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Preparation of Some Alkylthallium(III) Dichlorides and Their Reactions with Potassium and Copper Halides

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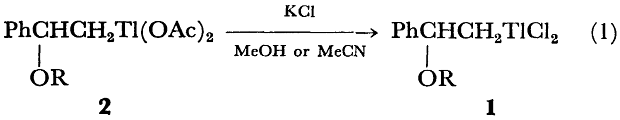
A simple synthesis is given for the stable monoalkylthallium(III) dichloride, $C_6H_5CH(OR)CH_2TlCl_2$ (**1**) from the corresponding diacetate (**2**) and potassium chloride in methanol or acetonitrile. **1**(R=Me) reacts slowly with potassium and copper(I) halides to give mainly α-methoxystyrene and $C_6H_5CH(OMe)CH_2X$ (X=Cl, Br, I), respectively. It is concluded that **1**(R=Me) is less susceptible than **2**(R=Me) to S_N1, S_N2, and S_Ni reactions.

In contrast to the readily prepared monoarylthallium(III) dihalides, monoalkylthallium(III) dihalides are unstable[1,2] and their successful isolation has so far been limited to pyridiomethylthallium(III) dichloride[3] and neopentylthallium(III) dihalide.[4] We report herewith on the preparation of 2-alkoxy-2-phenylethylthallium(III) dichlorides and their behavior towards metal halides in various solvents.

Results and Discussion

Preparation of 2-Alkoxy-2-phenylethylthallium(III) Dichloride (1). It was found that the reaction shown below proceeds at the refluxing temperature of the solvent (Table 1).

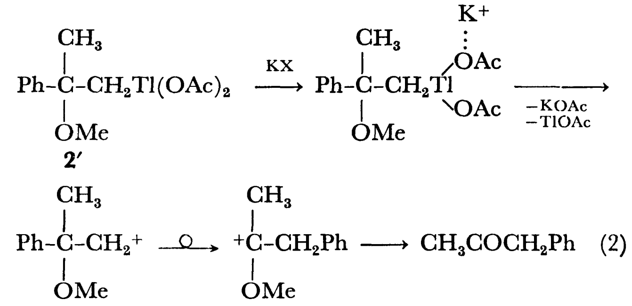


$$\underset{\substack{\mathrm{OR}\\ \mathbf{2}}}{\mathrm{PhCHCH_2Tl(OAc)_2}} \xrightarrow[\text{MeOH or MeCN}]{\text{KCl}} \underset{\substack{\mathrm{OR}\\ \mathbf{1}}}{\mathrm{PhCHCH_2TlCl_2}} \qquad (1)$$

(R=Me, Et, *n*-Pr, *i*-Pr)

Isolation of **1** was carried out by evaporating the filtrate under reduced pressure and also by adding water to the filtrate. The former procedure gave a colorless tarry residue soluble in organic solvents such as methanol, DMSO and pyridine. The NMR spectrum of the residue showed the presence of monoalkylthallium(III) species other than **2** and dialkylthallium(III) species from several coupling constants J_{Tl-H} (Table 2). The latter procedure gave a white amorphous solid, sparingly soluble in almost all solvents, together with 10—15% of phenylacetaldehyde. Recrystallization of the solid from a large volume of acetonitrile gave **1** (Table 1). The difference in solubility of the tarry residue and **1** may be due to the difference in the mode of association.

It has been reported that the reaction of methyl thallium(III) diacetate with aqueous sodium chloride gives methyl chloride instead of the corresponding dichloride. The difference in behavior of methylthallium(III) diacetate and **2** to chloride ion can be ascribed to their difference in susceptibility to S_N2 reaction. Since **2** has a bulky $C_6H_5CH(OR)$-group on the carbon which bears Tl moiety, it seems that the attack of chloride anion from the rear to expel $Tl(OAc)_2$ is hindered profoundly. We therefore attempted to isolate a similar compound by the reaction of KCl with 2-methoxy-2-methyl-2-phenylethylthallium(III) diacetate (**2'**)[5] which has more bulky substituent than **2**. However, even in the reaction in MeCN at room temperature for 1 h, neither the corresponding alkylthallium(III) dichloride nor alkyl chloride was obtained, benzyl methyl ketone being produced instead in 83% yield. The ketone was also obtained in 85—95% yield with use of KBr, KI, or even KOAc in place of KCl, while almost all of **2'** was recovered (only 6% yield of ketone) under similar conditions without potassium salt. The results suggest that potassium cation prompts the decomposition of **2'** to a thallium(I) salt and an alkyl cation, the latter giving the ketone after phenyl migration (Scheme 2). The reason why phenyl migration is more prominent in the reaction of **2'** than in that of **2** might be explained by the difference in the steric crowding in **2'** and **2**. The thermal instability of **2'** as compared to **2** has been observed in many cases.[6]



$$\underset{\substack{\mathrm{OMe}\\ \mathbf{2'}}}{\overset{\mathrm{CH_3}}{\mathrm{Ph\text{-}C\text{-}CH_2Tl(OAc)_2}}} \xrightarrow{\mathrm{KX}} \underset{\mathrm{OMe}}{\overset{\mathrm{CH_3}}{\mathrm{Ph\text{-}C\text{-}CH_2Tl}}}\!\!\begin{smallmatrix}\mathrm{K^+}\\ \vdots\\ \mathrm{OAc}\\ \mathrm{OAc}\end{smallmatrix} \xrightarrow[-\mathrm{TlOAc}]{-\mathrm{KOAc}}$$

$$\underset{\mathrm{OMe}}{\overset{\mathrm{CH_3}}{\mathrm{Ph\text{-}C\text{-}CH_2^+}}} \xrightarrow{\curvearrowright} \underset{\mathrm{OMe}}{\overset{\mathrm{CH_3}}{\mathrm{^+C\text{-}CH_2Ph}}} \longrightarrow \mathrm{CH_3COCH_2Ph} \qquad (2)$$

Comparison of Reactivities of 1(R=Me) and 2(R=Me) under Various Conditions (Table 3). First, the stability of **1**(R=Me) was checked by heating **1**(R=Me) in acetonitrile, 1,4-dioxane, and methanol for 5 h for comparison with that of **2**(R=Me). In acetonitrile and methanol almost no decomposition occurred. In 1,4-dioxane the total yields of the decomposition products were only 20% as shown in Scheme 3, while **2**(R=Me) gave 40—80% yield of the decomposition products under the same conditions. The fact that **3**(X=Cl) and **5** were scarcely obtained suggests both S_Ni and S_N1 type reactions of **1** to be very slow. Second, in the reaction with potassium halide only a low yield of **3** was obtained, showing that S_N2 displacement of thallium moiety in **1** by halide anions is very slow. A considerable amount of α-methoxystyrene(**4**) was obtained in methanol especially in the reaction with KI or KBr, while **4** was not produced from **2** under the same conditions.[5] We confirmed that **3**(X=I or Br) is not the precursor of **4** under the reaction conditions. Although the details of this dehydrothallation reaction giving **4** are not yet

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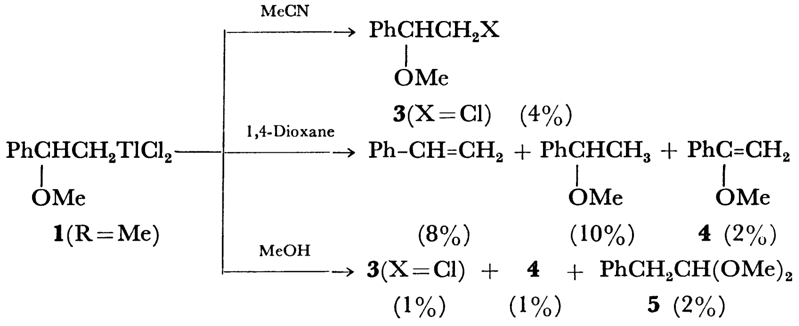

(3)

clear, such reaction is not common in organothallium compounds. So far it has been proposed only in the allylic oxidation of cyclohexene by $Tl(OAc)_3$ to explain the formation of 2-cyclohexenyl acetate.[7] The reaction of **1**(R=Me) with copper(I) salt was carried out. The yield of **3** was low except in the case of copper(I) bromide. Almost no reaction occurred with copper(I) cyanide and thiocyanate in contrast to the case of **2**(R=Me) from which **3** was obtained in a good yield by use of many kinds of copper(I) salts.[5] This also shows that **1**(R=Me) is less reactive than **2**(R=Me).

From all results on reactivities of **1** described above it can be concluded that **1** is less susceptible to S_N1, S_N2, and S_Ni reactions than **2**.

Experimental

The IR spectra were taken with Hitachi EPI-S2 and Perkin-Elmer 521 spectrometers in paraffin mull and KBr disks. The far-infrared spectra (400—30 cm^{-1}) were taken with a Hitachi FIS-3 spectrometer in paraffin mull or liquid film. The NMR spectra were recorded with Varian A-60 and EM-360 and JEOL MH-100 spectrometers in suitable solvents, using TMS as an internal standard. GLC analyses were carried out on a Shimadzu 5APTF apparatus, using Apiezon L(30%)-Celite(1 m) and PEG 6000(25%)-Chromosorb W (3 m) columns (N_2 as the carrier gas).

Materials. All the organic materials except **2**[5] and **2'**[5] were purified by distillation before use, while commercial inorganic materials were used without further purification.

TABLE 1. PREPARATION AND PROPERTIES OF 2-ALKOXY-2-PHENYLETHYLTHALLIUM(III) DICHLORIDE (**1**)

2 (mmol) R		KCl (mmol)	Solvent[a] (ml)		Yield[b] (%)	**1**[c] Mp (dec.) (°C)	**1**[c] Found (Calcd) C	H	Tl
Me	5	20	MeCN	25	33	146—147	26.4(26.3)	2.7(2.7)	49.1(49.8)
Me	3	6	MeOH	15	24				
Et	3	12	MeOH	15	45	89—91	28.3(28.3)	3.2(3.1)	48.4(48.1)
Et	3	12	MeCN	15	22				
n-Pr	3	12	MeOH	15	43	105—107	30.9(30.0)	3.7(3.5)	47.3(46.6)
i-Pr	3	12	MeOH	15	32	78—79	30.5(30.0)	3.4(3.5)	47.7(46.6)

a) The reaction was carried out at refluxing temperature for 1 h. In the case of R=*i*-Pr, for 0.5 h. b) Crude product, based on the amount of **2**. c) Recrystallized from a large amount of acetonitrile.

TABLE 2. J_{Tl-H} (IN Hz) AND δ (IN ppm) OF SOME ORGANOTHALLIUM(III) COMPOUNDS

Compound	Solvent	J_{Tl-H_B} (δ_B)	J_{Tl-H_C} (δ_C)	J_{Tl-H_A} (δ_A)
$\text{Ph-}\overset{\text{OEt}}{\text{C}}\text{H}_A\text{CH}_B\text{H}_C\text{TlCl}_2$[a,b] **1**(R=Et)	d_6-DMSO	757 (2.56)	917 (2.62)	630 (4.65)
	CD_3OD	755 (2.86)	932 (2.93)	671 (4.74)
$\text{Ph-}\overset{\text{OEt}}{\text{C}}\text{H}_A\text{CH}_B\text{H}_C\text{Tl(OAc)}_2$[c] **2**(R=Et)	d_6-DMSO	780 (2.67)	934 (2.88)	701 (4.52)
	CD_3OD	780 (2.93)	937 (3.06)	741 (4.69)
	$CDCl_3$[d]	768 (3.08)	921 (3.11)	737 (4.82)
$(\text{Ph-}\overset{\text{OMe}}{\text{C}}\text{H}_A\text{CH}_B\text{H}_C)_2\text{TlCl}$[c]	$CDCl_3$	274 (2.50)	486 (2.69)	325—345 (4.85—4.95)

a) In the form of a colorless tarry residue. b) Similar *J* values were obtained in the cases of **1**(R=Me, *n*-Pr, and *i*-Pr). c) White amorphous solid, prepared by the method given in Ref. 5. d) Reported in Ref. 5.

TABLE 3. REACTION[a] OF **1**(R=Me) (1 mmol) WITH KX AND CuX

KX or CuX (2 mmol)	Solvent (10 ml)	Products (yield,[b] %)		
		3	**4**	**5**
—	MeOH	1	1	2
—	MeCN	4	0	—
KCl	MeOH	1[c]	1	2
KCl	MeCN	4[c]	0	—
KBr	MeOH	7[d]	24	2
KBr	MeCN	6[d]	0	—
KI	MeOH	8[e]	44	0
KI	MeCN	11[e]	9	—
CuCl	MeCN	19[c]	0	—
CuBr	MeCN	51[f]	0	—
CuI	MeCN	20[g]	0	—

a) At reflux for 5 h. b) Based on the amount of **1**. c) X=Cl. d) X=Br. e) X=I. f) X=Br (43%) and X=Cl (8%). g) X=I (19%) and X=Cl (1%).

*Preparation of 2-Methoxy-2-phenylethylthallium(III) Dichloride (**1**, R=Me).* A white heterogeneous mixture of **2**(R=Me) (2.29 g, 5 mmol) and potassium chloride (2.38 g, 20 mmol) in acetonitrile (25 ml) was stirred under reflux** for 1 h (Table 1). The white precipitate (1.8 g) composed of a mixture of TlCl and KCl was filtered off. The filtrate was evaporated at 20 Torr leaving a colorless tarry residue (*ca.* 2.5 g), a part of which being used for NMR measurement. For isolation, 150 ml of ice-water was added to the filtrate, and a white voluminous solid formed was filtered and washed three times with small portions of ether (0.67 g, 33% yield). Recrystallization from 300 ml of acetonitrile afforded 0.43 g of a white amorphous solid (21% yield) of **1**(R=Me); mp 146—147 °C (dec.). IR; 1454 (m), 1100 (s), 765 (s), 700 (s), 640 (m), 420 (s), and 405 (sh) cm^{-1} (weak absorptions are not shown). The spectrum clearly shows the absence of absorptions due to ν_{CO_2} characteristic of **2**(R=Me)[5] and also that of strong absorptions at 162 and 100 cm^{-1} which bis(2-methoxy-2-phenylethyl)thallium(III) chloride has. The IR spectrum of the latter compound is as follows: 1450 (s), 1093 (s), 761 (s), 698 (s), 640 (m), 569 (m), 274 (m), 233 (m), 162 (s), and 100 (s) cm^{-1}.

GLC analysis of the organic layer after the usual work-up of the filtrate revealed the presence of 1.17 mmol of phenylacetaldehyde (23% yield), 0.09 mmol of methyl α-methylbenzyl ether (1.6%), and trace amounts of unidentified compounds.

*Preparation of **1**(R=Et, n-Pr, i-Pr, n-Bu, and i-Bu).* In the case of **1**(R=Et, *n*-Pr, and *i*-Pr), the white solid (*ca.* 1—1.5 g) obtained by the method described above was washed three times with methanol (10 ml × 3) to remove water and some organic products, leaving crude **1**. Each compound (Table 1) was obtained by washing the crude product with 20 ml of MeOH and by evaporating the methanol washing. We could also isolate crude **1**(R=*n*-Bu and *i*-Bu) as a white solid by a similar treatment in 30—50% yield, but the analysis was unsatisfactory.

*Reaction of **1**(R=Me) with KI.* To a white suspension of **1**(R=Me) (0.82 g, 2 mmol) in methanol was added 0.67 g (4 mmol) of KI and the resulting yellow heterogeneous mixture was stirred under reflux for 5 h. After being cooled down to room temperature the mixture was filtered from the yellow precipitate(0.55 g; a mixture of **1**, KI, and thallous salts) and water(100 ml) was added to the filtrate which was extracted with benzene. GLC analysis of a part of the extract revealed the presence of α-methoxystyrene (**4**) (44%), **3**(X=I) (8%), styrene (5%), and methyl α-methylbenzyl ether (5%) (butyrophenone as an internal standard). Distillation gave 30 mg of almost pure **4**(bp 58—60 °C/22 Torr). The NMR and IR spectra and retention time in GLC of **4** was identical with those of an authentic sample prepared by the reported method.[8]

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** At room temperature the reaction was incomplete even after 5 h, the separation of **1**(R=Me) from the unreacted **2**(R=Me) being difficult.