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Preliminary communication

Optically active stibonium iodide

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SUMMARY

The first preparation of an optically-active stibonium iodide, viz. (+)-PhMeEt(i-Pr)SbI, is described.

Optically active quaternary phosphonium and arsonium salts are well known and their reactions have been much studied. The preparation of the asymmetric stibonium iodide MeEtPrBuSbI has been described recently[1], but no optical resolution of an asymmetric quaternary stibonium salt has been reported[2]. We describe below the first preparation of an optically active stibonium iodide, *viz.* (+)-PhMeEt-i-PrSbI, [(+)-I].

The stibonium iodide PhMeEt-i-PrSbI (I) was prepared by the reaction of PhMe-i-PrSb[3] with triethyloxonium fluoroborate[4] in methylene chloride, followed by treatment with potassium iodide in methanol. Compound (I) was also obtained from PhMe-i-PrSbS and Et_2InI, which has been reported to react with Me_3SbS to give Me_3EtSbI[5]. Treatment of (I) with silver-(—)-dibenzoylhydrogentartrate (DBHT)[6] in methanol, followed by recrystallization from ethyl acetate, gave PhMeEt-i-PrSb-(—)-DBHT of $[\alpha]_D^{18}$ −66.5° (*c* 1.023 in methanol). Treatment of dibenzoylhydrogentartrate with potassium iodide in methanol gave dextrorotatory stibonium iodide [(+)-I] of $[\alpha]_D^{26}$ +4.10° (*c* 0.634 in methanol), which was found to be optically stable as a solid and in solution.

The properties and PMR data of the asymmetric compounds obtained are shown in Table 1.

TABLE 1

THE PROPERTIES AND PMR DATA OF THE ASYMMETRIC ANTIMONY COMPOUNDS

Compound	*M.p.* (°C)	*Solvent for recrystallization*	*Analysis found (calcd.) (%)*		*PMR*[a]		*Assign*
			C	*H*	*δ (ppm)*	*J (Hz)*	
PhMe-i-PrSbS[b]	74–75	ethanol	41.24	5.17	1.42 d	7.5[c]	C(CH$_3$
			(41.55)	(5.23)	1.45 d	7.5[c]	
					1.64 s		SbCH$_3$
					2.60 m		SbCH
(±)-PhMeEt-i-PrSbI	117–118	methylene chloride/benzene	34.78	5.00	1.56 d	7.5[c]	C(CH$_3$
			(34.90)	(4.88)	1.58 d	7.5[c]	
					1.54 t	7.5[d]	SbCH$_2$
					2.19 s		SbCH$_3$
					3.13 m		SbCH$_2$
					3.98 m		SbCH
PhMeEt-i-PrSb-(−)-DBHT[e]	115–116	ethyl acetate	55.78	5.28	1.19 d	7.5[c]	C(CH$_3$
			(56.01)	(5.17)	1.20 d	7.5[c]	
					1.19 t	7.5[d]	SbCH$_2$
					1.62 s		SbCH$_3$
					2.43 m		SbCH$_2$
					3.20 m		SbCH
					5.87 s		DBHT
(+)-PhMeEt-i-PrSbI	107	methylene chloride/benzene	34.66	5.00			
			(34.90)	(4.88)			

[a] In $CDCl_3$ at room temperature; δ (ppm) downfield from internal TMS. [b] This compound was prepared from PhMe-i-PrSbBr$_2$ (ref. 3) and $Na_2S \cdot 9H_2O$ in methanol under nitrogen atmosphere. [c] $J(CH_3-CH)$. [d] $J(CH_3-CH_2)$ [e] DBHT = dibenzoylhydrogentartrate.

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