Chemistry

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1961

SovietRxiv

Abstract

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Separation of Quaternary Arsonium Compounds into Optical Antipodes by Asymmetric Adsorption on Natural Dissymmetric Adsorbents

(Presented by Academician B. A. Arbuzov on 21 III 1961)

Usually, the separation of asymmetric onium compounds into optical antipodes has been carried out by the classical method ($^{1-4}$), which consists in using some optically active reagent, with the formation of diastereoisomers, their subsequent decomposition, and the isolation of the optically active substance subjected to separation, according to the scheme:

$$\mathrm{l_1d_1} + \mathrm{d_2} \begin{cases} \longrightarrow \mathrm{l_1d_2} \longrightarrow \mathrm{l_1} + \mathrm{d_2} \\ \longrightarrow \mathrm{d_1d_2} \longrightarrow \mathrm{d_2} + \mathrm{d_2'} \end{cases}$$

where $\mathrm{l_1d_1}$ is the racemate under investigation, $\mathrm{d_2}$ is the optically active reagent, $\mathrm{l_1d_2}$ and $\mathrm{d_1d_2}$ are a pair of diastereoisomers, and $\mathrm{l_1}$ and $\mathrm{d_1}$ are the optical isomers of the substance under investigation.

The presence in this method of three successive operations—formation of a pair of diastereoisomers, separation of this pair, and decomposition of the pure diastereoisomer—makes it laborious and not very effective, especially in the case of poor crystallization of the diastereoisomers or low stability of the optically active isomers. The latter, probably, may explain the failures of numerous investigators in the separation of racemates.

In the present work, the separation of quaternary arsonium compounds was carried out by asymmetric adsorption on natural dissymmetric adsorbents ($^{5-7}$). The separation was studied of ethyl-*n*-amylphenylbenzylarsonium bromide, which had previously been carried out (^{8}) according to the scheme described above, for which $[\alpha]_D^{20} = +16.5^\circ$ had been found.

It was therefore of interest, on the one hand, to use the new method for separating asymmetric arsonium compounds and, on the other, to confirm the previously obtained results.

Experiments on the separation of a racemic mixture of ethyl-*n*-amylphenylbenzylarsonium bromide on a column filled with dextrorotatory piezoquartz obtained by vibrogrinding in water (column diameter 0.9 cm; adsorbent height 23 cm; weight 8.5

Fig. 1

Figure 1: Fig. 1

g; specific surface area 28.1 m^2/g; according to X-ray analysis, 70% crystalline phase) were carried out as follows: a solution of 0.5 g of the substance in 1 ml of absolute alcohol was placed on the column and eluted with chloroform. With the appearance of arsenic in the eluate (qualitative reactions for arsenic), fractions of 7 ml each were collected. In the third fraction it was found that the solution possessed optical activity, measurement of which showed: $[\alpha]_D^{20} = +22.1^\circ$ ($\alpha_D^{20} = +0.24^\circ,\ l = 1.9$). It was not possible in this case to isolate the levorotatory isomer.

For the purpose of isolating the levorotatory isomer, experiments were carried out on a column with levorotatory quartz (column diameter 0.9 cm; adsorbent height 17 cm; quartz weight 6.5 g; specific surface area 15.4 m^2). A solution of 0.3 g of ethyl-*n*-amylphenylbenzylarsonium bromide in 1 ml of absolute alcohol, eluted with chloroform, was passed through the column.

The third fraction, with the presence of arsenic in the solution, was active and had: $[\alpha]_D^{20} = -19.56^\circ$ ($\alpha_D^{20} = -0.09^\circ,\ l = 1.9$).

Table 1

Compound	Amount of substance, g	Amount of solvent, ml	α_D^{20}, deg.	$[\alpha]_D^{20}$, deg.	Tube length, dm
$[C_2H_5 \setminus C_5H_{11} / As \setminus C_6H_5 / C_7H_7]$ Br	0.0402	7	+0.24	+22.10	1.9
$[C_2H_5 \setminus C_5H_{11} / As \setminus C_6H_5 / C_7H_7]$ Br	0.0190	7	−0.09	−19.56	1.9

Further, from consideration of the dependence of the concentration of the solution under study (Fig. 1), when working with *d*- and *l*-quartz, on the amount of fractions collected, an increase and decrease in the concentration of one of the isomers and a constant value of the concentration of the antipode are seen. Consequently, the impossibility of isolating both isomers when working with both *d*- and *l*-quartz is explained by the excessively large adsorption capacity of active quartz with respect to one of the isomers.

Fig. 1

Consideration of the dependence of the specific rotation of the solution on the amount of fractions collected when working with *d*- and *l*-quartz with the isolation, respectively, of isomers with $[\alpha]_D^{20} = +22.10^\circ$ and $[\alpha]_D^{20} = -19.56^\circ$ (with an insignificant absolute discrepancy equal to 2.5°) convinces us that, in the absence of a large selective adsorption of quartz toward one of the isomers, we would have obtained both isomers with identical optical activity (Fig. 2).

Fig. 2

Figure 2: Fig. 2

Fig. 2

When the separation of a racemic mixture of ethyl-*n*-amylphenylbenzylarsonium bromide was carried out on a column with lactose, no reliable results were obtained. It should be noted that both the right- and left-handed isomers of ethyl-*n*-amylphenylbenzylarsonium bromide, separated on a column with optically active quartz, changed within an hour into the racemate.

Thus, for the separation of racemates of quaternary arsonium compounds, the method of asymmetric adsorption on natural dissymmetric adsorbents was used; with its aid the left-handed isomer with $[\alpha]_D^{20} = -19.56°$ was isolated for the first time.

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Received
9 III 1961

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