

## The Synthesis of Iodmethyltrialkyl(aryl)arsonium Diiododibromocadmates(II)

Givi Tsintsadze\*, Tea Lobzhanidze\*\*, Mikheil Gverdtsiteli\*\*

\* Academy Member, Georgian Technical University, Tbilisi

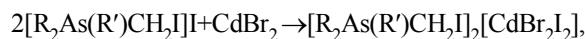
\*\* I. Javakhishvili Tbilisi State University

**ABSTRACT.** The specificity of preparation of mixed diiododibromocadmates(II) on the basis of iodmethyltrialkyl(aryl)arsonium salts in the alcohol-water solution is investigated. The structure of synthesized compounds is determined by physico-chemical methods. © 2010 Bull. Georg. Natl. Acad. Sci.

**Key words:** acido-complexes, mercurometric method, electroconductivity.

Acido-complexes of tetrasubstituted arsonium, whose arsenic is in the composition of cation, have been thoroughly investigated [1,2]. But the synthesis of tetraalkyl(aryl)arsonium complexes of cadmates, with mixed ligands, has not been carried out practically to date. The reason is that a method does not exist by which the different halogens can be determined at their simultaneous presence in arsenic-organic compounds.

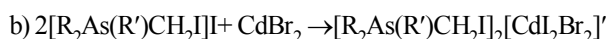
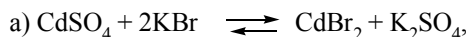
As iodmethyltrialkyl(aryl)iodides were accessible to us [3], we decided to study the possibility of obtaining mixed diiododibromocadmates(II) on the basis of iodmethyltrialkyl(aryl)arsonium salt. The process can be represented according to the equation:



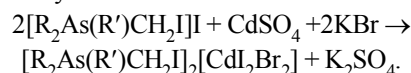
where  $\text{R}=\text{C}_3\text{H}_7$ ;  $\text{iso-C}_3\text{H}_7$ ;  $\text{C}_4\text{H}_9$ ;  $\text{iso-C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$ .

It should be noted that during the synthesis of tetrasubstituted diiododibromocadmates(II) it is not necessary to use cadmium bromide as the initial compound - other water-soluble salts of cadmium can also be used. But if we wish the reaction to proceed in a desirable direction, the presence of bromide ion is obligatory in solution. 3-5% more must be used than the theoretical quantity to block the existence of iodide ions in the mixture and to increase the yield of products. The

following consecutive reactions are achieved according to the scheme:



or in summary



The only great obstacle encountered by us in studying bromide coordination compounds of cadmium was quantitative determination of halogens (bromide, iodide) in the sample. We solved this problem by the mercurometric method [4]: on the basis of mathematical calculations we obtained a formula which allows calculating the summary content of bromide and iodide (Table 1). The Table shows that elementary analysis of halogens and arsenic proved unequivocally the formation of mixed-ligand cation-anion coordination compounds of the type:  $[\text{R}_2\text{As}(\text{R}')\text{CH}_2\text{I}]_2[\text{CdI}_2\text{Br}_2]$ .

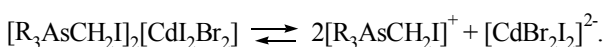
The synthesized acido-complexes with mixed ligands are white-yellow compounds. They are insoluble in water, alcohol, benzene and other aprotic solvents. They are solved relatively well in dimethylformamide. Their electroconductivity ( $\mu$ ) was determined in the latter

Table 1

Some physical-chemical constants of tetrasubstituted arsonium dibromodiiodocadmates(II)

№	R	R'	T, °C	$\mu, \text{om}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Found		Gross-formula	Calculated	
					As	Hlg		As	Hlg
1	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	230-231	101.5	11.80	54.48	C <sub>20</sub> H <sub>46</sub> As <sub>2</sub> CdI <sub>4</sub> Br <sub>2</sub>	12, 3	54.91
2	iso-C <sub>3</sub> H <sub>7</sub>	iso-C <sub>3</sub> H <sub>7</sub>	210-211	100.0	12.09	55.01	C <sub>20</sub> H <sub>46</sub> As <sub>2</sub> CdI <sub>4</sub> Br <sub>2</sub>	12.33	54.91
3	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	71-72	99.5	10.92	50.02	C <sub>30</sub> H <sub>50</sub> As <sub>2</sub> CdI <sub>4</sub> Br <sub>2</sub>	11.19	49.83
4	iso-C <sub>4</sub> H <sub>9</sub>	iso-C <sub>4</sub> H <sub>9</sub>	199-200	94.8	11.49	51.92	C <sub>26</sub> H <sub>58</sub> As <sub>2</sub> CdI <sub>4</sub> Br <sub>2</sub>	11.53	51.36
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	128-129	91.9	10.71	47.79	C <sub>38</sub> H <sub>34</sub> As <sub>2</sub> CdI <sub>4</sub> Br <sub>2</sub>	10.56	47.02

solvent.  $\mu$  of the substance under study range within 91-102  $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  and it corresponds to three-ionic electrolytes [5]. The electrolytic dissociation of the synthesized substances proceeds according to the scheme:



Apart from chemical analysis, the composition and structure of the compounds were investigated by physical-chemical methods as well. The analysis of IR spectra of these compounds shows that they are largely identical with the IR spectra of the initial tetrasubstituted arsonium iodides, where as it is present in the composition of cation (Fig. 1). IR spectra contain a band of absorption at  $\sim 440\text{-}470 \text{ cm}^{-1}$ , which is characteristic of As-C atom bonds and the band of absorption at  $\sim 610\text{-}650 \text{ cm}^{-1}$  [6], which is characteristic of As-C<sub>Aliph</sub> bonds. This proves that arsenic is present in quaternized state ( $\text{sp}^3$ -hybridization). The synthesized compounds were studied by derivatography method. The thermogravigrams of iodmethyltripropylarsonium dibromodiiodo-

cadmate (a) and iodmethyltributylarsonium dibromodiiodocadmate (b) are presented in Fig. 2. The thermolysis of these compounds starts at a temperature higher than the melting point and ends with the isolation of cadmium bromide. Iodmethyltripropylarsonium dibromodiiodocadmate loses 77.0% of its mass in the temperature range 200-400°C; this points to the loss of the "organic part" of the compound. Thus,  $2\text{CH}_2\text{I}_2$ ,  $2(\text{iso-C}_3\text{H}_7)_3\text{As}$  are isolated (77.6% theor.). It is more probable that in this temperature range ligands are isolated in parts.

The thermolysis can be represented by the scheme:

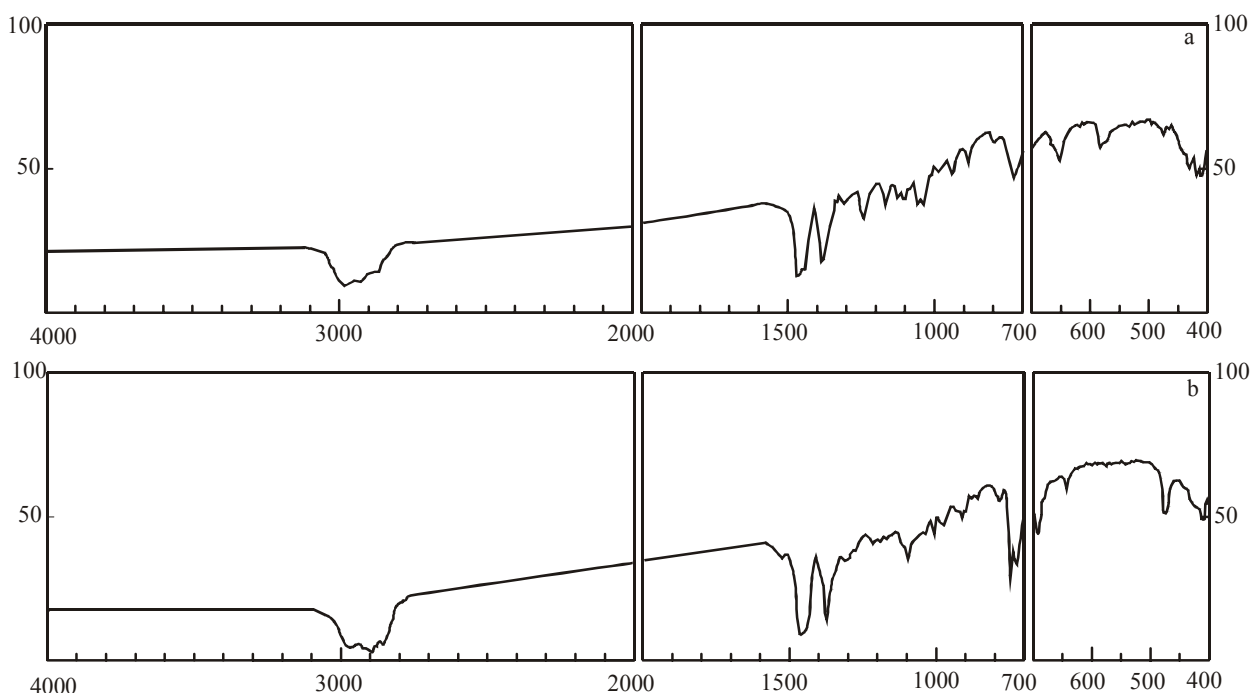
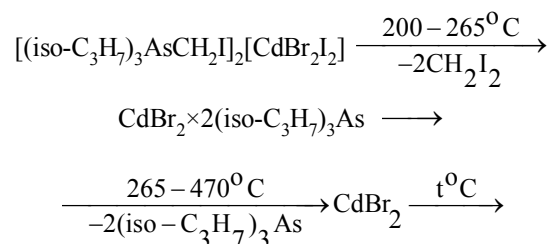


Fig. 1. IR- spectra of absorption in white paraffin oil; a)  $[(\text{C}_4\text{H}_9)_2\text{As}(\text{C}_6\text{H}_5)\text{CH}_2\text{I}]_2[\text{CdI}_2\text{Br}_2]$ ; b)  $[(\text{iso-C}_3\text{H}_7)_3\text{AsCH}_2\text{I}]_2[\text{CdI}_2\text{Br}]$

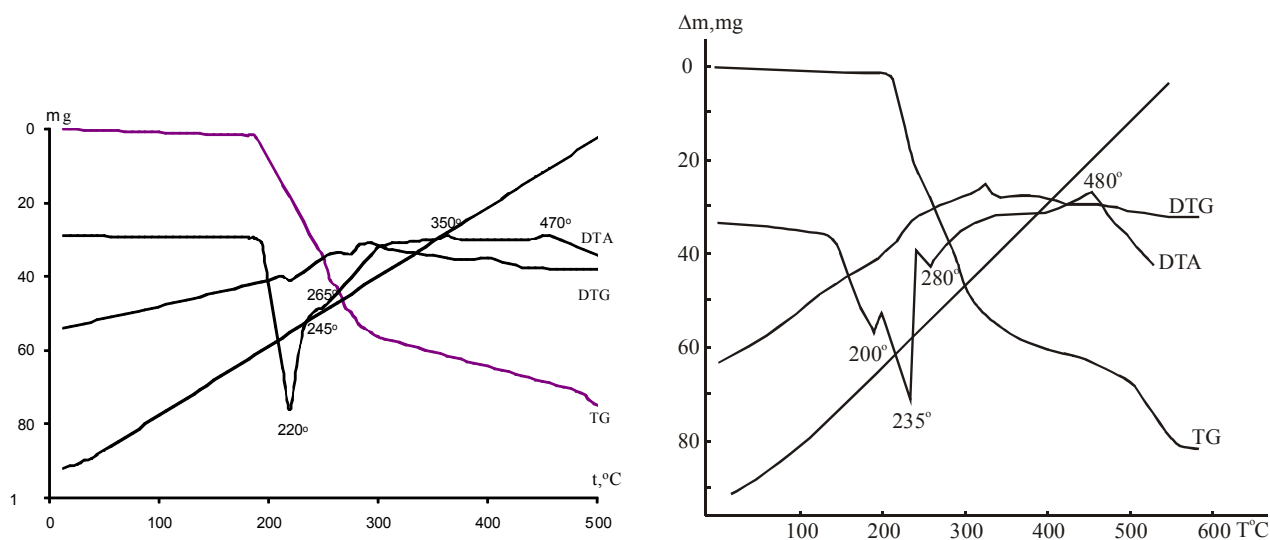


Fig. 2. Thermogram: a)  $[(\text{iso-C}_3\text{H}_7)_3\text{AsCH}_2\text{I}]_2[\text{CdI}_2\text{Br}_2]$ ; b)  $[(\text{iso-C}_4\text{H}_9)_3\text{AsCH}_2\text{I}]_2[\text{CdI}_2\text{Br}_2]$ .

Thus, as a result of the interaction of water-alcohol solutions of cadmium bromide and tetra-substituted arsonium iodide, in the presence of potassium bromide, a coordination compound with mixed ligand was found to be formed.

## Methods

### Iodmethyltriphenylarsonium diiododibromocadmiate(II).

2.5g(0.0043 mole) of iodmethyltriphenylarsonium iodide is dissolved in ethyl alcohol. Water-solution of 0.59g(0.00215 mol) of cadmium bromide and 0.0255g (0.021 mol) of potassium bromide is prepared in parallel. Both solutions are mixed. After one day, a white

crystalline compound is formed. It is filtrated, the precipitate is washed in distilled water, alcohol and dried in vacuum-(with  $\text{P}_2\text{O}_5$  and paraffin) until a constant mass is obtained. 2.63g (85.1%) iodmethyltriphenylarsonium diiododibromocadmiate(II) is obtained.  $T_{\text{melt}} = 128\text{--}129^\circ\text{C}$ . Experimentally it was found: % As 10.71; Hg 47.79.  $\text{C}_{38}\text{H}_{34}\text{AsCdI}_4\text{Br}_2$ : % As 10.56; Hg 47.02 was calculated.

Other tetrasubstituted arsonium diiododibromocadmiates are prepared analogously. The loading of the initial compounds and the yield of the products are presented in Table 2. Some physico-chemical constants of the synthesized compound are presented in Table 1.

Table 2

The loading of the initial compounds, obtaining of iodmethyltrialkyl(aryl)arsonium diiododibromocadmiates(II) and their yield

№	Loading of the initial compounds								The yield $[\text{R}_2\text{As}(\text{R}')\text{CH}_2\text{I}]_2[\text{CdBr}_2\text{I}_2]$		
	$[\text{R}_2\text{As}(\text{R}')\text{CH}_2\text{I}]\text{I}$				$\text{CdBr}_2$		$\text{KBr}$		g	mol	%
	R	R'	g	mol	g	mol	g	mol			
1	$\text{C}_3\text{H}_7$	$\text{C}_3\text{H}_7$	2.0	0.0042	0.57	0.0021	0.025	0.00021	2.26	0.0018	88.0
2	iso- $\text{C}_3\text{H}_7$	iso- $\text{C}_3\text{H}_7$	2.0	0.0042	0.57	0.0021	0.025	0.00021	2.25	0.0020	87.6
3	$\text{C}_4\text{H}_9$	$\text{C}_6\text{H}_5$	1.5	0.0028	0.38	0.0014	0.0165	0.00013	1.69	0.0012	90.2
4	iso- $\text{C}_4\text{H}_9$	iso- $\text{C}_4\text{H}_9$	1.5	0.0029	0.39	0.00145	0.017	0.00014	1.68	0.0013	89.9
5	$\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5$	2.5	0.0043	0.59	0.00215	0.0255	0.00021	2.63	0.0018	85.1

ზოგადი და არარორგანული ქიმია

## იოდმეთილენტრიალკილ(არილ)არსონიუმის დიოდდობრომკადმიატების(II) სინთეზი

გ.ცინცაძე\*, თ. ლობჯანიძე\*\*, მ. გვერდწითელი\*\*

\* აკადემიკოსი, საქართველოს ტექნიკური უნივერსიტეტი, თბილისი

\*\* ი.ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი

შესწავლილია იოდმეთილენტრიალკილ(არილ)არსონიუმის მარილების საფუძველზე შერეული დიოდდობრომკადმიატების(II) მიღების სპეციფიკა სპირტ-წყალხსნარში. კვლევის ფიზიკურ-ქიმიური მეთოდებით დადგენილია სინთეზირებული ნაერთების შედგენილობა-აღნაგობა.

### REFERENCES

1. R.D. Gigauri, M.A. Indjia, B.D. Chernokalski, G.N. Chachava (1978), Jour. Gen. Chem., **48** (4): 809-811,
2. R.D. Gigauri, B.D. Chernokalski, M.A. Indjia (1977), Proc. AN GSSR, **40**, 2: 353-356 (in Russian).
3. T.E. Lobzhanidze, R.D. Gigauri, M.Sh. Rusia (2003), GEN, 3: 116-120.
4. L.S. Khintibidze, R.D. Gigauri, B.B. Gvakharia, et al. (1989), Proc. AN GSSR, **134**, 3: 117-120.
5. G. Peyronel, W. Malavasi, A. Pignedoli (1982), Spectrochim. Acta, **38**, 10: 1069-1072.
6. M.A. Indjia, R.D. Gigauri, B. D. Chernokalski, et al. (1976). Proc. AN GSSR, 31: 81-84.

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