CHEMISTRY

Gilm KAMAI and Yu. F. GATILOV

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

Gilm KAMAI and Yu. F. GATILOV

ON THE RESOLUTION OF ASYMMETRIC ARSONIUM COMPOUNDS INTO OPTICALLY ACTIVE ANTIPODES

(Presented by Academician B. A. Arbuzov on 28 IX 1960)

At the present time there is a small number of works devoted to the resolution of salts of asymmetric quaternary arsonium compounds of the general type $RR'R''R'''AsHal$, where the optical activity undoubtedly depends on the asymmetric arsenic atom.

After the unsuccessful investigations in this direction by Michaelis ([1]) and Winmill ([2]), in 1921 Burrows and Turner ([3]) isolated the dextrorotatory component of methylphenylbenzyl-α-naphthylarsonium iodide with $M_D = 12°$, which on recrystallization passed into an inactive form. Later, one of us ([4]), by decomposing the d-π-bromocamphorsulfonate salt of ethyl-n-propyl-p-tolylbenzylarsonium with an aqueous solution of potassium iodide, succeeded in isolating the dextrorotatory component of ethyl-n-propyl-p-tolylbenzylarsonium iodide with $M_D = 41.5°$.

Continuing investigations in this field, by the interaction of phenylethylchloroarsine with organomagnesium compounds of the corresponding haloalkyls we synthesized various asymmetric arsines of the general type:

$$\begin{array}{c} C_6H_5 \\ A - R, \\ C_2H_5 \end{array}$$

where R is an aliphatic radical.

Some physical constants of the arsines studied are given in Table 1.

Table 1

Compound	B.p., °C at 10 mm	d_4^{20}	n_D^{20}	As, % calc.	As, % found
$(C_6H_5)(C_2H_5)(CH_3)\equiv As$	85–86	1.2023	1.5642	38.21	37.98
$(C_6H_5)(C_2H_5)(C_3H_7)\equiv As$	108–109	1.1415	1.5492	33.45	33.28
$(C_6H_5)(C_2H_5)(C_4H_9)\equiv As$	122–123	1.1187	1.5438	31.45	31.27
$(C_6H_5)(C_2H_5)(C_5H_{11})\equiv As$	133–134	1.0971	1.5371	29.70	29.59
$(C_6H_5)(C_2H_5)(C_6H_{13})\equiv As$	145–146	1.0862	1.5340	28.20	27.90
$(C_6H_5)(C_2H_5)(C_7H_{15})\equiv As$	163–164	1.0661	1.5271	26.72	26.53
$(C_6H_5)(C_2H_5)(C_8H_{17})\equiv As$	171–172	1.0514	1.5221	25.45	25.28
$(C_6H_5)(C_2H_5)(C_9H_{19})\equiv As$	181–182	1.0327	1.5170	24.29	24.23

The isolated tertiary asymmetric arsines are colorless liquids (with an unpleasant odor), which readily mix with alcohol, ether, benzene, and other organic solvents.

Further, by addition of allyl bromide or benzyl bromide to some of the indicated arsines, the following asym-

Table 2

Compound	M.p., °C at 10 mm	As, % calc.	As, % found	Br, % calc.	Br, % found	Yield, %
$\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}> As < \begin{matrix}CH_3\\C_3H_5\end{matrix}\right] Br$	84–85	23,30	23,62	25,10	25,10	93,1
$\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}> As < \begin{matrix}C_3H_7\\C_3H_5\end{matrix}\right] Br$	105–106	21,75	21,74	23,06	23,15	93,9
$\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}> As < \begin{matrix}C_4H_9\\C_3H_5\end{matrix}\right] Br$	77–78	20,95	21,14	22,35	22,25	87,8
$\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}> As < \begin{matrix}C_3H_7\\C_7H_7\end{matrix}\right] Br$	154,156	18,95	18,78	20,22	20,33	84,7
$\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}> As < \begin{matrix}C_5H_{11}\\C_7H_7\end{matrix}\right] Br$	108–109	17,69	17,60	18,88	18,94	79,2

⋯metric tetravalent arsonium compounds in crystalline form; some data on them are summarized in Table 2.

The asymmetric arsonium compounds obtained are white crystalline substances, soluble in alcohol, acetone, and water and insoluble in ether. They are hygroscopic. The allyl derivatives are more hygroscopic than the benzyl derivatives. Introduction of a benzyl radical into quaternary arsonium compounds leads to greater stability of the latter in air.

Table 3

Fraction No.	Quantity, g	Amount of solvent, l	α_D	$[\alpha]_D$	$[M]_\alpha$	Difference ΔM
1	0,0441	2	+0,35	+53,2	+347,7	+74,7
2	0,1491	2	+1,20	+53,4	+348,3	+75,3
3	0,0187	2	−0,10	−34,2	−222,3	−51,1

The resolution of asymmetric arsonium compounds was carried out with the aid of the optically active silver salt of *d*-π-bromocamphorsulfonic acid. On interaction of the indicated salts of arsonium bases with the silver salt of *d*-π-bromocamphorsulfonic acid, only the *d*-π-bromocamphorsulfonate of ethyl-*n*-amylphenylbenzylarsonium crystallized well. The remaining salts formed syrup-like substances.

The resolution experiment with ethyl-*n*-amylphenylbenzylarsonium bromide by means of the silver salt of *d*-π-bromocamphorsulfonic acid was carried out as follows.

An aqueous solution of 8.01 g of ethyl-*n*-amylphenylbenzylarsonium bromide was added to a solution of 7.91 g of the silver salt of *d*-π-bromocamphorsulfonic acid. After filtration of the silver bromide precipitate, the water was removed under vacuum. The *d*-π-bromocamphorsulfonate of ethyl-*n*-amylphenylbenzylarsonium remaining in the distillation flask crystallized. The contents of the flask were then dissolved in ethyl acetate. After distillation of part of the solvent and prolonged standing, the first fraction of crystals separated in the form of needles; then, after partial evaporation of the solvent and further standing, a second fraction of crystals was isolated. M.p. of the crystals of the first fraction 159°. Found, %: As 11,50; $C_{30}H_{42}O_4SBrAs$. Calculated, %: As 11,46.

M.p. of the crystals of the second fraction 156°. Found, %: As 11,48; $C_{30}H_{42}O_4SBrAs$. Calculated, %: As 11,46.

Crystals were also isolated from the remaining mother liquor.
Found, %: As 11.39; $C_{30}H_{42}O_4SBrAs$. Calculated, %: As 11.46.

The polarimetric measurements are given in Table 3. The measurements were carried out in a 3-cm tube.

Next, in order to obtain the optical isomers in pure form, decomposition of the diastereomers with an aqueous solution of potassium bromide was carried out. Only the decomposition of the diastereomers of the first fraction led to positive results—crystals with m.p. 111° were isolated. Found, %: As 16.99; $C_{20}H_{28}AsBr$. Calculated, %: As 17.69.

The polarimetric measurements showed: $\alpha_D = +0.10°$; $[\alpha]_D = +16.5°$; $[M]_D = +70.0°$.

This dextrorotatory component rather rapidly passed into the inactive form.

Thus, the dextrorotatory and levorotatory diastereomers were obtained:

$$d\left[\begin{array}{ccccc} C_6H_5 & \backslash & & / & C_5H_{11} \\ & & \mathrm{As} & & \\ C_2H_5 & / & & \backslash & C_7H_7 \end{array}\right]\text{-}d\text{-}\pi\text{-}C_{10}H_{14}OBrSO_3;$$

$$l\left[\begin{array}{ccccc} C_6H_5 & \backslash & & / & C_5H_{11} \\ & & \mathrm{As} & & \\ C_2H_5 & / & & \backslash & C_7H_7 \end{array}\right]\text{-}d\text{-}\pi\text{-}C_{10}H_{14}OBrSO_3$$

and *d*-bromoethyl-*n*-amylphenylbenzyl arsonium was isolated with $[\alpha]_D = +16.5°$; $[M]_D = +70.0°$.

Chemical Institute
Kazan Branch of the Academy of Sciences of the USSR

Received
24 IX 1960

CITED LITERATURE

1. A. Michaelis, Lieb. Ann., **321**, 159 (1902).
2. Winmill, J. Chem. Soc., **101**, 720 (1912).
3. Burrows, Turner, J. Chem. Soc., **119**, 426 (1921).
4. Gilm Kamai, ZhOKh, **4**, 184 (1934).

Note: Figure translations are in progress. See original paper for figures.