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Aromatic Bromination by the Use of Organic and Inorganic Thallium Salts[1]

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Using organic and inorganic Tl salts, the following aromatic brominations were carried out in a CCl_4 or HOAc solvent and were found to occur very smoothly; (A) aromatic bromination with $TlBr_3 \cdot 4H_2O$, (B) aromatic bromination with Br_2 in the presence of Tl(III) and Tl(I) salts, and (C) the bromination of arylthallium(III) compounds. From a study of the relative rates and selectivities of benzene and toluene, it was deduced that an arylthallium(III) compound was not involved as an intermediate in the A and B reactions, that Tl(III) salts were more effective catalysts than Tl(I) salts for the B bromination, and that the A reaction was essentially identical with the B reaction with the $TlBr_3 \cdot 4H_2O$ catalyst. By considering the difference in the catalytic behavior of Tl(III) and Tl(I) salts in the B reaction, probable mechanisms are suggested.

Aromatic bromination with bromine in the presence of metallic iron or Lewis acid catalysts (*e.g.*, $FeCl_3$, $FeBr_3$, $AlCl_3$, $AlBr_3$, and $ZnCl_2$) is a well-known reaction.[2] On the other hand, bromination with a certain metal halide itself, *e.g.*, $CuBr_2$, has also been reported.[3] In view of the effectiveness of Tl(III) halides as Lewis-acid catalysts,[4-6] it seems that it would be of interest to know their functions in the two types of bromination described above. Recently it was reported in a communication that, in the presence of Tl(III) acetate, bromine reacted with aromatics to give pure monobromocompounds.[7] In addition, although it has been known that arylmercury(II) compounds react smoothly with bromine to give aryl bromide,[8] there have been no reports about the analogous bromination of arylthallium(III) compounds. Hence, some characteristics of the following bromination reatcions were examined; (A) aromatic bromination with $TlBr_3 \cdot 4H_2O$, (B) aromatic bromination with bromine in the presence of Tl(III) and Tl(I) catalysts, and (C) the bromination of arylthallium(III) compounds with bromine. Some findings on the C reaction are of interest in connection with the problem of whether or not an arylthallium(III) compound is involved as an intermediate in the A and B reactions. Probable mechanisms for the Tl(III) and Tl(I) salt-catalyzed brominations were also considered on the basis of their selectivity data.

Results and Discussion

A. Aromatic Bromination with $TlBr_3 \cdot 4H_2O$. Aromatic compounds were added to a mixture of carbon tetrachloride (or acetic acid) and thallium(III) bromide tetrahydrate at the refluxing temperature. The reaction mixture was heterogeneous with molten Tl(III) salt in a CCl_4 solvent, while it was homogeneous in an acetic acid solvent. The red-brown color in the gas and liquid phases which was observed at the initial stage of the reaction because of the partial decomposition of $TlBr_3 \cdot 4H_2O$ [Eq.(1)] gradually disappeared as the reaction proceeded. Indeed, about a 9% conversion of $TlBr_3 \cdot 4H_2O$ to $TlBr \cdot TlBr_3$ in 1hr at 77°C was confirmed iodometrically by a blank experiment. Some

1) Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

2) See for example, R. C. Fuson, "Reactions of Organic Compounds," John Wiley & Sons, New York, N. Y. (1962), p. 58.

3) P. Kovacic and K. E. Davis, *J. Amer. Chem. Soc.*, **86**, 427 (1964).

4) "Friedel-Crafts and Related Reactions," Vol. I, ed. by G.A. Olah, Interscience Publisher, New York, N. Y. (1965), p. 256.

5) L. I. Kashtanov, *J. Gen. Chem(U.S.S.R)*, **2**, 515 (1932); *Chem. Abstr.*, **27**, 975 (1933).

6) E. C. Taylor and A. McKillop, *Accounts of Chem. Res.*, **3**, 338 (1970).

7) A. McKillop, D. Bromley, and E. C. Taylor, *Tetrahedron Lett.*, **1969**, 1623.

8) H. C. Brown and C. W. McGary, Jr., *J. Amer. Chem. Soc.*, **77** 2300 (1955).

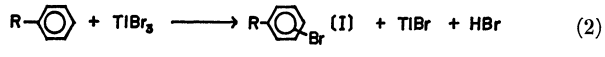
TABLE 1. REACTIONS OF AROMATICS WITH $TlBr_3 \cdot 4H_2O$ IN CCl_4[a]

Aromatics (100 mmol)	Products mmol (Yield[b] %) [I]	[II]	[III]	Tl^{3+} consumed[c] (%)
Benzene	1.9 (23)	0.4 (10)	0	35
Benzene[d]	1.9 (25)	—	0	32
Toluene	4.7[e] (59)	trace	trace	33
Toluene[d]	5.0[f] (47)	—	1.2 (12)	44
o-Xylene	8.3[g] (78)	0.3 (6)	1.4 (13)	44
p-Xylene	5.9 (60)	0.2 (5)	3.4 (33)	41
Ethylbenzene	4.9[h] (51)	0.7 (15)	0.5 (6)	40
Mesitylene[i]	3.9 (73)	0.4 (8)	—	29
Anisole	10.1[j] (65)	0.2 (3)	—	65
Bromobenzene	—	7.0[k] (77)	—	38

a) $TlBr_3 \cdot 4H_2O$ 24.2 mmol, CCl_4 80 ml, 77°C, 1 hr.
b) Calculated on the basis of the amount of consumed Tl^{3+} salt.
c) Determined by iodometry.
d) HOAc (80 ml) solvent.
e) $o/p=1.64$; trace of $C_6H_5CH_2Br$ is present.
f) $o/p=1.09$; traces of $C_6H_5CH_2Br$ and $C_6H_5CH_2OAc$ are present.
g) A mixture of approximately equal amounts of 3-bromo and 4-bromoderivatives.
h) $o/p=1.24$
i) 18.6 mmol of $TlBr_3 \cdot 4H_2O$ were used.
j) $o/p=0.049$
k) $o/p=0.33$

$$2TlBr_3 \cdot 4H_2O \longrightarrow Tl[TlBr_4] + Br_2 + 8H_2O \quad (1)$$

typical results are shown in Table 1. The products were monobromocompounds (major) and dibromocompounds (minor), and occasionally diarylmethanes were formed as by-products from alkylbenzenes. The yields of the products were calculated on the basis of the Tl(III) salt consumed according to Eqs. (2), (3), and (4). With less reactive aromatics, such as nitrobenzene,



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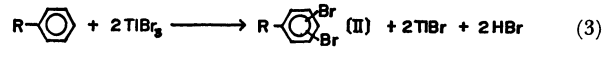

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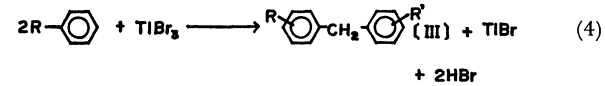


(4)

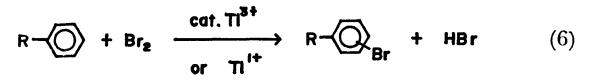
ethyl benzoate, and pyridine, no reaction occurred, even during a longer reaction time at the refluxing temperature. The reaction with benzene and toluene did not occur at 20°C, but with toluene it occurred slowly at 39°C, without any appreciable liberation of bromine. III, the yield of which changed greatly from run to run, could be formed *via* the corresponding benzyl bromides, which were formed by some route or other. A control experiment showed that benzyl bromide and toluene gave a 90% yield of phenyltolylmethane in the presence of $TlBr_3 \cdot 4H_2O$ (see Experimental section).

No evolution of hydrogen bromide was observed, probably because of the complexation with the $TlBr_3$ present [Eq.(5)] giving $HTlBr_4$ as with $HTlCl_4$.[9] This complex seems to suppress further bromination, because an elongation of the reaction time did not lead to an increase in the yields of bromocompounds. The same phenomenon had been observed in the $ZnCl_2$-catalyzed bromination of aromatics.[10]

$$TlBr_3 + HBr \longrightarrow H[TlBr_4] \quad (5)$$

As may be seen in the table, this bromination is rather slow and is apt to be accompanied by some side reactions, so the method is hopeless for preparative purposes.

B. Aromatic Bromination with Bromine in the Presence of Tl(III) and Tl(I) Catalysts. In the presence of small amounts of Tl(III) or Tl(I) salts, aromatics reacted with bromine smoothly in carbon tetrachloride at the refluxing temperature to give pure monobrominated compounds in good yields [Eq. (6)]. The mixtures were heterogeneous (under these experimental conditions only 29—33% of the Tl salts were dissolved in the solvent). In contrast to A reaction, the TlX_3-catalyzed reaction proceeded rather rapidly and a vigorous evolution of HBr gas was observed. Such a difference can be explained by assuming a stronger interaction of the Tl(III) salt with bromine than with



(6)

HBr. Some typical data are shown in Table 2. From toluene, a mixture of *o*- and *p*-bromotoluenes was rapidly obtained; in this mixture Tl(III) and Tl(I) catalysts favoured *o*-isomer formation and *p*-one formation respectively, while only traces of the *m*-isomer were

TABLE 2. AROMATIC BROMINATION BY Tl CATALYST[a]

Aromatics (100 mmol)	Catalyst (1.3mmol)	React. time (min)	Products [I] mmol (yield, %)
Benzene	$TlBr_3 \cdot 4H_2O$	5	22.2 (89)
Benzene	$Tl(OAc)_3$	5	20.7 (83)
Benzene	TlOAc	120	11.3 (45)
Benzene	TlBr	300	15.9 (64)
Benzene	$Hg(OAc)_2$	60	trace
Benzene	$Pb(OAc)_4$	60	trace
Benzene	—	60	—
Toluene	$Tl(OAc)_3$	5	24.2 (97)[b]
Toluene	$TlBr_3 \cdot 4H_2O$	5	23.0 (92)[c]
Toluene	TlBr	5	20.0 (80)[d]
Toluene	—	5	20.0 (80)[e]
Bromobenzene	$Tl(OAc)_3$	90	16.7 (67)

a) CCl_4 80 ml, Br_2 25 mmol, 77°C. b) $o/2p=0.67$ c) $o/2p=0.70$ d) $o/2p=0.24$ e) Only $C_6H_5CH_2Br$ was obtained.

9) R. J. Meyer, *Z. Anorg. Allg. Chem.*, **24**, 337 (1900).
10) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **78**, 4549 (1956).

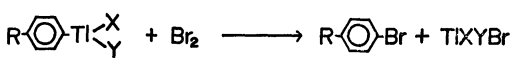
Table 3. Bromination of arylthallium (III) compounds[a]

ArTlXY	(mmol)	Br_2 (mmol)	React. time (min)	Products mmol (%)[b] [I]	[II]
$C_6H_5Tl(OAc)(ClO_4\cdot H_2O)$	10	25	120	6.5 (65)	1.3 (13)
	2.5	4	20	2.2 (88)	—
p-$CH_3C_6H_4Tl(OAc)(ClO_4\cdot H_2O)$	10	25	120	—	8.0 (80)
	1.6	2.6	20	1.1 (69)	trace
p-$CH_3C_6H_4Tl(OAc)Br$	1.6	1.6	20	1.1 (69)	trace
$(C_6H_5)_2TlBr$	5.8	11.6	60	10.1 (87)	—
$C_6H_5Tl(OAc)(ClO_4\cdot H_2O)$	10 [c]	10	3	1.63 (16.3)	trace
p-$CH_3C_6H_4Tl(OAc)(ClO_4\cdot H_2O)$	10 [c]	10	3	2.22 (22.2)	0.15 (1.5)

a) CCl_4 80 ml, 77°C. b) Calculated on the basis of Br_2. c) Competitive reaction, $k_T/k_B=1.45$.

formed (detected by studying the NMR spectra). When enough water to dissolve the Tl(III) salt (more than 0.9 g in this case) was added to the reaction mixture, the major product from toluene became benzyl bromide rather than bromotoluenes. Under comparable reaction conditions without a Tl(III) or Tl(I) catalyst, benzene gave no brominated compounds, while toluene gave only benzyl bromide, even in the dark. In sharp contrast to Tl(III) acetate, mercury(II) and lead (IV) acetates, which have an isoelectronic structure with the Tl(III) salt and which exhibit similar behavior in many reactions,[11] showed no catalytic action in this bromination. Tl(III) salts are more effective than Tl(I) salts as catalysts; this is clearly reflected by the yields of bromobenzenes from benzene.

C. Bromination of Arylthallium(III) Compounds with Bromine. When bromine was added to a suspension of arylthallium(III) compounds (ArTlXY) in carbon tetrachloride at the refluxing temperature, the desired brominated products were readily obtained in good yields regardless of the kinds of X and Y [Eq.(7)]. However, the presence of excess bromine resulted in the formation of dibrominated compounds [Eq. (8)]. Some typical data are shown in Table 3.



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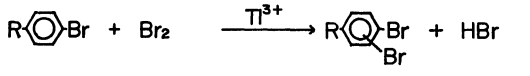


(8)

(R=H, CH_3; X,Y=OAc, ClO_4; OAc, Br; C_6H_5, Br)

From a competitive reaction of the phenylthallium(III) compound and the p-tolyl compound (X=OAc, Y=ClO_4) the relative rate ratio, k_T/k_B, was determined; its value was nearly 1.5 (in CCl_4 at 77°C). In the case of X=OAc and Y=Br, a similar value was obtained. Hence, it seems reasonable to assume that the k_T/k_B ratios for the bromination of $ArTlBr_2$ or $ArTl(OAc)_2$ are nearly 1 or 2. This means that the bromination of the phenylthallium(III) compounds and the p-tolyl compound proceeds at similar rates. These estimated k_T/k_B values differ from those values (7 and 24 for $TlBr_3\cdot 4H_2O$ and $Tl(OAc)_3$ respectively) obtained in the Tl(III) salt-catalyzed reaction B, to be described below. In the B reaction, if rate-determining aromatic thallation is involved, this disagreement can be understood. However, the reported k_T/k_B value (2.6) for aromatic thallation[12] also disagrees with the values for the B reaction. In addition, the following experimental fact must be noted. Although arylthallium (III) compounds reacted easily with KI to give aryliodides,[6] when a mixture of 10 mmol of $TlBr_3\cdot 4H_2O$ and 40 ml of HOAc was treated with 50 mmol of KI (H_2O:HOAc=1:1 solution) and 50 mmol of benzene at 100°C, no traces of iodobenzene and phenylacetate (the acetolysis product of iodobenzene) were formed. Aromatic thallation is rather slow and can usually occur in polar solvents and under acidic conditions when reactive aromatics or strong electrophilic Tl(III) salts such as $Tl(OCOCF_3)_3$ are used as substrates.[6,13] Therefore, in a nonpolar CCl_4 solvent the possibility of aromatic thallation seems very rare.[7] From all these facts, it can be deduced that the Tl(III)-catalyzed bromination does not proceed *via* an arylthallium (III) compound.

D. Relative Reactivities of Benzene and Toluene in the A and B Brominations. In order to ascertain the nature of the transition states of bromination using

11) See for example, W. Kitching, *Organometal. Chem. Rev.*, **3**, 35, 61 (1968).

12) P. M. Henry, *J. Org. Chem.*, **35**, 3083 (1970).

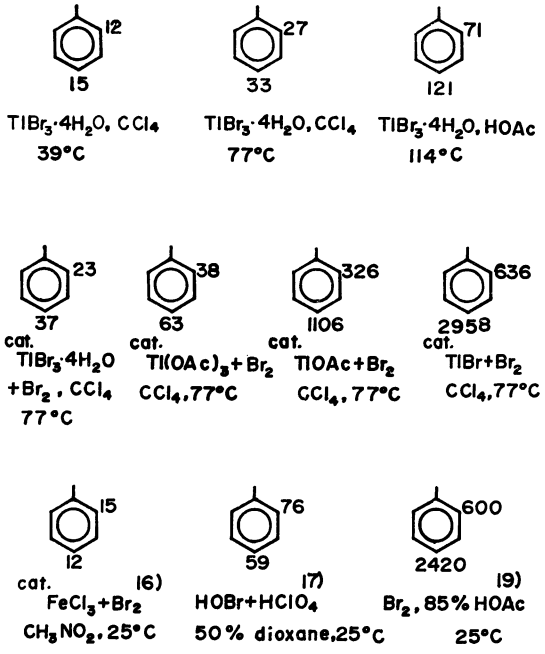
13) K. Ichikawa, S. Uemura, T. Nakano, and E. Uegaki, This Bulletin, **44**, 545 (1971).

Table 4. Competitive bromination of benzene and toluene[a)]

Tl salt (mmol)	Br_2 (mmol)	Solvent (80 ml)	React. temp. (°C)	React. time (min)	Bromotoluene[b)] k_T/k_B	Bromotoluene[b)] $o/2p$	Total[c)] yield (mmol)
$TlBr_3 \cdot 4H_2O$ (24.2)	—	CCl_4	77	5	15	0.80	4.7[d)]
$TlBr_3 \cdot 4H_2O$ (24.2)	—	CCl_4	39	120	6.5	0.84	6.9
$TlBr_3 \cdot 4H_2O$[e)] (24.2)	—	CCl_4	39	120	5.4	0.76	4.5
$TlBr_3 \cdot 4H_2O$ (24.2)	—	HOAc	114	5	44	0.59	4.7
$TlBr_3 \cdot 4H_2O$ (1.0)	25	CCl_4	77	5	7	0.67	17.5
$Tl(OAc)_3$ (1.3)	25	CCl_4	77	5	24	0.60	17.5
TlOAc[f)] (1.0)	10	CCl_4	77	5	293	0.30	8.0
TlBr[f)] (1.3)	10	CCl_4	77	5	705	0.22	7.6

a) Benzene (100 mmol), toluene (100 mmol). b) No or trace amounts of *m*-bromotoluene were formed. c) Sum of bromotoluene and bromobenzene; unless otherwise noted no dibromocompounds were found. d) Traces of dibromocompounds were found. e) Benzene (200 mmol), toluene (100 mmol). f) Benzene (100 mmol), toluene (10 mmol).

Table 5. Partial rate factors for bromination of toluene



Tl salts, competitive reactions of benzene and toluene were carried out under various conditions. Some data on the relative rate ratio (k_T/k_B) and on the isomer ratio ($o/2p$) in the bromotoluenes formed are shown in Table 4. Neither the k_T/k_B ratio nor the $o/2p$ ratio changed significantly when the reaction time for a TlX_3-catalyzed reaction was varied from 5 to 60 min. On the basis of these data, partial rate factors were calculated; they are listed in Table 5, together with some previously reported values. Table 4 shows that the positional selectivity (reflected by the $o/2p$ ratio) increases with an increase in the substrate selectivity (k_T/k_B ratio). This is a general correlation which has been established in several electrophilic substitutions of aromatics.[14)] Our data on relative reactivities are rather limited and are not precise enough for us to undertake a detailed discussion; however, at least the following qualitative deductions are possible. First, there are no significant differences in either the k_T/k_B or $o/2p$ ratio for the two bromination reactions (A and B) using $TlBr_3 \cdot 4H_2O$. This suggests that the A and B brominations are essentially the same. Second, the remarkable differences in both the k_T/k_B ratio and the partial rate factor between TlX_3- and TlX-catalyzed brominations suggests two distinct attacking species for the two reactions. In the Tl(III)-catalyzed reaction, the observed k_T/k_B ratios were of the same order as those for the reaction with other metal chlorides catalysts (*e.g.*, 10—31 for $AlCl_3$ in $C_6H_5NO_2$ at 30°C, and 10—21 in CH_3NO_2,[15)] 3.6—32 for $FeCl_3$ in CH_3NO_2 at 25°C,[16)] and 148 for $ZnCl_2$ in HOAc at 25.4°C[10)]). The partial rate factors obtained were also comparable to those values for the $FeCl_3$-catalyzed bromination with bromine (in CH_3NO_2)[16)] and the perchloric acid-catalyzed bromination with hypobromous acid (in 50% dioxane).[17)] For the latter reaction, kinetic evidence for the attack of Br^+ or its hydrated form has also been given.[18)] On the other hand, in the Tl(I)-catalyzed reaction, both values (the k_T/k_B ratios and the partial rate factors) were quite large and were comparable to those for a bromination without a catalyst (in 85% HOAc),[19)] in which molecular bromine is considered to be the reactive species.[18)] Recently Olah[20)] cited a clear correlation between the electrophilicity of the reagent and the nature of the transition state. He reached the following conclusions. When the electrophilic species is sufficiently reactive, *i.e.*, in the case of a low k_T/k_B value and a high $o/2p$ ratio, the position of the transition state is represented by a much earlier state resembling the starting aromatics (oriented π-complex-like); on the other hand, in the reaction with a weak electrophile (a high k_T/k_B value and a low $o/2p$

14) See for example, R. O. C. Norman, and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishers, (1965), p. 56.

15) S. Y. Caille and R. J. P. Corrin, *Chem. Commun.*, **1967**, 1251.

16) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, **86**, 1039 (1964).

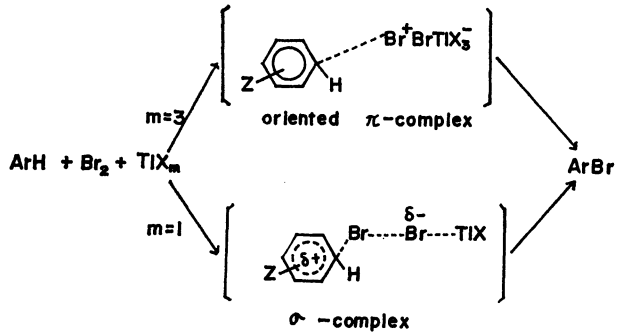
17) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, **1956**, 36.

18) a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed., Cornell Univ. Press (1969), p. 345. b) Ref. 14 p. 122 and p. 130.

19) H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 1421 (1957).

20) G. A. Olah, M. Tashiro, and S. Kobayashi, *ibid.*, **92**, 6369 (1970).

ratio), a late transition state resembling the intermediate (σ-complex-like) is involved. Taking account of this conclusion and the observed differences in selectivities, we propose the following reaction paths and transition states for these reactions. When the Tl (III) catalyst is used, the reaction may involve the initial formation of a polarized complex (probably an ion-pair containing Br^+) from Br_2 and TlX_3 and its subsequent attack on aromatics (oriented π-complex). The latter step would be rate-determining. In the case of the Tl (I) catalyst, the interaction between aromatics and Br_2 would be more important than that between Br_2 and TlX, for the Tl (I) salt is expected to be a rather weak Lewis acid because of two *s*-electrons in the outer shell. The transformation of the ArH·Br_2 (π-complex) to the ArH·Br^+ (σ-complex) would be essentially rate-determining, and Tl (I) salt may assist in breaking the Br-Br bond. The transition states for these reactions may be represented as follows:



Experimental

Materials. All the starting materials were used after distillation. The $TlBr_3 \cdot 4H_2O$ (mp 40—42°C, lit, 40°C;[21] the purity as determined by iodometry was greater than 97%), TlBr and TlOAc were commercial products. The $Tl(OAc)_3$ was prepared by dissolving Tl_2O_3 into acetic acid at 60°C for 20 hr, collecting white crystals after cooling, and drying over CaO (the purity was greater than 98%). The arylthallium (III) compound ($C_6H_5TlOAc \cdot ClO_4 \cdot H_2O$ and *p*-$CH_3C_6H_4TlOAc \cdot ClO_4 \cdot H_2O$) were prepared by the reaction of benzene or toluene with $Tl(OAc)_3$ in the HOAc-$HClO_4$ solvent. The synthetic method of these compounds was described in detail in a separate paper.[13] *p*-$CH_3C_6H_4TlOAcBr$ was prepared by the addition of an aqueous KBr solution to the aqueous *p*-$CH_3C_6H_4TlOAc \cdot ClO_4 \cdot H_2O$ solution at room temperature. The white precipitates which were formed instantly were recrystallized from benzene; mp>300°C (Found: C, 24.42; H, 2.22%. Calcd for $C_9H_{10}O_2TlBr$: C, 24.89; H, 2.32%). The phenyl analogues were prepared similarly. The diphenylthallium(III) bromide was prepared from phenylboric acid and $TlBr_3 \cdot 4H_2O$ in boiling water according to the reported method;[22] mp>300°C (Found: C, 32.86; H, 2.18%. Calcd for $C_{12}H_{10}TlBr$: C, 32.87; H, 2.30%).

Reaction of Aromatics with $TlBr_3 \cdot 4H_2O$. An aromatic compound (100 mmol) was added to a suspension of molten $TlBr_3 \cdot 4H_2O$ (24.2 mmol) in 80 m*l* of CCl_4 at the refluxing temperature (77°C). The reaction mixture was kept at that temperature for 1 hr, during which period the red-brown color of bromine which was observed at the initial stage gradually disappeared. Yellowish-white precipitates were filtered off, and the filtrate was washed with water and a sodium bicarbonate solution, dried over Na_2SO_4, and distilled. All the products were analyzed by g.l.c. and by a study of the IR and NMR spectra. The *o*/2*p* ratio of isomeric bromotoluenes (bp 72°C/20 mmHg), bromoethylbenzenes (bp 71°C/10 mmHg), and bromoanisoles (bp 77°C/7 mmHg) were also determined by g.l.c. and by a study of the NMR spectra (for example, methyl protons of *o*- and *p*-bromotoluenes were observed at τ 7.62 and 7.73 respectively).

Bromination of Benzene with Bromine in the Presence of the $TlBr_3 \cdot 4H_2O$ Catalyst. Benzene (100 mmol) was added to a mixture of CCl_4 (80 m*l*), Br_2 (25 mmol) and $TlBr_3 \cdot 4H_2O$ (1.3 mmol) at the refluxing temperature (77°C). After 5 min, the red-brown color of the solution completely disappeared. The reaction mixture was then cooled rapidly and treated as has been described above to give 22.2 mmol of bromobenzene; bp 50°C/20 mmHg (yield, 89%).

Reaction of p-*Tolylthallium(III) Acetate Perchlorate Monohydrate with Bromine.* Carbon tetrachloride (42 m*l*) containing 25 mmol of bromine was added to a mixture of the *p*-tolylthallium(III) compound (4.72 g, 10 mmol) and CCl_4 (38 m*l*) at 77°C. The red-brown color of bromine gradually disappeared, while the evolution of HBr gas was observed. After 2 hr, the reaction mixture was cooled and worked up as usual. The only products obtained were isomeric dibromotoluenes; no isomeric bromotoluenes was detected by g.l.c. Distillation gave a mixture of dibromotoluenes, which were shown by their IR spectra to be 1-methyl-2,4-dibromotoluene and 1-methyl-3,4-dibromotoluene. Yield, 2.0 g (80%); bp 100—130°C/3.5 mmHg.

Reaction of p-*Tolylthallium(III) Acetate Bromide with Bromine.* A CCl_4 (2.6 m*l*) containing 1.6 mmol of bromine was added to a mixture of *p*-tolylthallium(III) acetate bromide (1.6 mmol) and CCl_4 (27.4 m*l*) at 77°C. Within 1 min, the bromine disappeared; after 20 min, the reaction mixture was cooled rapidly and treated as has been described above. G.l.c. analysis with bromobenzene as the internal standard showed that 1.06 mmol (yield, 66%) of *p*-bromotoluene and a trace of dibromotoluene were the only products.

Competitive Bromination of Benzene and Toluene in the Presence of $TlBr_3 \cdot 4H_2O$ Catalyst. A mixture of benzene (100 mmol) and toluene (100 mmol) was added to a stirred mixture of CCl_4 (80 m*l*), Br_2 (25 mmol) and $TlBr_3 \cdot 4H_2O$ (1 mmol) at 77°C. After 5 min, the reaction mixture was cooled rapidly and worked up as usual. The amounts of bromobenzene and isomeric bromotoluenes and the *o*/2*p* ratio of the latter compounds were determined by g.l.c. analysis. The total yield of both bromocompounds was 76%, and the k_T/k_B value was 7.

Competitive Bromination of the Phenylthallium(III) Compound and the p-*Tolyl Compound.* A CCl_4 (40 m*l*) solution of bromine (10 mmol) was stirred into a suspension of equimolar (each 10 mmol) amounts of $C_6H_5TlOAc \cdot ClO_4 \cdot H_2O$ and *p*-$CH_3C_6H_4TlOAc \cdot ClO_4 \cdot H_2O$ in CCl_4 (40 m*l*) at 77°C. After 3 min, the reaction was stopped. G.l.c. analysis showed that bromobenzene (1.63 mmol), bromotoluenes (2.22 mmol), and dibromotoluenes (0.15 mmol) were thus formed.

Authentic Samples for G.l.c. Analysis. The bromobenzene, *o*-, *m*-, and *p*-bromotoluenes, *o*-, *m*-, and *p*-bromoanisoles, *o*- and *p*-dibromobenzenes, were commercial products. The bromoxylenes, bromomesitylene and bromoethylbenzenes were each isolated and determined by studying their NMR and IR spectra. The dibromoalkylbenzenes were prepared from bromine and the corresponding monobromoalkylbenzenes.

21) V. Thomas, *Ann. Chim. Phys.*, **11**, 204 (1907).
22) F. Challenger and B. Parker, *J. Chem. Soc.*, **1931**, 1462.

The isomeric phenyltolylmethanes (*o*- and *p*-) were prepared by heating benzyl bromide (20 mmol) and toluene (100 mmol) in the presence of the $TlBr_3 \cdot 4H_2O$ (25 mmol) catalyst at 77°C for 1 hr; yield, 3.1 g (18 mmol, 90%); *o*/*p*= 1.38; bp 100—102°C/2 mmHg. The *p*-tolyl-*p*-xylyl-methane was prepared from *p*-xylene, $Tl(OAc)_3$, and $HClO_4$ by a method reported in a separate paper.[13] Diarylmethanes from *o*-xylene and ethylbenzene could not be isolated in the pure form, but their NMR spectra revealed the presence of a methylene proton at τ 6.0—6.20.

Spectral Measurements. The NMR spectra were determined by a Varian A-60 spectrometer, using TMS as the internal standard in $CDCl_3$. The IR spectra were obtained by means of HITACHI EPI-2 and EPS-3T. G.l.c. analysis was carried out on a SHIMADZU 5APTF apparatus, using PEG 6000 (25%)-Chromosorb-W 3-m and Apz-L (30%)-Celite 3-m columns and on a HITACHI F-6 apparatus using Apz-L 1-m columns.