50, *BB'*, 4-H	3.80,[d] 4-H

[a] $CDCl_3$ as solvent. [b] Component parts of the *ABC* system. [c] Component parts of the ABX_3 system. [d] Component parts of the *AA'BB'* system for 1,4 disubstitution.

Triphenylantimony oxide, obtained by Ph_3Sb oxidation in acetone with 3 percent H_2O_2 which was dried in air (amorphous, associated form), was used. In a flask fitted with a stirrer and reflux condenser triphenylantimony oxide was suspended in methanol (10 ml per gram of oxide), the corresponding acid (3 mol per mol of oxide) was added in excess, (in the case of acrylic and methacrylic acids, 0.025% hydroquinone was added) and the mixture was brought to boiling point for ten minutes in a glycerol bath. It was filtered while hot in a pre-heated Büchner funnel. From the filtrate, crystals of the corresponding diester were separated out overnight by cooling or standing. Recrystallization of the preparations was carried out from methanol or ethanol. In this way, esters of formic, acetic, monochloroacetic, trichloroacetic, propionic, acrylic, methacrylic, benzoic, *o*-chlorobenzoic and *p*-aminobenzoic acids were obtained.

The obtained triphenylantimony diesters are soluble in methanol, ethanol, acetone, benzene, chloroform and CCl_4, and insoluble in petroleum ether.

The antimony content was determined titrometrically using the Schulek—Villecz method [8].

^1H NMR spectra (with integration) of the diester solutions were measured in CCl_4, or in deuteriochloroform adding tetramethylsilane (internal standard, 0 δ) at room temperature. Preparation yields, the determined and calculated Sb content and values of chemical shifts are given in Table 1.

References

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