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Note

Determination of the optical purity of chiral quaternary phosphonium salts by differential scanning calorimetry

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In order to evaluate the exact stereochemistry (i.e., the quantitative degree of stereoselectivity) of nucleophilic substitution reactions at chiral acyclic phosphorus compounds[1–4] the optical purities of all of the reactants as well as of the reaction products must be known. As the most reliable method for optical purity determination, the isotope dilution procedure[5], is rather tedious we looked for another method, equally reliable, which could be easily applied to chiral acyclic quaternary phosphonium salts.

As the small amount of racemate (e.g., 2%) contained in an enriched optically active enantiomer (thus of 98% optical purity) may be regarded as an "impurity" of the enantiomer, each kind of purity determination by calorimetric measurements (e.g., DSC[6,7]) should be suitable for the purpose of optical purity evaluation. This was first performed by Fouquey and Jacques[8], who determined the optical purity of some optically active carbon acids by DSC.

We found this DSC method[8] to be applicable to some of the chiral quaternary phosphonium salts whose stereospecific conversion reactions we were studying, namely: *S*-(+)-methyl-n-propylphenylbenzylphosphonium bromide (**1**) (ref. 9) and *R*-(+)-methylphenyl-α-naphtylbenzylphosphonium bromide (**2**) (refs. 2 and 10).

RESULTS

The following results were obtained with a Perkin-Elmer Model DSC 1B, using the method and calculation as given by Fouquey and Jacques[8]:

S-(+)-**1**

$[\alpha]_D = +36.7°$ (methanol), m.p. 207°C.

Anal. $C_{17}H_{22}BrP$ (337.3) calc. C = 60.55, H = 6.58; found C = 60.42, H = 6.52. Optical purity determined by DSC measurement: 99±1% (molar heat of fusion: 12.5 kcal mol^{-1}).

Additionally, the reliability of the DSC method was proved by investigating a number of artificially prepared mixtures of *S*-(+)-**1**, $[\alpha]_D = +36.7°$ and racemic **1**. A

second small peak was obtained in the DSC thermogram when adding as small an amount of racemic **1** as 1%; the presence of 0.5% of racemic **1** in the enantiomeric *S*-(+)-**1**, however, could not be detected as a second peak. The addition of 2% of racemic **1** produced a second peak with twice the area of the 1% addition. Table 1 contains the results of some of these DSC measurements.

TABLE 1

DSC MEASUREMENTS OF SOME MIXTURES OF ENANTIOMERIC *S*-(+)-**1** WITH RACEMIC **1**

No. of mixture	*Composition of the mixture*		*Optical purity* (%)	
	S-(+)-**1**, $[\alpha]_D$ = +36.7° (%)	*racemic* **1** (%)	*Calc. from the composition of the mixture (assuming S-(+)-1 with* $[\alpha]_D$ = +36.7° *to be 100% opt. pure)*	*calc. according to ref. 8*
1	100	0	100	99.0
2	99.01	0.99	99.01	98.5
3	97.86	2.14	97.86	97.6
4	94.58	5.42	94.58	94.8
5	91.00	9.00	91.00	90.4

R-(+)-**2**

$[\alpha]_D$ = +84.5° (methanol), m.p. 243 °C.

Anal. $C_{24}H_{22}BrP$ (421.3) calc. C = 68.42, H = 5.26, Br = 18.97; found C = 68.45, H = 5.48, Br = 19.12. Optical purity determined by DSC measurement: 98±2%. (molar heat of fusion: 11.0 kcal mol^{-1}).

The knowledge of the optical purities of the two chiral phosphonium salts *S*-(+)-**1** and *R*-(+)-**2** enables one to evaluate the optical purities of all of those chiral phosphorus compounds which can be converted to or derived from one of these salts in a complete stereospecific manner, i.e., either with 100% retention or with 100% inversion of configuration (cf., e.g. refs. 2–4, 10 and references cited therein).

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