

Preliminary communication

CHROMATOGRAPHIC RESOLUTION OF RACEMIC ORGANOTIN AND -GERMANIUM COMPOUNDS*

IVAN VANDEN EYNDE and MARCEL GIELEN*

Vrije Universiteit Brussel, TW-AOSC, Pleinlaan 2, B-1050 Brussels (Belgium)

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Summary

Seven racemic organotin and -germanium compounds have been partially resolved by inclusion chromatography on microcrystalline cellulose triacetate.

Introduction

Several optically active organotin compounds in which the tin atom is the only chiral center have already been synthesized [1], either in the classical way, through the coupling of a chiral auxiliary group with a functional group present on the starting racemate [2,3] or by asymmetric synthesis using either a chiral leaving group [4,5] or a chiral reagent [6], or finally by a stereoselective or -specific substitution reaction [7] performed on an optically active organotin compound prepared by one of the former methods. In general (see, however, ref. 2) their optical purity is not known and, in fact, no really efficient method was available for resolving the organotin compounds. No chromatographic resolution of organotin racemates has been described previously, although many resolutions of racemic organic compounds into optically pure enantiomers by chromatography on optically active adsorbents have been reported [8].

Microcrystalline cellulose triacetate, introduced by Hesse and Hagel [9], is a chiral adsorbent that has given astonishingly good resolutions [10]. A particularly favorable property of this adsorbent is that the racemate to be separated does not need any functional group for the adsorption on the chiral matrix because phenyl rings fit especially well into the gaps of the cellulose chain.

We have examined the efficiency of microcrystalline cellulose triacetate in resolving organotin and -germanium compounds.

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Results and discussion

The results are summarized in Table 1. We used for this preliminary work a rather small column with which only partial separations of organotin and -germanium compounds were achieved. However, we have obtained for several

TABLE 1

ROOM TEMPERATURE CHROMATOGRAPHIC RESOLUTION OF ORGANOTIN AND -GERMANIUM COMPOUNDS ON MICROCRYSTALLINE CELLULOSE TRIACETATE

Organotin racemate	Maximum α -value		Mean $[\alpha]_{365}^{25}$ [9] ($^{\circ}$)	Retention volume V_R (ml)
	First ORD peak ($^{\circ}$)	Second ORD peak ($^{\circ}$)		
MeNeopPhSnTrit ^a	-0.155	+0.097	60	30
BenzMePhSnTrit ^a	-0.040	+0.026	32	50
MeNeop <i>i</i> -PrSnTrit ^a	-0.012	+0.006	4.5	15
BenzMe <i>i</i> -PrSnPh ^a	-0.012	+0.008	4.0	40
BenzEt <i>i</i> -PrSnPh ^a	0		0	25
MeNpPhGeH ^a	+0.073	-0.020	+80	-42
($[\alpha]_D = 10^{\circ}$)				165
MeNpPhGeCl ^b	+0.007	-0.005	1.5	100

Column ($l = 35$ cm; intern. diameter 2 cm) filled with 55 g of microcrystalline cellulose triacetate (53–105 μ) in 95% ethanol; eluent^a 95% ethanol ^b diethyl ether; dead volume $V_0 = 60$ ml, 50–100 mg of organometallic compound; 200 ml/h ($p(N_2) = 300$ torr)

Me = methyl; Et = ethyl; *i*-Pr = isopropyl; Ph = phenyl; Benz = benzyl; Trit = trityl(triphenylmethyl); Neop = neophyl(2-phenyl-2-methylpropyl); Np = 1-naphthyl.

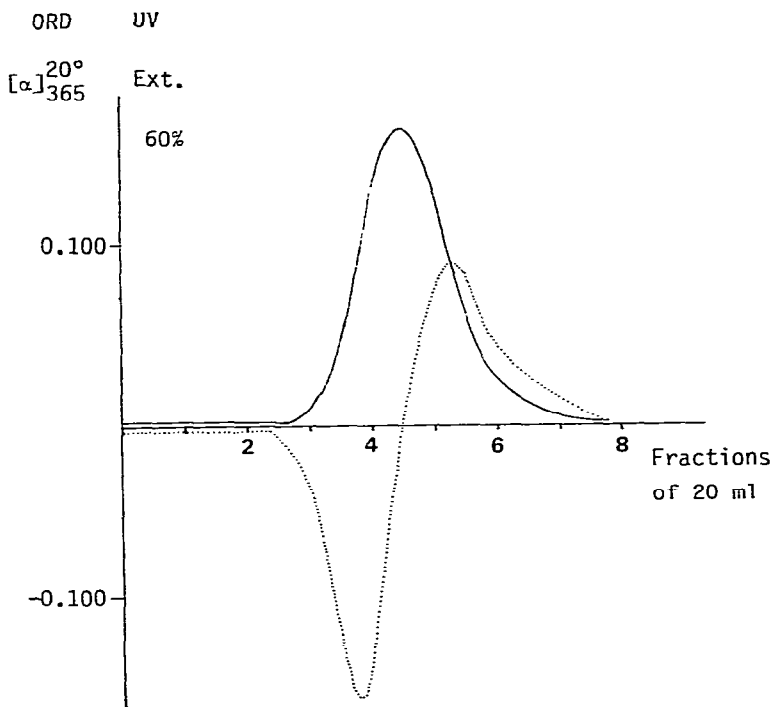


Fig. 1. Partial chromatographic resolution of 75 ng PhMeNeopSnTrit on cellulose triacetate (see Table 1). — UV ($\lambda = 275$ nm); - - - - ORD ($\lambda = 365$ nm).

compounds fractions with a high optical rotation. In particular tetraorganotin compounds with a triphenylmethyl substituent seem to be separated quite efficiently on cellulose triacetate (see Figure 1). Partially resolved methyl-1-naphthylphenylgermanium hydride ($[\alpha]_D^{20} = +10^\circ$) could be separated into two fractions characterized by $[\alpha]_{365}^{25} = +80^\circ$ and -42° , respectively. Even for the configurationally less stable methyl-1-naphthylphenylgermanium chloride, partial resolution was achieved.

These preliminary results show that microcrystalline cellulose triacetate can be used to separate enantiomeric organotin and -germanium compounds. Further experiments with a more efficient column will show if a complete resolution of racemic organometallic compounds into optically pure enantiomers is possible.

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