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Thallium(III) Oxide as an Oxidative Reagent in Organic Chemistry

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Abstract—Oxidative properties of thallium(III) oxide in various organic reactions were studied. Oxidative bromination of organic compounds in Tl_2O_3–KBr–trifluoroacetic acid system was carried out. New synthetic method for preparation of diphenylthallium salts from phenylhydrazine and thallium(III) oxide was developed.

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Oxides of various elements are widely used in organic chemistry as oxidants [1]. Among the most frequently used are MnO_2, SeO_2, PbO_2, CrO_3, etc. The oxidation with the transition metal salts [2] and thallium(III) salts was also mentioned[3]. Among the inorganic thallium compounds thallium(III) oxide is the most available, but its oxidative properties in the organic reactions were studied poorly up to now [4]. Inasmuch as the redox potential Tl^{3+}/Tl^{+} is 1.25 V it could be expected that thallium(III) oxide is a mild oxidant, and that the oxidative reactions with its participation should proceed sufficiently easyly.

The aim of this work was to study the oxidative properties of thallium(III) oxide in the oxidative organic reactions.

We investigated the oxidative properties of thallium(III) oxide in the oxidative bromination. It was shown that in the heterogenic Tl_2O_3–KBr–CF_3COOH system the bromination of the aromatic compounds takes place. Thallium(III) oxide in this reaction acts as a mild oxidant.

$$\text{Ar–X} + Tl_2O_3 + \text{KBr} \xrightarrow{CF_3COOH} \text{Br}C_6H_4\text{–X}, \qquad (1)$$

Ar = Ph, X = Cl, Br, Me, *t*-Bu, NO_2; Ar = 4-$CH_3C_6H_4$, X = NO_2.

The bromination proceeds at room temperature, and it is not complicated by side reactions. Yields of bromoarenes reach 80–90% and depend on the reaction time and chosen conditions.

Freshly precipitated brown thallium(III) oxide exhibiting higher activity as compared to the black modification was used. It follows from the table that the arenes with electron-donating substituents react much faster as compared to those with the electron-acceptor ones. For example, *tert*-butylbenzene gives 98% yield of the bromination product in 6 h, while in the case of nitrobenzene 25% yield is achieved in 12 days in the presence of a double excess of oxidant and KBr. In the case of 4-nitrotoluene yield of brominated product increases with the reaction time. Isomeric composition of the bromination products (*ortho*/*para*) evaluated by GLC is as follows: 18:82 (X = Br), 21:79 (X = Cl), 39:61 (X = Me), 14:86 (X = *t*-Bu). In the case of nitrobenzene m-bromonitrobenzene is formed.

Bromination of arenes in the presence of thallium(III) oxide permits to exclude molecular bromine and to solve the problem of utilization of hydrogen bromide, the side product of bromination with molecular bromine. Besides, in this reaction there is no need to use catalysts as in the bromination with the molecular bromine. Thallium(III) oxide used in this process as an oxidant is easily recovered by chemical methods. Freshly isolated Tl_2O_3 and thallium(I) halides may be used repeatedly.

Thallium(III) oxide easily oxidizes arylhydrazines. Phenylhydrazine reacts with Tl_2O_3 in benzene at room temperature to give organothallium compounds. The subsequent reaction of intermediate compounds with acids HX yields diphenylthallium salts and the corresponding thallium(I) salts.

Bromination of aromatic compounds in Tl_2O_3–KBr–CF_3COOH system

ArX	Molar ratio of reagents ArX:Tl_2O_3:KBr:CF_3COOH	Reaction time, h	Yield[a] of bromoarenes, %
PhBr	5.4:5.0:5.4:130	26	82
PhCl	5.0:5.0:5.0:130	47	98
PhMe	8.0:5.0:5.0:130	9	99
PhBu-*t*	10.0:5.0:5.0:130	6	98
$PhNO_2$	2.5:5.0:5.0:130	264	25
4-$MeC_6H_4NO_2$	5.0:5.0:5.0:130	70	30
4-$MeC_6H_4NO_2$	5.0:10.0:10.0:195	145	89
4-$MeC_6H_4NO_2$	5.0:10.0:10.0:195	165	98

[a] Total yield of brominated arenes was evaluated from the mass of the isolated bromine-containing products considering that after dilution of reaction mixtures with water and four-time extraction with chloroform complete separation of reaction products and unreacted arenes takes place.

$$PhNH{-}NH_2 \xrightarrow[(2)\ HX]{(1)\ Tl_2O_3{-}\text{benzene}} Ph_2TlX + TlX + N_2 + Ph_2 + H_2O, \quad (2)$$
$$X = CF_3COO,\ CH_3COO,\ Br,\ Cl,\ BF_4.$$

In the reaction (2) 1.4 mol of phenylhydrazine is consumed per 1 mol of Tl_2O_3. In the course of the process dark brown Tl_2O_3 precipitate becomes brighter, and finally light beige solid is formed. This precipitate without isolation is treated with the corresponding acids to form diphenylthallium salts. In the case of HBF_4, acetic and trifluoroacetic acids Ph_2TlX salts were separated from TlX ones by washing with water, and in the case of HCl and HBr, with DMF. Reaction (2) proceeds with the liberation of nitrogen to give Tl(I) salts and a small amount of biphenyl as the side products. Formation of biphenyl shows that the reaction (2) has a radical nature. The developed procedure is the universal method for preparation of diphenylthallium salts because various acids HX can be involved in the reaction.

Hence, a new method of formation of C–Tl bond was found, and on this basis new universal method of formation of diphenylthallium salts was developed.

Reaction of 4-nitrophenylhydrazine with Tl_2O_3 in benzene in the presence of trifluoroacetic acid leads to 4-nitrobiphenyl in 58.5% yield.

$$4\text{-}O_2N{-}C_6H_4NH{-}NH_2 + Tl_2O_3 \xrightarrow{\text{benzene}{-}HX} C_6H_5{-}C_6H_4NO_2\text{-}4 + 2TlX + N_2 + H_2O, \quad (3)$$
$$X = CF_3COO.$$

We found that thallium(III) oxide oxidizes benzyl alcohol to benzaldehyde (40% yield) while boiling it in water in the presence of sulfuric acid.

$$C_6H_5{-}CH_2OH + Tl_2O_3 \xrightarrow[t,\ ^\circ C]{H_2O{-}H_2SO_4} C_6H_5{-}CHO. \quad (4)$$

The compounds obtained were identified by means of TLC, GLC, elemental analysis, and IR spectroscopy (see Experimental).

Hence, the oxidative properties of thallium(III) oxide were studied. It is established that Tl_2O_3 is a mild oxidant and may be successfully used in organic chemistry.

EXPERIMENTAL

IR spectra were registered on a Specord-80 spectrometer in mineral oil and hexachlorobutadiene. Chromatographic analysis of the isolated bromination products was carried out on an LKhM-80M chromatograph equipped with a flame ionization detector and a 3000×3 mm column filled with 3% of XE-60 on a Chezasorb AW-HMDS, carrier gas nitrogen, column temperature programming in the range 60–240°C.

Amorphous brown Tl_2O_3 was prepared from tallium(III) nitrate by precipitation with ammonium hydroxide. The precipitate formed was filtered off, repeatedly washed with hot water, and dried at 40°C in a vacuum.

Potassium bromide of “chemically pure” grade was used without additional purification. Arenes of “chemically pure” grade were distilled. Trifluoroacetic acid of “pure” grade was dried over P_2O_5 and then distilled. Physicochemical constants of arenes and trifluoroacetic acid were consistent with the reported data [5–7]. Aluminum oxide of the chromatographic grade and the Brockman activity III was used.

2-Bromo-4-nitrotoluene. A mixture of 0.686 g of p-nitrotoluene, 1.19 g of KBr, 4.567 g of Tl_2O_3, and 15 ml of trifluoroacetic acid was stirred for 165 h at room temperature, diluted with 50 ml of water and 4 times extracted with chloroform. The extract was twice washed with water and dried over sodium sulfate. Chloroform was slowly distilled off, and the sample was kept in a vacuum to give 1.07 g of the residue. It was subjected to TLC on Al_2O_3, elution with 1:2 chloroform–petroleum ether (bp 40–68°C), development with the iodine vapor. By means of reference substances it was shown that the residue contained 2-bromo-4-nitrotoluene (R_f 0.79). The sample was crystallized from ethanol to give the product with mp 74°C, reported data [6] mp 75°C. Found, %: C 38.86, H 2.84. $C_7H_6BrNO_2$. Calculated, %: C 38.92, H 2.80.

4-Bromo-*tert*-butylbenzene. A mixture of 1.342 g of *tert*-butylbenzene, 0.595 g of KBr, 2.284 g of Tl_2O_3, and 10 ml of trifluoroacetic acid was stirred for 25 h at room temperature. After that the reaction mixture was treated with 34 ml of water and four times extracted with chloroform. The extract was twice washed with water, dried over sodium sulfate and subjected to TLC on aluminum oxide, elution with petroleum ether (40–68°C), development with iodine vapor. It was found that the extract contained 4-bromo-*tert*-butylbenzene (R_f 0.81). Petroleum ether was distilled off, and the residue was kept in a vacuum to give the oily product. It was treated with hexane, and 4-bromo-*tert*-butylbenzene was separated from the other substances by column chromatography on aluminum oxide, elution with hexane. The eluate was evaporated to give 0.92 g (86%) of 4-bromo-*tert*-butylbenzene, n_D^{20} 1.5412, bp 231–232°C, reported data [6] bp 232°C.

Diphenylthallium trifluoroacetate. To a suspension of 2.538 g of Tl_2O_3 in 30 ml of benzene stirred with a magnetic stirrer a solution of 0.768 g of phenylhydrazine in 5 ml of benzene was added dropwise at room temperature in the course of 30 min under argon. Liberation of nitrogen was observed immediately, and the dark brown suspension gradually became lighter. Finally the light beige precipitate was formed. The reaction mixture was stirred for 2 h, 0.95 ml of trifluoroacetic acid was added, and stirring was continued for additional 0.5 h. The precipitate was filtered off, yield 3.2 g. It was several times washed with water and dried to give 0.50 g of diphenylthallium trifluoroacetate, yield 30% with respect to phenylhydrazine. The product obtained was crystallized from ethyl acetate, mp 274–276°C. IR spectrum, ν, cm^{-1}: 3062, 1624, 1570, 1480, 1435, 1196, 1150, 1140, 702. Found, %: C 35.56, H 2.24, Tl 43.10. $C_{14}H_{10}F_3O_2Tl$. Calculated, %: C 35.66, H 2.14, Tl 43.34.

Thallium(I) trifluoroacetate, 2.5 g, mp 109–110°C, was isolated from aqueous filtrate. Benzene filtrate was subjected to TLC on Al_2O_3, elution with 1.5:1 hexane-chloroform, development with I_2. Using the authentic substance we have found that filtrate contains biphenyl (R_f 0.87). Benzene was distilled off, biphenyl was isolated and purified by column chromatography on Al_2O_3, elution with hexane, yield 0.017 g, mp 70°C, reported data [6] mp 71°C.

Diphenylthallium acetate was obtained analogously. Yield 32%, mp 258–263°C , reported data [9] mp 267–262°C. IR spectrum, ν, cm^{-1}: 3059, 2935, 2862, 1635, 1580, 1551, 1484, 1458, 1437, 1380, 1161, 1140, 1201. Found, %: C 40.18, H 3.21, Tl 48.76. $C_{14}H_{13}O_2Tl$. Calculated, %: C 40.26, H 3.14, Tl 48.94.

Diphenylthallium tetrafluoroborate was obtained as described above. Yield 30.5%, mp 305–307°C. Reported data [9] mp 306–308°C. IR spectrum, ν, cm^{-1}: 3050, 2964, 2925, 1581, 1479, 1433, 1035, 765, 725, 686.

Diphenylthallium bromide was obtained as described above. It was isolated from precipitate by extraction with DMF. Yield 30.8%, mp 295°C. Found, %: C 32.74, H 2.34, Tl 46.80. $C_{12}H_{10}BrTl$. Calculated, %: C 32.87; H 2.30, Tl 46.61.

4-Nitrodiphenyl. To a suspension of 2.350 g of Tl_2O_3 in 35 ml of benzene 0.78 ml of trifluoroacetic acid was added, and an argon flow was bubbled through the reaction mixture. After that it was heated to 50°C and 0.788 g of 4-nitrophenylhydrazine in 150 ml of benzene heated to 50°C was gradually added. The mixture obtained was stirred for 2 h at 50°C and then heated to boiling. The solvent was distilled off, and an oily cherry-colored residue was obtained. It was examined by TLC on Al_2O_3, elution with 3:1 petroleum ether (40–68°C)–chloroform. 4-Nitrodiphenyl was found, R_f 0.69. It was purified by column chromatography on Al_2O_3, elution with 3:1 petroleum ether-chloroform, to give 0.6 g (58.5%) of compound with mp 112°C, reported data [6] 113°C.

Benzaldehyde. Thallium(III) oxide, 2.284 g, was treated with 50 ml of water, 2.569 g of sulfuric acid, and 1.081 g of benzyl alcohol. Reaction mixture was refluxed with stirring for 4 h. After that it was cooled, and residual thallium(III) oxide was filtered off. Filtrate was 3 times extracted with 20 ml of ether, washed with water, dried over sodium sulfate, and ether was distilled off until the residual volume about 3 ml. This residue was examined by TLC on Al_2O_3, elution with 3:1 petroleum ether (45–58°C)–chloroform, development with iodine vapor. Using the reference substance it was established that the mixture obtained contains benzaldehyde (R_f 0.75) and unreacted benzyl alcohol (R_f 0.15). Benzaldehyde was separated from benzyl alcohol by column chromatography on Al_2O_3, elution with 3:1 petroleum ether–chloroform to give 0.43 g of benzaldehyde, yield 40%, bp 179°C, n_D^{20} 1.5418. Constants of the isolated benzaldehyde agreed with the reference data [6, 7].

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