Journal of Organometallic Chemistry, 78 (1974) 107—113

SPATIAL EFFECTS AND THE STRUCTURE OF ORGANOANTIMONY ALDEHYDES AND KETONES*

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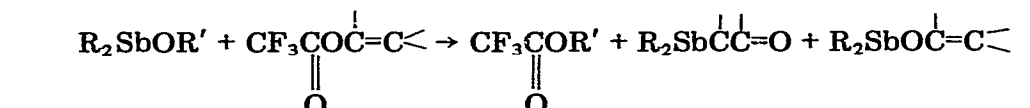
(Received March 21st, 1974)

Summary

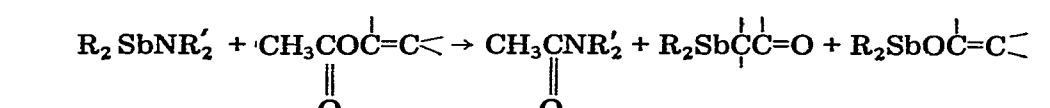
A number of organoantimony aldehydes and ketones have been synthesised. An increase in the spatial hindrance at either the α-carbon or the antimony increases the *O*-isomer relative content.

Recently, the structures and syntheses of carbonyl derivatives of elements of Groups IVB and VB have drawn a great deal of attention [1, 2]. The compounds may behave as stable *O*- or *C*-isomers or else one of these may be thermodynamically less stable and rearrange to give the other isomer [1]. The *O/C* tautomerism was found for the derivatives of germanium [3], tin [4], or antimony [5]. To clarify the effect of spatial factors upon the structure of organoantimony aldehydes and ketones, we wanted to synthesize a number of the organoantimony derivatives containing substituents of variable size at the carbonyl.

The compounds were synthesized (Table 1) using our previous methods, starting with alkoxystibines and enol trifluoracetates (method A) [5, 6], or dialkylaminostibines and enol acetates (method B) [5].



method A



method B

* In honour of Academician A.N. Nesmeyanov on the occasion of his 75th birthday.

It should be noted that absolutely pure aminostibines react via path B slower than do the compounds contaminated with the chlorostibine or the diaminostibine. For example, di-tert-butyldimethylaminostibine is practically not affected when kept with diethyl ketone enol acetate for two days, heating the mixture at 80° for 7 h gives as low as 50% yield of the terminal compound, whereas the reaction is complete if 5% (mol/mol) di-tert-butylchlorostibine are added under these conditions.

Attempts to obtain organoantimony aldehydes via method B resulted in significant amounts of enamines. This may be explained by assuming that the organoantimony carbonyl compound reacts with the aminostibine.

$$R_2SbNR'_2 + CH_3COC(=O)C\!< \rightarrow CH_3CNR'_2 + R_2SbCC(=O)\!< \xrightarrow{R_2SbNR'_2}$$

$$\rightarrow \left[R_2SbCC(OSbR_2)\!< \right] \rightarrow >C=C\!< + (R_2Sb)_2O$$

A special experiment showed that even the diethylantimony derivative of isobutyric aldehyde, an enolate, reacts with the aminostibine quantitatively and gives the enamine.

$$(C_2H_5)_2SbOCH=C(CH_3)_2 + (C_2H_5)_2SbN(CH_3)_2 \rightarrow (CH_3)_2C=CHN(CH_3)_2 + [(C_2H_5)_2Sb]_2O$$

Apparently, this reaction of the aminostibine as well goes via the isobutyric aldehyde *C*-derivative which is equilibrated with the *O*-derivative and the concentration of which is below the sensitivity of spectral methods.

When method B is applied to the ketone syntheses, enamines are, to all practical purposes and intents, not formed, but yields of the diethylantimony compounds are not very high, probably due to autocondensation in situ. Method A is, as a rule, more efficient, but enol trifluoroacetates [7] are not as easy to synthesize as enol acetates, so method B may in some cases turn out to be more convenient.

The organoantimony carbonyl derivatives (Table 1) are yellowish oils. Those boiling below 100° may be prepared in the analytically pure form.

Compounds of the type $(CH_3)_2SbX$ (X is Hal, OCH_3) readily disproportionate [$2R_2SbX \rightarrow R_3Sb + RSbX_2$] and are therefore inapplicable to a study of the structure. The diethylantimony derivatives are more stable while the di-tert-butyl derivatives were not observed to disproportionate at all.

The stability towards autocondensation depends on the structure. The acetaldehyde derivatives are unstable at room temperature. The enolate compounds may be stored at room temperature in argon for months whereas the *C*-derivatives start decomposing in a week. Note that the di-tert-butyl derivatives are much more stable than their diethyl analogues.

Table 1 shows that the organoantimony aldehydes and ketones may exist in the form of both *C*- and *O*-isomers. Let us collate carbonyl derivatives of arsenic, antimony, and tin, neighbours in the Periodic System. Unlike organoarsenic compounds (*C*-structured in all cases) [8], organoantimony compounds may have also enolate structures. On the other hand, the antimony derivatives reveal a stronger tendency to exist as the *C*-isomers than do the tin derivatives (cf. refs. 4 and 9 and the data in Table 1). Like in organotin carbonyl compounds [4], in which *O/C* tautomeric equilibria exist, similar equilibria may be in some cases observed spectrally (IR, NMR) in organoantimony carbonyl derivatives such as the diethylantimony derivative of cyclohexanone [5], di-tert-butylantimony derivatives of cyclopentanone [5] and diethyl ketone. The equilibrium for the latter compound, in contrast to the first two, is reached only in a month (in several days in the presence of di-tert-butylchlorostibine).

For the derivative of diethyl ketone, the *C/O* equilibrium coexists with the *O*-species *cis/trans* equilibrium.

An IR spectrum of the di-tert-butylantimony derivative of diethyl ketone contains an intense band at 1680 cm^{-1}, a characteristic of organoantimony carbonyl compounds, and a less intense band at 1640 cm^{-1} assignable to the *O*-isomer double bond.

The PMR spectrum contains the tert-butyl signals (a singlet for the *cis-O*-species, a singlet for the *trans-O*-species, two singlets for the diastereotopic *C*-species), and two vinyl quadruplets assignable to the *cis*- and *trans*-isomers (see Table 2). It should be noted that the di-tert-butylantimony derivative of diethyl ketone, similarly to the cyclohexanone derivative [5], is markedly enriched in the *O*-isomer after having subjected it to slow distillation; the 1640 cm^{-1} band intensity becomes much greater than that at 1680 cm^{-1} while the *O*-species tert-butyl PMR signals increase noticeably, with the *cis*-isomer signals growing predominant. When kept for three days under ambient conditions, the system regains its initial *C/O* and *cis/trans* equilibrium states. The equilibrium *O*-isomer content is 53% at room temperature, and 40% of this amount is due to the *trans*-isomer.

The tautomerism was observed for just three organoantimony derivatives of aldehydes and ketones, however, we believe that, like in organotin carbonyl compounds [4], the tautomeric transformations exist in all the compounds obtained, although they may be unobservable spectrally when the second isomer concentration is low. Stronger spatial hindrance due to the introduction of alkyl substituents in the α-position, and more bulky substituents introduced to the antimony, lower the *C*-isomer stability.

The relative stability of *O*- and *C*-isomers of organoantimony derivatives of carbonyl compounds depend mainly on the type and structure of the carbonyl compound, in other words on the enol stability of the carbonyl compound and on the spatial factors.

Aldehydes compared with ketones are more apt to form the *O*-isomers, but the most important role is played by substituents on the α-carbon of the carbonyl compound. An increase in the spatial hindrance at the α-carbon of an organoantimony carbonyl compound sharply lowers the *C*-isomer stability. Indeed, all organoantimony derivatives containing the group $SbCH_2C(O)R$ are stable as their *C*-isomers (irrespective of the size of R) whereas introducing two, or even one, alkyls to the α-carbon of an aldehyde (e.g., isobutyric or

TABLE 1

ANALYTICAL DATA

No.	Starting carbonyls	Starting stibines $R_2Sb—OR'$ / $R_2Sb—NR'_2$		Yield (%) via method A	Yield (%) via method B	Terminal stibine structure Sb-OC=C *O*-isomer (%)	Terminal stibine structure Sb-C-C=O *C*-isomer (%)
		R	R'				
1	$CH_3C(H)=O$	C_2H_5	C_2H_5	[a]			100
		t-C_4H_9	CH_3	[a]			100
2	$CH_3(CH_2)_2C(H)=O$	t-C_4H_9	CH_3	62		100 [b]	
3	$(CH_3)_2CH—C(H)=O$	t-C_4H_9	CH_3	82		100	
		C_2H_5	CH_3	83		100	
4	CH_3CCH_3 (=O)	C_2H_5	C_2H_5	77			100
		C_2H_5	CH_3		44		100
		t-C_4H_9	CH_3	57 [c]			100
5	$CH_3CC(CH_3)_3$ (=O)	t-C_4H_9	CH_3		85		100
		t-C_4H_9	CH_3	92			100
		C_2H_5	CH_3		43		100
6	$C_2H_5CC_2H_5$ (=O)	t-C_4H_9	CH_3		78	53 [d]	47
7		t-C_4H_9	CH_3		64	20	80
8		t-C_4H_9	CH_3	79		100	
		t-C_4H_9	CH_3		79	100	
		C_2H_5	CH_3	[a]		[e]	

[a] The compound failed to be distilled. [b] The *cis*-isomer content is 67%, the *trans*-isomer content is 33%, in the equilibrated mixture; the ratio is independent of temperature. [c] Synthesised from isopropenyl trichloroacetate. [d] The *cis*-isomer content is 60%, the *trans*-isomer content is 40%, in the mixture equilibrated at room temperature; an increase in the temperature raises the *trans*-isomer content. [e] See ref. 5.

butyric aldehydes) stabilises just the enolate structure. For ketones, branching at the α-carbonyl lowers the *C*-isomer stability compared with the enolate stability, that is, the *C*- and *O*-isomer contents become comparable in the tautomeric mixture. An increase in the size of alkyls attached to the antimony stabilises the *O*-isomer, i.e., it lowers the *C*-isomer content, as is clearly seen on comparing the structures of diethyl- and di-tert-butylantimony derivatives of cyclohexanone.

Thus, increasing spatial hindrance at either the α-carbon or the antimony increases the *O*-isomer relative content.

B.p. (°C/mmHg)	n_D^{20}	Empirical formula	Found (calcd.) (%)		
			C	H	Sb
		$C_6H_{13}OSb$	32.39, 32.62	5.59, 5.70	
			(32.32)	(5.90)	
45-47/3·10^{-2}	1.5115	$C_{12}H_{25}OSb$	46.31, 46.55	8.07, 8.02	
			(46.93)	(8.21)	
44-45/5·10^{-2}	1.5125	$C_{12}H_{25}OSb$	46.51, 47.09	8.25, 8.35	
			(46.93)	(8.21)	
42-43/1.5·10^{-2}	1.5350	$C_8H_{17}OSb$	37.83, 37.75	6.70, 6.92	48.26, 48.47
			(38.28)	(6.83)	(48.51)
45-46/1·10^{-2}	1.5440	$C_7H_{15}OSb$	35.31, 34.99	6.37, 6.17	51.32, 51.14
			(35.42)	(6.56)	(51.29)
73-75/2	1.5440				
48-49/2·10^{-2}	1.5300	$C_{11}H_{23}OSb$	44.29, 44.88	7.89, 7.92	41.75, 41.68
			(45.08)	(7.91)	(41.56)
67-68/5.6·10^{-2}	1.5170	$C_{14}H_{29}OSb$	49.58, 49.30	8.64, 8.70	36.35, 37.15
			(50.20)	(8.73)	(36.35)
70-71/4·10^{-2}	1.5170				
58-59/2·10^{-2}	1.5120	$C_{10}H_{21}OSb$	42.16, 42.22	7.16, 7.10	43.98, 43.61
			(43.03)	(7.59)	(43.64)
65-70/6·10^{-2}		$C_{13}H_{27}OSb$	48.05, 47.88	8.77, 8.89	37.44, 37.64
			(48.62)	(8.48)	(37.93)
80-90/6·10^{-2}		$C_{13}H_{25}OSb$	49.27, 49.23	7.73, 7.94	37.93, 38.11
			(48.95)	(7.90)	(38.17)
89-90/4·10^{-2}	1.5295	$C_{14}H_{27}OSb$	50.60, 50.33	8.40, 8.37	36.85, 36.78
			(50.47)	(8.15)	(36.56)
89-90/4·10^{-2}	1.5300				
		$C_{10}H_{19}OSb$	42.93, 43.03	6.38, 6.47	
			(43.35)	(6.26)	

Experimental

All operations were carried out in a dry argon atmosphere. IR spectra were recorded in thin films on an IKS-22 two-beam spectrometer. PMR spectra were obtained on an RS-60 machine using hexamethyldisiloxane as internal reference.

1. Di-tert-butylmethoxystibine

A solution of di-tert-butylchlorostibine [10] (45.2 g, 0.165 mol) in 100 ml hexane was added over a period of 1 h to a stirred solution of sodium methoxide

TABLE 2

SPECTRAL DATA

a b c
$R_2SbCR'_2COR''$

a d b
$R_2SbOCH{=}CR_2$

No.	Compound		PMR Spectra δ(ppm)				IR Spectra ν(cm^{-1})	
			H_a	H_b	H_c	H_d	C=O	C=C
1	$(C_2H_5)_2SbCH_2CH{=}O$			2.50	9.63		1700	
2	$(C_2H_5)_2SbCH_2COCH_3$			2.64	1.98		1690	
3	$(t\text{-}C_4H_9)_2SbCH_2CH{=}O$		1.12	2.70	9.70		1690	
4	$(t\text{-}C_4H_9)_2SbCH_2COCH_3$		1.20	2.56	2.12		1680	
5	$(C_2H_5)_2SbCH_2COC(CH_3)_3$			2.52	0.98		1660	
6	$(t\text{-}C_4H_9)_2SbCH_2COC(CH_3)_3$		1.22	2.64	1.12		1670	
7	$(C_2H_5)_2SbOCH{=}C(CH_3)_2$			1.47		6.26		1650
8	$(t\text{-}C_4H_9)_2SbOCH{=}C(CH_3)_2$		1.19	1.39 1.50		6.30		1650
		cis	1.22	4.02[a]		6.21		
9	$(t\text{-}C_4H_9)_2SbOCH{=}CHC_2H_5$							1630
		trans	1.20	4.63[a]		6.36		
10	$(t\text{-}C_4H_9)_2SbCH(CH_3)COC_2H_5$		1.26 1.30	2.50			1680	
		cis	1.26	4.22[a]				
11	$(t\text{-}C_4H_9)_2SbOC(C_2H_5){=}CHCH_3$							1650
		trans	1.23	4.40[a]				
12	$(t\text{-}C_4H_9)_2SbO$– 		1.2	4.38[c]				1630
13	$(t\text{-}C_4H_9)_2SbO$– 		1.32	4.73[c]				1640

[a] Proton chemical shifts for =CHR. [b] PMR data for the di-tert-butylantimony derivative of cyclopentanone and the diethylantimony derivative of cyclohexanone may be found in ref. 5. [c] Vinyl proton chemical shift.

placed in a cold water bath, obtained from sodium metal (4 g, 0.174 mol) and 100 ml absolute methanol. A white precipitate formed immediately. The mixture was maintained at 50-60° for 1 h. The precipitate was centrifuged, the centrifugate was evaporated, and two distillations of the residue gave di-tert-butylmethoxystibine, 37 g (84%), b.p. 54-56°/7 mm. Found: C, 39.67, 39.61; H, 7.56, 7.41; Sb, 45.84, 45.96. $C_9H_{21}OSb$ calcd.: C, 40.49; H, 7.93; Sb, 45.59%.

2. Diethylmethoxystibine

The compound was obtained in a similar way from sodium methoxide and diethylbromostibine; yield 80%, m.p. 30°, b.p. 43-47°/7 mm. Found: C, 28.54, 28.60; H, 6.08, 6.12; Sb, 56.87, 56.92. $C_5H_{13}OSb$ calcd.: C, 28.48; H, 6.23; Sb, 57.76%.

3. Diethyldimethylaminostibine

A cold solution of dimethylamine (9 g, 0.2 mol) in 50 ml absolute light petroleum was added dropwise to a vigorously stirred, cold (−40°) solution of n-butyllithium (0.166 mol) in a light petroleum. A white voluminous precipitate was formed. The mixture was stirred at room temperature for 1 h, excess di-

methylamine liberated vigorously. The mixture was cooled down to —40° again, and treated by a solution of diethylbromostibine [11] (41.9 g, 0.162 mol) added to the reaction flask for a period of 15 min. The cooling was switched off and the mixture was stirred at room temperature for 1 h. The precipitate was centrifuged, the residue was evaporated in vacuo and distilled twice, to give diethyldimethylaminostibine, 28 g (77.5%), b.p. 48-50°/10 mm. Found: C, 32.50, 32.02; H, 6.96, 6.96; Sb, 54.93, 53.84, 54.48; N, 5.96. $C_6H_{16}NSb$ calcd.: C, 32.10; H, 7.22; Sb, 54.40; N, 6.25%.

4. Diethylantimony derivative of isobutyric aldehyde

β,β-Dimethylvinyl trifluoroacetate [7] (11.4 g, 0.068 mol) was added dropwise at 10° to a stirred diethylmethoxystibine (12 g, 0.057 mol). The mixture was maintained at 40° for 20 min and distilled in vacuo, the lower-boiling fraction being collected in a trap cooled down to —70°. The contents of the trap was distilled to give methyl trifluoroacetate, 5.5 g (75%), b.p. 41-43° (lit. [12] 41-43°), n_D^{20} 1.3040 (lit. [12] 1.3053). The residue was twice distilled in a high vacuum to give β, β-dimethylvinyloxydiethylstibine (11.8 g).

The compound does not change when stored for a year. All other compounds synthesized through method A (Table 1) were prepared in a similar way.

5. Reaction of di-tert-butyldimethylaminostibine with pinacoline enol acetate

Di-tert-butyldimethylaminostibine (15.2 g, 0.0544 mol) was added to a vigorously stirred pinacoline enol acetate (9.4 g, 0.0662 mol). The reaction is exothermic. It was maintained at 80-90° for 4 h, and distilled in vacuo. The low-boiling fraction was collected in a trap cooled down to —70°. The contents of the trap and the collector was distilled again, to give *N,N*-dimethylacetamide, 4.0 g (84.7%), b.p. 45°/7 mm (lit. [13] 165-175°/760 mm), n_D^{20} 1.4300 (lit. [13] 1.4308).

The residue twice distilled in a high vacuum gave α-(di-tert-butylstibyl) pinacoline (15.5 g).

All other compounds synthesized by method B were prepared in similar way (Table 1).

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