BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 545—550 (1971)

Reaction of Aromatics with Thallic Salts——Preparation of Arylthallic Compounds[1]

Katsuhiko Ichikawa, Sakae Uemura,* Takeshi Nakano, and Eizo Uegaki
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto
**Institute for Chemical Research, Kyoto University, Uji, Kyoto*

(Received September 8, 1970)

Arylthallic acetate perchlorate monohydrates, Ar-Tl(OAc)(ClO_4)·H_2O, were obtained as the major products of the reaction between thallic acetate and aromatics in acetic acid containing perchloric acid. As the minor products, various types of oxidation products including oxidative coupling were obtained. Reactivity order of the aromatics and the isomer distributions in the products were the same as those in the usual electrophilic aromatic substitution. With thallic nitrate, sulfate, and chloride, no arylthallic compounds could be obtained.

Aromatic mercuration has been well known as one of the family of electrophilic aromatic substitution.[2,3] Davidson and Triggs reported the possibilities of aromatic substitution with heavy metals such as thallation, plumbation, auration, palladation, and platination.[4] Since aromatic heavy metal compounds are not always stable, isolation of the compounds from direct substitution products was successful only in the case of thallation.[4] We have also studied the aromatic thallation under the similar conditions independently and wish to present our results, since our experiments were to develope a synthetic method of preparation of arylthallic compounds and different from those by Davidson and Triggs which were rather for mechanistic study.

So far, several methods of preparation of aromatic thallium compounds (using no metal exchange reaction) have been reported, for example, the reaction of thallic chloride with dibenzofuran[5] and the reaction of thallic isobutyrate with benzene and alkoxybenzenes.[6,7] Very recently, McKillop *et al.* found that thallic trifluoroacetate reacts with various aromatics to give arylthallic di-trifluoroacetates in good yields at room temperature.[8]

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[1] Presented partly at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April 1968 and at the 22nd Annual Meeting, Tokyo, April 1969.

[2] H. C. Brown and C. W. McGary, *J. Amer. Chem. Soc.*, **77**, 2300 (1955).

[3] W. Kitching, *Organometal. Chem. Rev.*, **3**, 35 (1968).

[4] J. M. Davidson and C. Triggs, *J. Chem. Soc.*, *A*, **1968**, 1324.

[5] H. Gilman and R. K. Abbott, *J. Amer. Chem. Soc.*, **65**, 122 (1943).

[6] V. P. Glushkova and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1957**, 1186.

[7] V. P. Glushkova and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **103**, 615 (1955); **116**, 233 (1957).

[8] A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, **1969**, 2423.

Results and Discussion

Aromatic compounds were added to acetic acid solutions of various thallic salts such as acetate, sulfate, nitrate, and chloride at various temperatures. The mixtures were homogeneous except in the case of thallic sulfate. As the reaction proceeded, formation of insoluble thallous salts was observed. Product distribution depends on the several factors such as the structure of aromatics, the kind of thallic salt used, the addition of mineral strong acid, and the conditions. Structures of the identified products are shown in Chart 1.

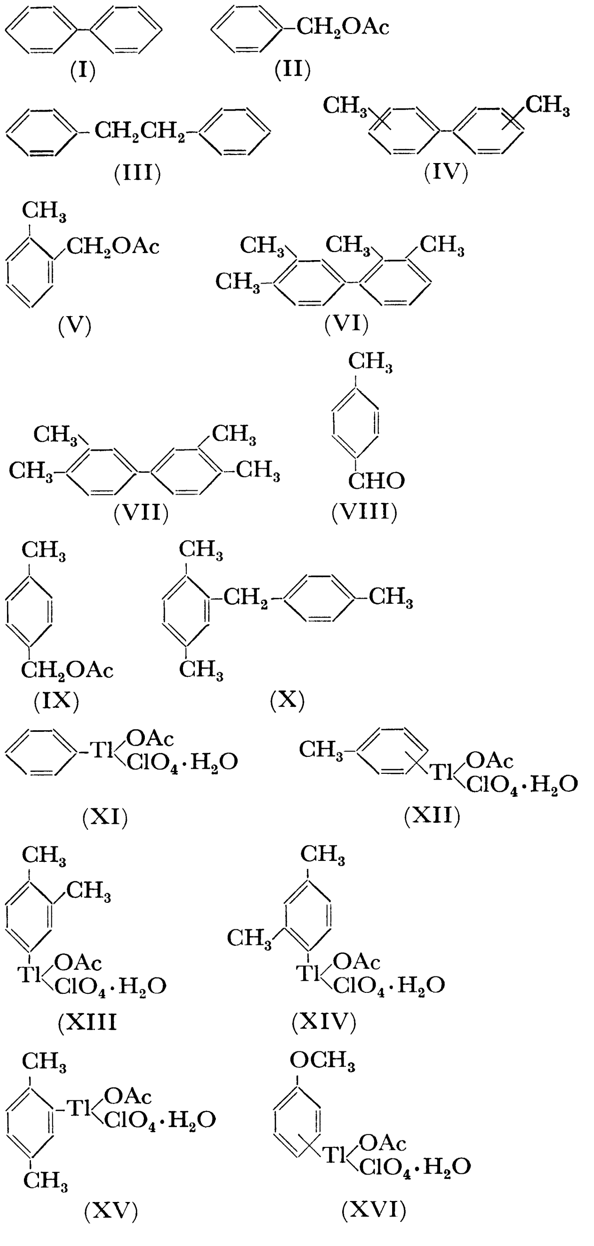
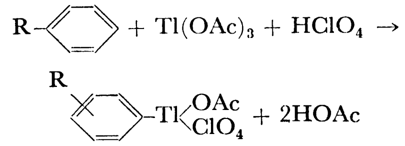
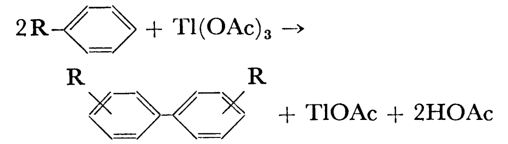


Chart 1. Structures of products.

Reaction with Thallic Acetate. In Table 1, the experimental results are summarized. Sluggish reactions between aromatics and thallic acetate were accelerated remarkably by the addition of perchloric acid to the reaction mixtures. Sulfuric acid, nitric acid and boron trifluoride showed the same effect, but were not so effective. The main products were arylthallic acetate perchlorate monohydrate, $ArTl(OAc)(ClO_4)\cdot H_2O$. Oxidative coupling products were also obtained along with small amounts of oxidation products of side chain. The yields were calculated according to the following equations on the basis of thallic acetate used.



(1)



(2)

Material balance of oxidation-reduction by Eq. (2) was very poor, probably because acetic acid was oxidized with thallic acetate, particularly in the presence of perchloric acid. In fact, 97% of thallic acetate (0.35 M) dissolved in acetic acid containing perchloric acid (0.6 M) were reduced to thallous salt after refluxing for 7 hr. It has been reported also that the yield of thallic acetate was poor when thallic oxide was dissolved in refluxing acetic acid.[9]

Fairly good yields of arylthallic compounds have been obtained by the reaction of benzene, toluene, xylenes, and anisole. Prolonged reactions at higher temperature resulted in the decrease in the yields of arylthallic compounds and in the increase of the oxidation products. No quantitative relationship, however, appears to exist between the two types of the reaction. It was also noted that some of the arylthallic salts oxidize acetic acid as solvent at refluxing temperature gradually and form thallous salt without giving oxidative coupling products.

Anisole reacted readily even at lower temperature to give anisylthallic derivative. At refluxing temperature, however, no organothallium and only a trace of oxidation products could be obtained even after short reaction time, despite that thallic salt was reduced to thallous state completely. With mesitylene the same phenomenon was observed. Aromatic compounds with electron withdrawing group such as nitro and chloro did not react at all. Therefore, the reactivity order of aromatics appears to be similar to that in the usual electrophilic aromatic substitution.

The structures of arylthallic compounds were identified to be arylthallic acetate perchlorate monohydrate by the results of elemental analyses and IR and NMR spectra measurements. IR spectra (KBr disc) showed strong absorption at 1570—1530 and 1420—1380 cm^{-1} due to carboxylate group and at 1150—1080 cm^{-1} due to perchlorate anion. As a typical example, in Figs. 1 and 2, are shown the spectra of XI together with that of thallic acetate for a con-

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[9] A. South and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7064 (1968).

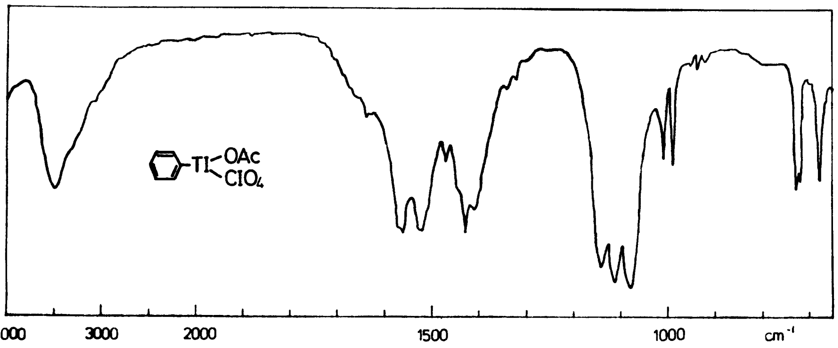

Fig. 1. IR spectrum of XI.

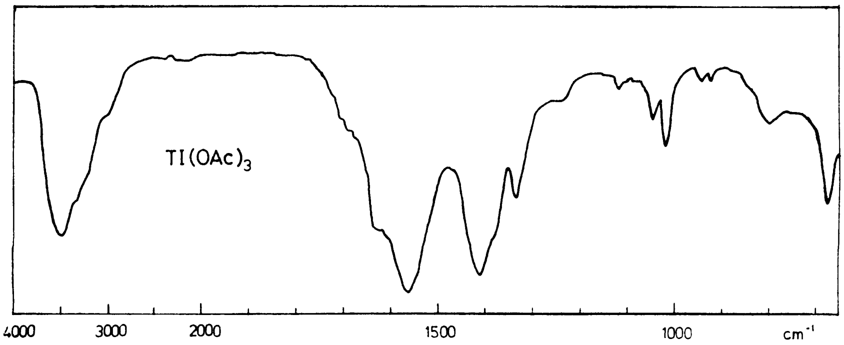

Fig. 2. IR spectrum of thallic acetate.

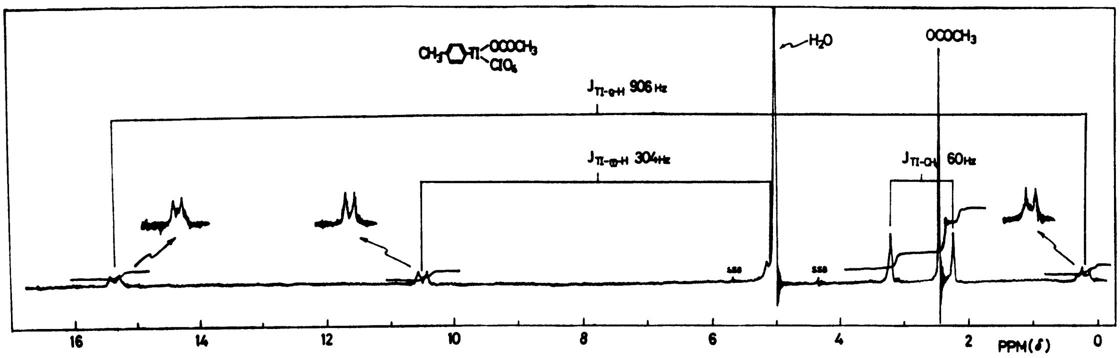

Fig. 3. NMR spectrum of p-isomer of XII (solvent D_2O)

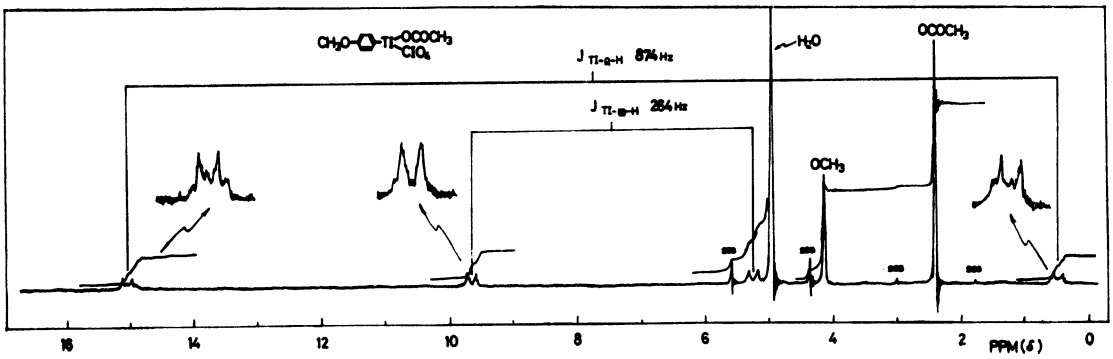

Fig. 4. NMR spectrum of p-isomer of XVI (solvent D_2O).

TABLE 1. REACTION OF AROMATICS WITH $Tl(OAc)_3$

Aromatic (mol)	$Tl(OAc)_3$ (mol)	HOAc (m*l*)	$HClO_4$ (mol/*l*)	React. temp. (°C)	React. time (hr)	Product (yield[a]%)
Benzene 0.25	0.05	80	0.5	90	6	I (2.0) XI (54.9)
Benzene 0.10	0.05	100	0.5	105	13	I (13.0)
Toluene 0.10	0.05	60	0.5	115	3	II (2.8) III (2.0) IV (1.3) XII (47.4)
Toluene 0.24	0.05	80	0.5	115	14	II (4.3) III (4.2) IV (1.8)
Toluene 0.10	0.02	40	0.5	115	2	XII (73.1)
Toluene 0.10	0.02	40	0.5	80	8.5	XII (67.0)
Toluene 0.10	0.05	65	—	112	18	II, III, IV (trace)
o-Xylene 0.10	0.05	80	0.5	112	2	V (trace) VI (1.2) VII (0.6) XIII (38.4)
o-Xylene 0.10	0.05	100	0.5	110	14	V (4.1) VI (5.0) VII (5.7)
m-Xylene 0.10	0.05	80	0.5	114	2	XIV (51.3)
p-Xylene 0.10	0.056	80	0.5	112	2	VIII, IX (trace) X (6.5) XV (22.6)
p-Xylene 0.10	0.034	100	0.5	115	13	VIII (6.0) IX (trace) X (21.8)
p-Xylene 0.10	0.05	60	—	115	23	VIII (4.2) IX (1.5)
Anisole 0.05	0.012	50	0.5	35	1	XVI (44.0)

a) Calculated on the basis of used thallic acetate

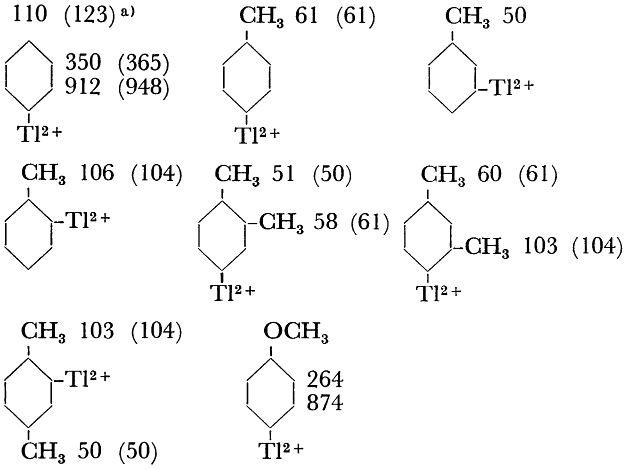

Chart 2. $J_{Tl^{205}\text{-}H}$ and $J_{Tl^{205}\text{-}CH_3}$ of arylthallic compounds.

a) The values reported by Maher and Evans are in parenthesis.

venience of comparison. Absorptions at about 3500 cm^{-1} due to water were observed in all of XI—XVI. Elemental analyses show that they are monohydrated. NMR spectra (in D_2O) shows the presence of aromatic protons and acetyl protons. From the comparison of the intensities of the two types of protons, it is concluded that ratio of aromatic nucleus and acetyl group is 1 : 1. In Figs. 3 and 4, the NMR spectra of *p*-isomers of, XII and XVI are given as typical examples. $J_{Tl^{205}\text{-}H}$ and $J_{Tl^{2\ 5}\text{-}CH_3}$ values (Chart 2), which agreed well with those reported by Maher and Evans,[10] were useful for determining the substituted position of thallium and rough isomer distribution. For example, crude tolylthallic compound from toluene was found to be mixture of *o*-/*m*-/*p*-isomers of 12/6/82 in one run and 16/6/78 in the other run.

The arylthallic compounds are stable in air, soluble in water, acetone, methanol, ethanol, pyridine, DMF, and DMSO, insoluble in ether, ligroin, and benzene, and can be recrystallized from acetic acid to give white crystalline products. All of them reacted with bromine in carbon tetrachloride to give corresponding bromobenzenes.[11] XI gave diphenylthallic chloride (mp >300°C) upon treating with excess of aqueous sodium chloride and phenylthallic acetate bromide with one mole of aqueous potassium bromide.

Concerning the oxidation products according to Eq. (2), the following remarks should be added to the data shown in Table 1. Throughout the experiments no acetoxylated products of aromatic nucleus could be detected. NMR data showed that IV from toluene

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[10] J. P. Maher and D. F. Evans, *J. Chem. Soc.*, **1965**, 637.

[11] S. Uemura, K. Sohma, M. Okano, and K. Ichikawa, Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1970.

contained unidentified Ar–CH_2–Ar′ type product other than those in Table 1 (NMR τ 6.15, methylene protons). In the case of *p*-xylene, fairly good yield of X was obtained. This type of oxidative coupling of *p*-xylene has been reported by Kovacic and Wu[12] as a side reaction in the preparation of *p*-tolyl-di-*p*-xylylmethane by the reaction of *p*-xylene with ferric chloride.

Reaction of Other Thallic Salts than Acetate with Aromatics. Several attempts to obtain arylthallic compounds by the reaction of aromatics with other thallic salt than acetate were unsuccessful. Under the conditions similar to those with thallic acetate in Table 1, the yields of organic products containing no thallium were also low.

With 50 mmol of thallic nitrate (at 105—115°C, 12 hr) the following products were isolated: From benzene (0.1 mol); nitrobenzene (1.6 mmol) and I (trace). From toluene (0.1 mol); benzaldehyde (trace), II (4.7 mmol), IV (trace), *o*-nitrotoluene (7.0 mmol). and *p*-nitrotoluene (5.9 mmol). From *p*-xylene (0.1 mol); VIII (7.5 mmol), IX (10.6 mmol), *p*-toluic acid (16.2 mmol), and nitro-*p*-xylene (6.1 mmol). All amounts of thallic salt were reduced to thallous salt.

With thallic sulfate (at 110—114°C, 1 hr) the following products were obtained: From benzene; I (trace). From toluene; IV (6.4%, calculated on the basis of thallic salt used). From *p*-xylene; X (9.3%). The amount of reduced thallic salt was 70—80%.

With thallic chloride, the reaction was very slow and only 22—27% of thallic salt was reduced at refluxing temperature in 14 hr. The following products were obtained: From benzene; nothing. From toluene; III (2.0%) and IV (0.3%). From *p*-xylene; VIII (1.8%) and X (1.6%). Addition of perchloric acid gave little effect on the reaction.

Experimental

Materials. All starting organic materials were used after distillation. Thallic acetate was prepared by dissolving thallic oxide into acetic acid at 60°C in 20 hr, collecting white crystals after cooling and drying over P_2O_5 (purity by iodometry was more than 98%). Thallic chloride and nitrate were commercial products. Thallic sulfate was prepared by dissolving the oxide into hot aqueous sulfuric acid.

Reaction of Alkylbenzene with $Tl(OAc)_3$: Formation of Organothallium Compounds. The following example shows a typical experimental procedure. Toluene (200 mmol) was added to a solution of thallic acetate (45.5 mmol) in 80 m*l* of acetic acid containing 8 g of 70% perchloric acid (*ca.* 0.5 M) at refluxing temperature (115°C). The reaction mixture was kept at 110°C under stirring. The color of the mixture turned from pale yellow to purple red. After 3 hr's duration the hot mixture was filtered off from white precipitates formed (4.78 g). When the filtrate was allowed to stand at room temperature, the same precipitates(0.60 g) were obtained again. These precipitates (5.38 g, 17.7 mmol) were identified as thallous perchlorate ($TlClO_4$) by the IR spectrum. Distillation of most part of acetic acid from the filtrate under reduced pressure gave 7.40 g of pale yellow crystals which were identified as XII (decomposed at 126°C 15.7 mmol, 34.6%). The residue from which XII was filtered off was diluted with water and extracted with benzene. The benzene extract was washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. Upon removal of benzene, there was obtained 0.66 g of residue, which was found to be consisted of benzene, toluene, benzaldehyde (trace), II (5%), III (68%), and IV (14%, mainly *p,p′*-isomer) by gas chromatographic analysis. The yields of II, III, and IV were calculated to be 0.2 mmol (0.4%), 2.5 mmol (5.4%), and 0.5 mmol (1.1%), respectively. Recrystallization of XII three times from acetic acid gave white crystals which were pure *p*-isomer. XII was stable in air, soluble in water, methanol, ethanol, acetone, pyridine, DMF, DMSO, and hot acetic acid, and insoluble in ether, ligroin, benzene, and chloroform. IR spectrum of XII is very similar to that of XI (Fig. 1). NMR spectrum of XII (*p*-isomer) in D_2O is shown in Fig. 3.

XI, XIII, XIV, and XV were obtained similarly by the method described above. They all decomposed without melting and showed almost the same solubility as those of XII. The IR spectra were similar to that of XI, showing the strong absorption bands due to carboxylate group and perchlorate ion. Coupling constants of Tl^{205}–H in NMR determination (D_2O solvent) are summarized in Chart 2. Analytical data are as follows:

	Dec. p. (°C)	Calcd for $ArTl(OAc)ClO_4\cdot H_2O$		Found	
		C	H	C	H
XI	174	20.98	2.20	21.06	2.25
XII	145	22.88	2.56	22.79	2.40
XIII	165	24.71	2.90	24.72	2.91
XIV	175	24.71	2.90	24.52	2.47
XV	176	24.71	2.90	24.40	2.87

Reaction of Anisole with $Tl(OAc)_3$: Formation of XVI. Anisole (50 mmol) was added to a solution of thallic acetate (12 mmol) in 50 m*l* of acetic acid containing 4 g of 70% perchloric acid (*ca.* 0.5 M) at 35°C. The reaction mixture was kept at 35°C for 1 hr under stirring. The color of the mixture changed from white to red brown. White precipitates thus formed (0.30 g, 1 mmol) were filtered off and acetic acid was evaporated from the filtrate to give brownish crystals of XVI (2.60 g, 5.33 mmol, 44.0%). NMR spectra showed that main constituent of XVI was para-isomer. Recrystallization from acetic acid gave 2.20 g of pure *p*-isomer of XVI which decomposed slightly at 157°C and completely at 177°C. (Found: C, 22.15; H, 2.48%. Calcd for $C_9H_{12}O_8TlCl$: C, 21.89; H, 2.42%.)

Reaction of Benzene with $Tl(OAc)_3$: Formation of I. Benzene (100 mmol) was added to a solution of thallic acetate (50 mmol) in 100 m*l* of acetic acid containing 8 g of 70% perchloric acid (*ca.* 0.5 M) at 117°C. The reaction mixture was kept at 105°C (refluxing temp.) for 10 hr under stirring. After cooling to room temperature white precipitates thus formed ($TlClO_4$, 13.0 g, 42.9 mmol) were filtered off. The fitrate was diluted with water and extracted with benzene. The extract was washed with saturated aq. $NaHCO_3$ and dried over Na_2SO_4. After removing benzene white crystals of I (1.0 g, 13%) were obtained as residue. Recrystallization from ethanol gave pure I, mp 69—70°C.

Reaction of p*-Xylene with $Tl(OAc)_3$: Formation of X.*

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[12] P. Kovacic and C. Wu, *J. Org. Chem.*, **26**, 762 (1961).

Reaction between *p*-xylene (100 mmol) and thallic acetate (34 mmol) was carried out in 100 m*l* of acetic acid at 117°C for 13 hr. Yellowish white precipitates thus formed ($TlClO_4$, 9.0 g, 29.7 mmol) were filtered off from the resulting black solution. The filtrate was treated as mentioned above. There was obtained a mixture which was analyzed to contain *p*-xylene, VIII (0.23 g, 5.8%), and X (1.47 g, 20.7%). Distillation of the mixture gave pure X (bp 128—131°C/2.5 mmHg, $n_D^{20}=1.5678$). NMR ($CDCl_3$) τ 3.0—3.20 (m.) 7H, 6.17 (s.) 2H, 7.75 (s.) 6H, and 7.85 (s.) 3H. (Found: C, 91.62; H, 8.93%; Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63%.)

Reaction of XV with p*-Xylene in Acetic Acid.* A mixture of XV (2.14 mmol) and *p*-xylene (10 mmol) dissolved in 40 m*l* of acetic acid containing 70% perchloric acid (2.3 g, *ca.* 0.4 M) was stirred at 110°C for 2 hr. The color of the reaction mixture turned from clear pale yellow to purple red and white precipitates were formed. After removing the precipitates ($TlClO_4$, 0.50 g, 76%) the filtrate was treated as described above. Gas chromatographic analysis showed that the products were VIII (4.3%), X (1.6%), and unidentified material (3.5 times as large as X in peak area). Any amount of xylenyl acetate could not be detected.

Reaction of Toluene with $Tl_2(SO_4)_3\cdot 7H_2O$: Formation of IV. Toluene (100 mmol) was added to a milky suspension of thallic sulate (22 mmol) in 100 m*l* of acetic acid at 114°C under stirring. After 10 hr the black reaction mixture was cooled to room temperature and white precipitates were filtered off. The precipitates were found to be consisted of 33.4 mmol of thallous salt and 13.7 mmol of thallic salt. The filtrate was treated as mentioned above and 0.51 g (2.8 mmol, 15.2%) of IV (mainly *p,p'*-isomer) was obtained. Distillation gave almost pure *p,p'*-isomer of ditolyl, bp 100—115°C/3mmHg, mp 110—115°C. Recrystallization from ether gave pure *p,p'*-isomer of IV, mp 120°C.

Authentic Samples for Gas Chromatography. I, II, III, V, VIII, nitrobenzene, *o*- and *p*-nitrotoluenes, and benzaldehyde were commercial products. VI and VII were prepared by the reaction of palladium chloride and sodium acetate with *o*-xylene.[13] Nitro-*p*-xylene was prepared by the method reported in the literature,[14] bp 109°C/9 mmHg. IX (bp 104—108°C/13 mmHg) was prepared by acetylation of *p*-methylbenzyl alcohol (mp 58°C) with acetic anhydride at 50°C for 1 hr in the presence of zinc chloride catalyst.

Spectral Measurements. IR spectra were obtained by Hitachi EPI-2 and EPS-3T. NMR spectra were determined by JEOL-3H-60 and Varian A-60 using TMS as internal standard in $CDCl_3$ in the case of organic products and in D_2O (without internal standard) in the case of organothallium compounds. Gas chromatographic analyses were carried out on Hitachi K-53 using Apiezon-L 1 m and PEG 20 M 1 m columns and Shimadzu 4APT using the similar 3 m colunns.

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[13] R. van Helden and G. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

[14] H. R. Snyder and F. J. Pilgrim, *J. Amer. Chem. Soc.*, **70**, 3787 (1948).