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Gilm KAMAI and G. M. RUSETSKAYA

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Abstract

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Gilm KAMAI and G. M. RUSETSKAYA

ON THE QUESTION OF THE RESOLUTION OF PHOSPHONIUM COMPOUNDS WITH AN ASYMMETRIC PHOSPHORUS ATOM

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At the present time there is a considerable number of works devoted to the study of the stereochemistry of asymmetric phosphonium compounds of the general type *abcd*PHal ([1]). However, attempts to resolve the indicated compounds into optical antipodes over a period of almost 5–10 years were unsuccessful. Holliman and Mann ([2]) were the first to isolate the *d*-form of one heterocyclic phosphorus-containing compound, namely *d*-bromo-2-phenyl-2-hydroxyphenyl 1:2:3:4-tetrahydroisophosphinolinium with M_D 32.9°. In 1956 one of us ([3]), together with L. A. Khismatullina, succeeded in isolating two diastereomeric *dπ*-bromocamphorsulfonates of ethylphenylbenzylallylphosphonium. Recently Camley, McEwen, and VanderWerf ([4]) successfully resolved methyl ethylphenylbenzylphosphonium iodide into optical isomers with the aid of the dextrorotatory and levorotatory silver salts of dibenzoyltartaric acid.

Continuing investigations in this direction, we set ourselves the goal of improving the method for obtaining asymmetric tertiary phosphines and of testing other methods for the resolution of asymmetric phosphonium compounds.

Previously, asymmetric tertiary phosphines were synthesized by us by the method of J. Meisenheimer, by thermal decomposition of chlorides of dialkylphenylbenzylphosphoniums in an atmosphere of carbon dioxide. But this method is very complicated and is a rather difficult route for isolating pure asymmetric alkylphenylbenzylphosphines.

As the starting substance for asymmetric tertiary phosphines we used phenylethylchlorophosphine, obtained by a comparatively simple method based on the action of tetraethyllead on phenyldichlorophosphine at elevated temperature, according to the equation:

$$3C_6H_5PCl_2 + Pb(C_2H_5)_4 \rightarrow 3\ \begin{matrix} C_6H_5 \\ PCl \\ C_2H_5 \end{matrix} + C_2H_5Cl + PbCl_2.$$

Further, by the action of phenylethylchlorophosphine on solutions of magnesium-organic compounds of the corresponding alkyl halides, asymmetric phosphines were isolated. Some data on them are given in Table 1.

The asymmetric phosphines synthesized by us are highly mobile, colorless liquids with an unpleasant odor; they mix readily with many organic solvents and are oxidized in air.

By addition of allyl bromide and monobromoacetic ester to the indicated phosphines, asymmetric phosphonium compounds were obtained. Some physicochemical and analytical data of these compounds are summarized in Table 2. The isolated asymmetric phosphonium compounds are white crystalline substances, readily soluble in water and alcohol, on heating soluble in benzene and acetone, and insoluble in dry ether.

By hydrolysis of methyl ethyl phenyl ethoxycarbonylmethylphosphonium bromide, an acidic salt was obtained—methyl ethyl phenyl carboxymethylphosphonium bromide with m.p. 135–137°. On treatment of ethyl propyl phenyl allylphosphonium bromide with the silver salt of *d*-bromocamphorsulfonic acid, after removal of silver bromide from the aqueous solution we isolated a syrup-like substance, which did not crystallize even on prolonged standing in a vacuum desiccator over sulfuric acid.

Table 1

No.	Compound	B.p., °C/mm	d_4^{20}	n_D^{20}	AR_D^P	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.
1	$C_6H_5\backslash$ CH_3*	82/4 84/9	0,9603	1,5555	9,61	71,04	71,05	8,61	8,55	20,35	20,39
2	$C_6H_5\backslash$ C_3H_7	109/4 111/9	0,9320	1,5360	9,71	73,35	73,33	9,48	9,44	17,15	17,22
3	$C_6H_5\backslash$ C_4H_9	121/4 123/11	0,9255	1,5325	9,89	74,30	74,23	9,95	9,79	15,91	15,98
4	$C_6H_5\backslash$ C_5H_{11}	129/4 131/10	0,9237	1,5299	9,83	75,13	75,00	10,18	10,09	15,05	14,90
5	$C_6H_5\backslash$ C_6H_{13}	123/4 125/5	0,9212	1,5255	9,81	—	—	—	—	14,09	13,97

* First synthesized by Horner, Beck, and Hoffmann (5).

Table 2

No.	Compound	M.p., °C	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.	Br, % found	Br, % calc.	Yield, %
1	$[CH_3, C_2H_5, C_6H_5, C_3H_5P]Br$	97–98	52,67	52,75	6,37	6,59	11,40	11,34	—	—	61,1
2	$[C_2H_5, C_7H_7, C_8H_5, C_3H_5P]Br$	131–133	55,87	55,81	7,09	7,31	10,22	10,30	—	—	68,9
3	$[C_2H_5, C_4H_9, C_8H_5, C_3H_5P]Br$	73–74	57,33	57,14	7,73	7,62	9,95	9,84	—	—	67,7
4	$[C_2H_5, C_5H_{11}, C_{16}H_5, C_3H_5P]Br$	58–60	47,58	47,36	8,05	7,90	9,67	9,42	—	—	66,7
5	$[C_2H_5, C_6H_{13}, C_{16}H_5, C_3H_5P]Br$	50–52	59,75	59,48	8,43	8,16	8,83	9,03	—	—	70,0
6	$[CH_3, C_2H_5, C_6H_5, C_{10}H_9OC_2H_5P]Br$	71–73	48,94	48,90	6,34	6,26	9,75	9,71	25,18	25,07	71,0
7	$[CH_3, C_2H_5, C_6H_5, C_{13}H_{11}OC_2H_5P]Br$	135–137	45,17	45,36	5,99	5,49	10,55	10,45	27,51	27,48	—

By fractional crystallization of the quinine salt of methyl ethyl phenyl carboxymethylphosphonium bromide, four fractions were isolated with $[\alpha]_D^{20}$: −81,35°, −102,03°, −143,43°, and −136,17°, but upon decomposition of these individual fractions no optically active salt was obtained.

Attempts were made to resolve asymmetric phosphonium salts by chromatography on dissymmetric adsorbents (quartz, glucose, lactose, fructose, and starch). Mixtures of solvents in various ratios were tested as eluents: heptane–ethyl acetate, heptane + benzene, and heptane + chloroform.

When methyl ethyl phenyl allyl phosphonium bromide and ethyl propyl phenyl allyl phosphonium bromide were tested on right- and left-rotating quartz, no separation was observed. The work was carried out in small chromatographic columns.

Table 3

Fraction No.	Amount of substance (g)	α, (in °C)	$[\alpha]_D^{20}$	Amount of substance (in % of charge)	Tube length (cm)
1	0,0042	—	—	—	10
2	0,0298	0,039	9,23 (c 0,423 ethyl acetate)	5,39	10

Fraction No.	Amount of substance (g)	α, (in °C)	$[\alpha]_D^{20}$	Amount of substance (in % of charge)	Tube length (cm)
3	0,0130	0,031	16,07 (c 0,186 ethyl acetate)	2,35	10
4	0,0230	0,023	−5,37 (c 0,428 ethyl acetate)	5,42	10

Slight resolution of phosphonium salts was observed on soluble and insoluble starch. Methyl ethyl phenyl allyl phosphonium bromide was somewhat resolved on insoluble starch (see Table 3).

On soluble starch, for the same salt, $\alpha = 0,022^\circ$, $[\alpha]_D^{20} = 11,95^\circ$ was obtained. For salts with heavier radicals, the following data were obtained (see Table 4).

Table 4

Adsorbent: soluble starch. Eluent: heptane + ethyl acetate

Fraction No.	Compound	Amount of substance (g)	α	$[\alpha]_D^{20}$	Amount of substance (in % of charge)	Tube length (cm)
1–2	$\begin{bmatrix} C_2H_5 \\ C_3H_7 \end{bmatrix} > P < \begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}$ Br	–	–	–		
3	$\begin{bmatrix} C_2H_5 \\ C_3H_7 \end{bmatrix} > P < \begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}$ Br	0,0157	0,013	8,35 (c 0,0824 ethyl acetate)	7,99	19,009
4	$\begin{bmatrix} C_2H_5 \\ C_3H_7 \end{bmatrix} > P < \begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}$ Br	0,0105	0,024	14,84 (c 0,1617 ethyl acetate)	7,84	10,00
1–6	$\begin{bmatrix} C_2H_5 \\ C_4H_9 \end{bmatrix} > P < \begin{matrix} C_6H_5 \\ C_3H_5 \end{matrix}$ Br	–	–	–		

Fraction No.	Compound	Amount of substance (g)	α	$[\alpha]_D^{20}$	Amount of substance (in % of charge)	Tube length (cm)
7	$\left[\begin{matrix}C_2H_5\\C_4H_9\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,0120	0,026	18,36 (c 0,0708 ethyl acetate)	2,52	20,00
8	$\left[\begin{matrix}C_2H_5\\C_4H_9\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,0376	0,022	4,68 (c 0,235 ethyl acetate)	4,68	20,00
9	$\left[\begin{matrix}C_2H_5\\C_4H_9\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,0211	0,010	3,57 (c 0,28 ethyl acetate)	4,44	20,00
1	$\left[\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,0083	0,025	18,10 (c 0,138 ethyl acetate)	6,92	10,00
2	$\left[\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,0494	0,018	2,18 (c 0,824 ethyl acetate)	41,23	10,00
1–3	$\left[\begin{matrix}C_2H_5\\C_6H_{13}\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	–	–	–		
4	$\left[\begin{matrix}C_2H_5\\C_6H_{13}\end{matrix}>P<\begin{matrix}C_6H_5\\C_3H_5\end{matrix}\right]Br$	0,1003	0,028	1,467 (c 1,0036 ethyl acetate)	87,52	19,009

The work on the resolution of asymmetric phosphonium salts on dissymmetric adsorbents was carried out by one of us in the Laboratory of Organic Chemistry named after N. D. Zelinskii under the direction of E. I. Klabunovskii, to whom we express our deep gratitude.

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

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