Carboxylation of some Aromatic Hydrocarbons with Thallium(III) Chloride Tetrahydrate in Carbon Tetrachloride

By SAKAE UEMURA,* OSAMU SASAKI, and MASAYA OKANO
(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)

Summary Certain aromatic hydrocarbons react with thallium(III) chloride tetrahydrate in carbon tetrachloride to give the corresponding benzoic acids together with the expected chlorinated compounds.

WHILE studying the aromatic halogenation by thallium salts, we found a unique example of carboxylation in the ternary system, ArH–CCl_4–$TlCl_3$. When thallium(III) chloride tetrahydrate and benzene were heated in carbon tetrachloride under reflux (78°) for 2 h, chlorobenzene (52%)† and benzoic acid (46%)† were obtained, while the thallium(III) salt was reduced to thallium(I). Similarly, toluene and the three isomeric xylenes yielded both kinds of products (see Table). During the reaction considerable evolution of phosgene and hydrogen chloride was observed and a blank experiment without the aromatic hydrocarbons showed that this was due to the thallium(III) salt-catalysed hydrolysis of carbon tetrachloride. Another experiment showed that a catalytic amount of thallium(III) chloride was efficient in promoting benzotrichloride hydrolysis. Aromatics with an electron-withdrawing group (*e.g.* nitrobenzene and halogenobenzenes) did not react for 2 h. Anisole reacted rapidly at 50°, but the yields of the products were low.

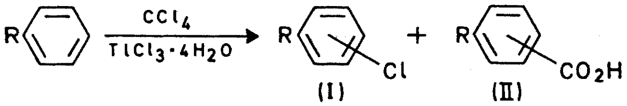
Product distribution from the reaction of thallium(III) *chloride and aromatic hydrocarbons*

($TlCl_3 \cdot 4H_2O$, 25 mmol; CCl_4, 100 ml)

Aromatic hydrocarbon (100 mmol)	Reaction temp. (°)	Reaction time (h)	Product[a] (mmol) (I)	(II)	Phosgene[b] (mmol)	HCl[b] (mmol)	Tl^ICl[c] (mmol)
Benzene	78	2	8·9	7·9	10·6	85·0	17·1
Benzene	50	2	0·4	2·9	trace	trace	—[d]
Toluene	78	2	7·1[e]	5·2[f]	10·2	82·5	16·1
o-Xylene[g]	78	2	10·8	1·2	12·4	76·2	16·3
m-Xylene[g]	78	2	10·2	2·8	13·9	87·2	14·8
p-Xylene	78	2	11·4	2·6	11·8	71·2	19·4

[a] Determined by g.c. (column, Apz-L and PEG-20M); (II) was determined as its methyl ester.
[b] Phosgene and HCl swept out of the system by N_2 into an ether solution of aniline and determined as diphenylurea and aniline hydrochloride, respectively.
[c] Determined gravimetrically.
[d] Not determined.
[e] $o:p = 1:1$ (by n.m.r.)
[f] $o:p = 1:1{\cdot}5$ (by g.c.).
[g] Both (I) and (II) consist of mixtures of 2 isomers.

The $o:p$ product ratio of (I) from toluene is similar to the value obtained for the chlorination using antimony chloride, but differs from that for the reaction using chlorine gas in the presence of antimony or iron(III) chloride catalyst.[1] This suggests that chlorination with thallium(III) chloride resembles other Lewis-acid metal salt halogenation in mechanism. On the other hand, the mode of formation of (II) is not yet fully understood: the following results are of



(I) (II)

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† Based on thallium(III) salt consumed, assuming that 1 mol of Tl^{III} salt reacted to give 1 mol of product.

interest. Phosgene, which reacted with aromatic hydrocarbons in the presence of aluminium chloride to give substituted benzoic acids or diaryl ketones[2] did not take part in our reaction system; no (I), (II), or diaryl ketone was formed when thallium(III) chloride was used as the catalyst for the reaction of benzene or toluene with phosgene. The iron(III) or copper(II) chloride-catalysed radical addition of carbon tetrachloride to olefin has been reported;[3] however, no carbon tetrachloride–oct-1-ene adduct formation was observed in our system containing thallium(III) chloride.

It has been reported[4] that Lewis acids such as the chlorides of iron, gallium, and antimony interact with carbon tetrachloride to form a metal–chlorine bridged complex which equilibrates with a small amount of reactive trichloromethyl carbonium ion–metal halide pair. If it is assumed that a similar reactive species is involved as an attacking agent in our reaction system, then the selective formation of *o*- and *p*-isomers in the carboxylation of toluene can be reasonably explained.

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[1] "Friedel–Crafts and Related Reactions," ed. G. A. Olah, Interscience, New York, 1965, vol. IV, p. 113.

[2] "Friedel–Crafts and Related Reactions," ed. G. A. Olah, Interscience, New York, 1965, vol. I, p. 120; E. Ador and F. Meier, *Ber.*, 1879, **12**, 1968.

[3] M. Assher and D. Vofsi, *J. Chem. Soc.*, 1963, 1887.

[4] M. E. Hill, *J. Org. Chem.*, 1960, **25**, 1115.