

Concurrent Chlorination and Carboxylation of Aromatic Hydrocarbons with Thallium(III) Chloride Tetrahydrate in Carbon Tetrachloride †

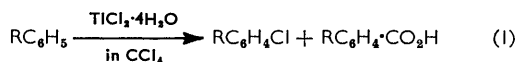
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In contrast to aromatic bromination with $TlBr_3 \cdot 4H_2O$, the reaction of lower aromatic hydrocarbons (C_6-C_8) with molten $TlCl_3 \cdot 4H_2O$ in boiling carbon tetrachloride afforded the corresponding benzoic acids together with the expected chlorinated aromatic compounds. At lower temperatures, carboxylation was considerably favoured. Possible mechanisms for chlorination and carboxylation have been discussed.

CERTAIN metal chlorides (e.g., $SbCl_5$ and $FeCl_3$) are known to effect direct chlorination of aromatic hydrocarbons, and an interpretation that has been given, is that the chlorinating ability of a metal chloride may be associated with its co-ordination ability, oxidation-reduction potential, and its solubility in organic phase.¹ Since mild Lewis acid activities of thallium halides² and the favourable reduction potential of Tl^{III} ion³ are known, chlorination with this chloride itself would be expected. No such attempt, however, has been made, though its use as a carrier has been known for a long time.⁴ The present paper describes some findings on chlorination and unexpected carboxylation by molten $TlCl_3 \cdot 4H_2O$ in carbon tetrachloride.

RESULTS AND DISCUSSION

When a lower aromatic hydrocarbon (C_6-C_8) in carbon tetrachloride was treated with $TlCl_3 \cdot 4H_2O$ at appropriate temperatures above its melting point (37°), nuclear chlorinated and carboxylated compounds were obtained [equation (1)]. The reaction was accompanied



by considerable evolution of phosgene and HCl from the hydrolysis of carbon tetrachloride by hydrated Tl^{III} salt.⁵ Several results are collected in Table 1.

The chlorination is rather slow, as in the case of bromination with $TlBr_3 \cdot 4H_2O$,⁶ and yields are generally low [cf. the experiment performed neat (Table 1, run 16)]. Direct carboxylation of aromatic compounds is an interesting reaction, though yields are not so high, and is characteristic for only this reaction system. No such transformation has been realized for a similar system with $TlBr_3 \cdot 4H_2O$.⁶

Both sets of products from toluene or ethylbenzene were composed of *o*- and *p*-isomers without any traces of the *m*-isomer. Observed orientation clearly predicts that both chlorination and carboxylation would be essentially electrophilic. The reaction with anisole or dimethylaniline (both generally reactive towards electro-

philes), however, was almost unsuccessful owing to their high sensitivity towards the oxidizing agent. With less reactive compounds such as chlorobenzene and nitrobenzene, no reaction occurred under our reaction conditions; but the Tl^{III} -catalysed chlorination with chlorine gas has been observed previously.⁴

TABLE I

Reaction of aromatic hydrocarbons with $TlCl_3 \cdot 4H_2O$ in carbon tetrachloride [$TlCl_3 \cdot 4H_2O$ (25 mmol); CCl_4 (100 ml)]

Aromatic hydrocarbon (100 mmol)	$T/^\circ C$	t/h	Chlorinated product ^a (mmol)	Carboxylated product ^b (mmol)	$TlCl$ formed ^c (mmol)
1 PhH	78	2	8.9	7.9	17.1
2 PhH	50	5	0.8	4.2	1.1
3 PhH	50	10	1.0	10.0	2.4
4 PhMe	78	2	7.1 ^d	5.2 ^e	16.1
5 PhMe	55	30	3.5	18.6	4.4
6 PhEt	78	2	4.9 ^f	6.3 ^g	14.0
7 PhEt	55	25	2.8	2.8	9.3
8 <i>o</i> -Me ₂ C ₆ H ₄	78	2	10.8 ^h	1.2 ^h	16.3
9 <i>m</i> -Me ₂ C ₆ H ₄	78	2	10.2 ⁱ	2.8 ⁱ	14.8
10 <i>p</i> -Me ₂ C ₆ H ₄	78	2	11.4	2.6	19.4
11 <i>p</i> -Me ₂ C ₆ H ₄	50-60	24	6.2	1.4	6.7
12 PhPr ^l	78	2	Trace	0.5	18.6 ^j
13 PhOMe	50	8	0.3	Trace	23.4 ^j
14 PhH ^k	78	3	2.4	l	m
15 PhH ⁿ	78	2	1.4	7.9 ^o	m
16 PhMe ^{p,q}	78	2	8.4 ^r		m

^a Determined by g.l.c. ^b Determined by g.l.c. as its methyl ester. ^c Determined gravimetrically. ^d *o/p* = 1.0 (g.l.c.). ^e *o/p* = 0.7 (g.l.c.). ^f *o/p* = 1.0 (g.l.c.). ^g *o/p* = 0.6 (g.l.c.). ^h A mixture of 1,2,3- and 1,3,4-isomers (i.r.). ⁱ A mixture of 1,2,3- and 1,2,4-isomers (i.r.). ^j Consumed Tl^{III} was determined by iodometry. ^k Anhydrous $TlCl_3$ (18.3 mmol) was used instead of the hydrated salt. ^l No $\alpha\alpha\alpha$ -trichlorotoluene was formed. ^m Not determined. ⁿ $CuCl_2 \cdot 2H_2O$ (5 mmol) was added in the system. ^o Benzophenone (1.0 mmol) was formed also. ^p Without carbon tetrachloride. ^q Run at twice scale. ^r *o/p* = 1.1 (g.l.c.).

Lower reaction temperatures resulted in a decrease in the yields of chlorinated aromatic compounds and an increase in those of aromatic carboxylic acids. Independent variation in yields of both products by alternation of the reaction time were also confirmed. These facts suggest that both reactions proceed concurrently through different courses, and the hydrated Tl^{III} salt

³ See A. G. Lee, 'The Chemistry of Thallium,' Elsevier, Amsterdam, 1971, p. 16.

⁴ (a) A. G. Page, *Annalen*, 1884, **225**, 196; (b) V. Thomas, *Compt. rend.*, 1907, **144**, 32.

⁵ S. Uemura, F. Tanaka, O. Sasaki, and M. Okano, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1971, **49**, 97.

⁶ S. Uemura, K. Sohma, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 2490.

† Preliminary communication, S. Uemura, O. Sasaki, and M. Okano, *Chem. Comm.*, 1970, 1139.

¹ (a) P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491; (b) P. Kovacic and A. K. Sparks, *ibid.*, 1960, **82**, 5740; (c) P. Kovacic and K. M. Lange, *J. Org. Chem.*, 1965, **30**, 4251.

² (a) 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1963, vol. 1, p. 255; (b) L. I. Kashtanov, *J. Gen. Chem. (U.S.S.R.)*, 1932, **2**, 515; (c) S. Uemura, K. Sohma, and M. Okano, *Bull. Chem. Soc. Japan*, 1972, **45**, 860.

surely acts as a reactant for the former reaction and acts as both a catalyst and a substrate (a source of water) for the latter.

In order to get some knowledge on chlorination mechanism, 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/p) are shown in Table 2. Two important points are evident from these data. First, in the chlorination with $TiCl_3 \cdot 4H_2O$, the observed k_T/k_B value was similar in magnitude to that for the TiX_3 -catalysed chlorination or the chlorination with HOCl (in water), but the o/p ratio was dissimilar to that for each of them. For the latter reaction involving the attack of Cl^+ , the reported k_T/k_B and o/p ratios were 60 and 3.2, respectively.⁷ Secondly, considerable differences were found in k_T/k_B values between Ti^{III} - and Ti^I -catalysed chlorinations, indicating the presence of two distinct attacking species for these two reactions. As to the first feature, we reported somewhat different results in the bromination with $TiBr_3 \cdot 4H_2O$;⁶ there were no significant differences in either the k_T/k_B or o/p ratio for the bromination with the Ti^{III} salt and the Ti^{III} -catalysed bromination with bromine. Such a contrast between two halides may be attributed to the difference in their thermal stabilities. Although both halides tend to lose halogen easily to form thallose halides, the chloride is known to be somewhat stable compared with the bromide.⁸ The considerable stability of $TiCl_3 \cdot 4H_2O$ under our conditions was confirmed experimentally; *i.e.*, no consumption of the Ti^{III} salt and appreciable formation of $TiCl$ occurred by heating $TiCl_4 \cdot 4H_2O$ in boiling carbon tetrachloride for 2 h. All the foregoing results clearly indicate that the participation of chlorine, which might be formed from the salt, is very unlikely at least in our chlorination.

TABLE 2

Competitive chlorination of benzene and toluene in carbon tetrachloride [benzene, toluene (100 mmol each); CCl_4 (100 ml); 78°; 1–2 h]

Ti salt (mmol)	Cl_2 ^a	PhCl	MeC_6H_4Cl (<i>o</i> + <i>p</i>)	<i>o/p</i>	k_T/k_B
$TiCl_3 \cdot 4H_2O$ (2.5) ^b	—	0.23	6.0	1.1	26
$TiCl_3 \cdot 4H_2O$ (2.5)	+	0.55	23.6	1.8	43
$Ti(OAc)_3$ (2.5)	+	0.39	23.5	2.2	60
$TiCl$ (2.5) ^c	+	0.29	16.9	2.5	117
$TiCl$ (2.5) + H_2O (10) ^c	+	0.28	14.8	2.4	106
$TiOAc$ (2.5) + H_2O (10) ^c	+	0.37	24.7	2.3	133

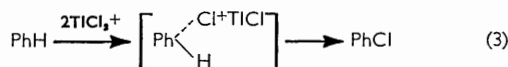
^a The total amount of the gas introduced was not measured. ^b The observed o/p and k_T/k_B values for carboxylation were 0.6 and 9, respectively. ^c Benzene (200 mmol), toluene (100 mmol).

The comparatively lower k_T/k_B value and abnormally low o/p ratio for our chlorination seems to imply that a reactive (probably positively charged) and somewhat

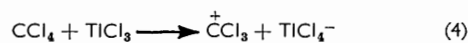
⁷ P. B. D. de la Mare, J. T. Harvey, M. Hassan, and S. Varma, *J. Chem. Soc.*, 1958, 2756.

⁸ See (a) J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' vol. 5, Longmans, London, 1924, pp. 443 and 452; (b) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Interscience, London, 1966, p. 440.

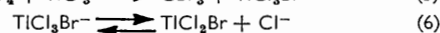
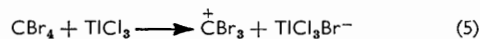
bulky attacking species is involved, as in the case of chlorination with $SbCl_5$.¹⁵ Thus the most probable electrophile would be the $TiCl_2^+$ ion (presumably as an ion-pair). Since the equilibrium [equation (2)] in methanol is already known,⁹ the existence of such active species in the molten phase containing water would be reasonable [equation (3)].



Our carboxylation resembles the $AlCl_3$ -catalysed condensation of aromatic compounds with carbon tetrachloride;¹⁰ however, the latter reaction usually affords a di- or tri-aryl compound rather than a monoaryl one, except for a few cases.¹¹ Since the ready hydrolysis of $\alpha\alpha\alpha$ -trichlorotoluene with $TiCl_3 \cdot 4H_2O$ has been known,⁵ its isolation would be difficult in our reaction system, even if it were formed. Moreover, an attempt to obtain such kind of intermediate by the use of the anhydrous salt was unsuccessful and gave only chlorinated product in a slight yield (run 14 in Table 1). Since a reasonable assumption of CCl_3^+ being the intermediate in the hydrolysis of carbon tetrachloride with $SbCl_5$, $GaCl_3$, and $FeCl_3$ has been made,¹² the generation of the same cation by the action of $TiCl_3$ would be expected also [equation (4)]. In connection with this, when our reaction with

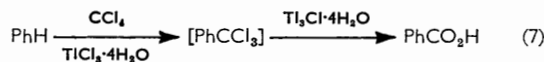


toluene was carried out in carbon tetrabromide–cyclohexane instead of a carbon tetrachloride solution, *p*-bromotoluene was formed as one of the main products, together with *p*-chlorotoluene (see Experimental section). This can be explained as a result of bromination with $TiCl_2Br$ formed by reactions (5) and (6).



By a competitive reaction between benzene and toluene, the k_T/k_B value for the carboxylation was determined. The observed low value (see footnote in Table 2)

does not conflict with the assumption that $\overset{+}{C}Cl_3$ ion (probably as an ion-pair) would be the reactive species. Thus the most plausible route leading to an aromatic acid may be expressed by reaction (7).



Since the $FeCl_3$ - or $CuCl_2$ -catalysed radical addition of carbon tetrachloride to olefins is known,¹³ we further examined the problem of whether or not a radical is involved in the $TiCl_3 \cdot 4H_2O$ -carbon tetrachloride system.

⁹ See ref. 3, p. 46.

¹⁰ (a) Ref. 2a, 1964, vol. II, p. 450; (b) R. C. Fuson, 'Reactions of Organic Compounds,' Wiley, New York, 1962, p. 74.

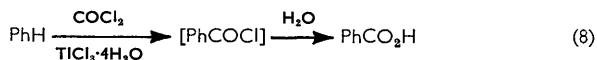
¹¹ H. Hart and R. W. Fish, *J. Amer. Chem. Soc.*, 1961, **83**, 4460.

¹² M. E. Hill, *J. Org. Chem.*, 1960, **25**, 1115.

¹³ M. Assher and D. Vofsi, *J. Chem. Soc.*, 1963, 1887.

However, reaction with oct-1-ene (at 78° for 2 h) gave no radical adduct (or hydrolysis product). Therefore, the attack of trichloromethyl radical is not worth consideration.

Two other possible routes *via* different intermediates can be formulated [equations (8) and (9)]. With regard



to the former route, the AlCl_3 -catalysed aromatic carboxylation with phosgene to afford diaryl ketones rather than aroyl chlorides is known.¹⁴ However, a separate reaction indicated that $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ was too weak to catalyse the carboxylation of toluene with phosgene (see Experimental section). The latter route involves the presumed formation of an arylthallium(III) intermediate; but, except for the metallation of reactive dibenzofuran, no other example of aromatic thallation with thallium(III) halides has ever been known.¹⁵ Moreover, when phenylthallium dichloride was used as a starting compound, instead of benzene, the following five products were formed by the reaction with $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$: chlorobenzene, *o*- and *p*-dichlorobenzenes, benzoic acid, and benzophenone (see Experimental section). Dichlorobenzenes and benzophenone were the products which could not be found in original reaction, and this result seemed to eliminate the possibility of the pathway (9). Two other products would be easily derived from benzene, which may be formed from the phenylthallium compound by the action of aqueous HCl present in the reaction system. This route was confirmed by an independent experiment (see Experimental section).

The catalytic action of other metal chlorides for carboxylation (or trichloromethylation) was also examined. All following chlorides, however, were ineffective for the reaction between benzene and carbon tetrachloride at 78°: anhydrous and hydrated FeCl_3 , anhydrous TiCl_3 (see run 14 in Table 1), anhydrous SbCl_5 , and hydrated TiCl . On the other hand, the known AlCl_3 -catalysed condensation (at 2°) afforded only dichlorodiphenylmethane as sole product, even under our conditions where a large excess of carbon tetrachloride was present. Thus, the $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ -carbon tetrachloride system seemed to be specific for direct carboxylation. It may be of interest to note here that the addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 equiv. to the Ti^{III} salt) to our system to oxidize Ti^{II} to Ti^{III} resulted in an additional formation of benzophenone rather than an increase in the yield of chlorobenzene (run 15 in Table 1).

Finally, the effect of solvents on the reaction was considered. The use of more polar but basic solvents such as acetonitrile and nitromethane led to a complex formation with the Ti^{III} salt, and the reaction was completely hindered, even when only small amounts (*ca.*

2 mol. equiv.) of acetonitrile were added in a carbon tetrachloride solvent. Surprisingly, the reaction was almost unsuccessful in boiling chloroform. No suitable explanation is found at present for the lack of chlorination, but insufficient interactions between metal halides with chloroform, as are shown by its use as solvent in metal halide-catalysed hydrolysis of trichloromethyl compound,¹² may result in the failure of carboxylation.

EXPERIMENTAL

Materials.—All organic starting materials were used after distillation. Commercial $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ and other metal chlorides were used without purification. The purity of $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ was found to be >98% (iodometry). Anhydrous TiCl_3 was prepared by dehydration of $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ with thionyl chloride.¹⁶ Phenylthallium(III) dichloride was produced from phenylboric acid and $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ according to the procedure reported; ¹⁷ m.p. 233–234° (lit.,¹⁷ 234°).

Reaction of Aromatic Compounds with $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$.—To a stirred suspension of molten $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ (9.5 g, 25 mmol) in CCl_4 (100 ml), an aromatic compound (100 mmol) was added dropwise at prescribed temperature. The mixture was stirred at that temperature for a definite period. The mixture, freed from gaseous products, was filtered to remove the precipitate of TiCl and unchanged TiCl_3 , which was determined by iodometry [the former was determined gravimetrically (after treatment with aqueous HCl to dissolve the latter salt)]. The filtrate was washed with water three times, dried (Na_2SO_4), and treated with ethereal diazomethane. Removal of unchanged aromatic compound and carbon tetrachloride left a liquid, which was examined by g.l.c. Chlorinated and carboxylated products were identified by comparison of retention times, and i.r. and n.m.r. spectra with those of authentic samples, and their amounts were also determined by adding a known amount of benzaldehyde as an internal standard for g.l.c. The analysis was carried out on SHIMADZU 5APTF apparatus [with PEG 20M(25%)–Shimalite (3 m), PEG 6000(25%)–Chromosorb-W (3 m), Apiezon-L (30%)–Celite (1 m), and DEGS(25%)–Shimalite (3-m) columns].

Competitive Chlorinations of Benzene and Toluene.—To a stirred mixture of benzene (100 or 200 mmol), toluene (100 mmol), and the appropriate Ti^{I} or Ti^{III} salt (chloride or acetate) (2.5 mmol) in CCl_4 (100 ml), chlorine gas was introduced slowly at 78°. After 1 or 2 h, the mixture was cooled rapidly and worked-up as usual. The amounts of chlorobenzene, *o*- and *p*-chlorotoluenes were determined by g.l.c.

Reaction of Toluene with $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ in the Presence of Carbon Tetrabromide in Cyclohexane.—A mixture of toluene (9.2 g, 100 mmol) and carbon tetrabromide (33.2 g, 100 mmol) in cyclohexane (40 ml) was added dropwise to a stirred mixture of $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ (9.5 g, 25 mmol) and cyclohexane (60 ml) at 83°. After stirring for 2 h at that temperature, the mixture was worked-up as before with CCl_4 . Evaporation left a liquid. G.l.c. indicated that it consisted of two major components, *p*-chloro- and *p*-bromotoluenes (in the ratio *ca.* 1:3), and several minor components including trace amounts of 2,4-dibromotoluene. No appreciable amounts of isomeric toluoic acid esters were found.

Attempted $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ -catalysed Reaction of Toluene with

¹⁴ Ref. 2a, p. 120.

¹⁵ See W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 57.

¹⁶ H. Hecht, *Z. anorg. Chem.*, 1947, **254**, 46.

¹⁷ F. Challenger and B. Parker, *J. Chem. Soc.*, 1931, 1462.

Phosgene.—To a 30% solution (56 g) of phosgene (100 mmol) in toluene (500 mmol) in an autoclave, $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$ (9.5 g, 25 mmol) was added, and the mixture was heated with stirring at 80° for 2 h. The mixture was worked-up as before. After removal of most of the toluene, the residual liquid was analysed (g.l.c.). No traces of isomeric toluoates and ditolyl ketones were found.

Reaction of Phenylthallium Dichloride with $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$.—A mixture of phenylthallium dichloride (3.5 g, 10 mmol) and $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$ (3.8 g, 10 mmol) was heated in CCl_4 (80 ml) with stirring at 78° for 2 h. The mixture was worked-up as before. Evaporation left a liquid, which was shown by g.l.c. to be a mixture of five components: chlorobenzene (1.2 mmol), *o*-dichlorobenzene (0.3 mmol), *p*-dichlorobenzene

(0.6 mmol), methyl benzoate (1.5 mmol), and benzophenone (0.5 mmol).

Reaction of Phenylthallium Dichloride with Conc. HCl.—In the presence of conc. HCl (*ca.* 1 ml), phenylthallium(III) dichloride (3.5 g, 10 mmol) in CCl_4 (80 ml) was heated at 78° for 2 h with stirring. The mixture was worked-up similarly. Evaporation afforded a mixture of benzene (6.3 mmol), benzoic acid (trace), and the unchanged thallium compound (3.0 mmol), in which the former two were confirmed by g.l.c.

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