Synthesis of Alkoxythallium(III) Compounds of Olefins and Their Reaction with Copper Halides and Pseudohalides

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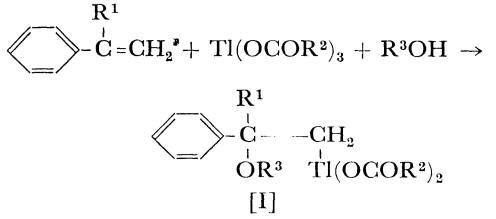
Some new alkoxythallium(III) compounds of olefins, $C_6H_5C(R^1)(OR^3)CH_2Tl(OCOR^2)_2$ [I], are prepared from styrene and α-methylstyrene with thallium(III) acetate and isobutyrate in various alcohols. I(R^1=H) reacts with copper(I) iodide, bromide, chloride, cyanide and thiocyanate to afford the corresponding alkyl halides and pseudohalides, $C_6H_5CH(OR^3)CH_2X$ [II], in various organic solvents, acetonitrile being the solvent of choice for the purpose of preparing II. The addition of potassium salt has a remarkable effect in improving the yield of II. The halo- and pseudohalodethallation occur at the position where thallium is attached previously to alkyl carbon. An ionic concerted intermolecular scheme is proposed as a reaction mechanism for the preparation of II. The data of NMR and IR spectra of I are briefly discussed.

Compared to the corresponding mercury(II) compounds, oxythallium(III) compounds of olefins are known to be unstable, and so far only a few compounds have been isolated since the first report by Criegee.[1] The compounds from styrene,[2] *o*-allylphenol,[2] norbornene,[3] norbornadiene[3] and isobutylene[4] are the known examples. Recently oxythallation products from acetylene[5,6b] and allene[6a] have also been isolated from the reaction mixture in methanol or acetic acid. Earlier work on the decomposition of oxythallium(III) compounds of olefins has revealed that the carbon-thallium bond is cleaved to leave a carbonium cation which gives the oxidation products of olefins.[2] A recent report by Mitani *et al.*[7] that carbon-thallium bond fission of the compound occurs easily with potassium thiocyanate to give 1-methoxy-2-thiocyanoalkanes in good yield may add another use of oxythallation in organic synthesis. We have reported some reactions of arylthallium(III) compounds with copper halides and pseudohalides where the aryl carbon-thallium bond was cleaved, resulting in the introduction of halogens[8a] or pseudohalogens[8b,c] to the aromatic ring. In connection with this observation, it might be interesting to examine how alkyl carbon-thallium bonds of oxythallium(III) compounds of olefins behave to these copper salts. We have investigated the synthesis of some new oxythallium(III) compounds of olefins and also some reactions of the resulting compounds with copper(I) iodide, chloride, bromide, cyanide, and thiocyanate. As a result a number of new oxythallium(III) compounds have been isolated from styrene and α-methylstyrene and the replacement of thallium group in these compounds by halogens or pseudohalogens has been achieved in good yield.

Results and Discussion

Synthesis of Alkoxythallium(III) Compounds of Olefins. Kabbe has reported the synthesis of α-methoxy-β-diacetatothallium ethylbenzene from styrene and thallium(III) acetate in methanol.[2] Similarly we obtained various α-alkoxy-β-diacetatothallium ethylbenzenes in 60—86% yield by stirring a mixture of styrene and thallium(III) acetate in various alcohols at room temperature for 0.5—24 hr. The reaction proceeded with decreasing order through the following series of alcohols as solvent; methyl>ethyl>*n*-propyl, *n*-butyl>*i*-propyl, *i*-butyl≫*t*-butyl, reflecting both steric and polar factors of the solvents. Thus in methanol the reaction was almost completed at 0 °C after 15 min, while the corresponding compound was scarcely obtained in *t*-butanol even by stirring at 20 °C for 2 days. Thallium(III) isobutyrate could also be used instead of the acetate for the preparation of methoxy- and ethoxy-thallium(III) compounds of styrene, but a longer reaction time was required. Similar oxythallium(III) compounds were obtained from α-methylstyrene using thallium(III) acetate in methanol or ethanol, but not in higher alcohols under similar reaction conditions. All the compounds isolated were white amorphous solids, soluble in polar solvents and recrystallized from benzene. The reaction conditions for the preparation of I and the yields, melting points, and analytical data of I are summarized in Table 1 (Eq. (1)).



(1)

[I]

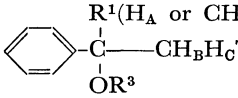
IR spectra (paraffin and hexachlorobutadiene mulls) of I (R^1=H, R^2=R^3=CH_3) showed four strong absorption bands in the acetate region which are assignable to two ν_{asym} (CO_2) (1600 and 1525 cm^{-1}) and two ν_{sym} (CO_2) (1422 and 1390 cm^{-1}) (Table 2). This suggests the presence of two types of acetate group, namely a bridging acetate group (1525 and 1422 cm^{-1}; strong and slightly broad) and a non-bridging one (1600 and 1390 cm^{-1}; strong and sharp), as in the case of methyl, ethyl and phenylthallium(III) dicarboxylates which were reported by Kurosawa and Okawara,[9] and Lee.[10] The expected large Tl–H spin-spin couplings were observed in NMR spectra (in $CDCl_3$ or CD_3OD) of I, but the clear separation of $J_{^{205}Tl-H}$ and $J_{^{203}Tl-H}$ was not obtained. Contrary to the known result that in ethyl-or *n*-propylthallium(III) compounds $J_{Tl-\beta-H}$ is generally larger than $J_{Tl-\alpha-H}$,[9a,11] the coupling constants of Tl-methylene protons ($J_{Tl-H_B \text{ or } H_C}$) in I were larger than that of Tl-methine proton (J_{Tl-H_A}) (Table 2). Similar result has been reported in the acetoxythallated compound of norbornene where

Table 1. Reaction conditions of alkoxythallation of styrene and α-methylstyrene and characterization of I

Olefin R^1 (mmol)	Tl-salt R^2 (mmol)	Alcohol R^3 (50 ml)	React. temp. (°C)	React. time (hr)	I Yield[a] (%)	I Mp(dec) (°C)	I Analysis Found (Calcd) C	I Analysis Found (Calcd) H
H	CH_3	CH_3	20	0.5	86	127—128[b]	33.9(34.1)	3.6(3.7)
H	CH_3	C_2H_5	20	1.3	60	115	35.5(35.6)	4.1(4.0)
H	CH_3	n-C_3H_7	20	4	72	103	37.0(37.2)	4.3(4.3)
H	CH_3	i-C_3H_7	20	22	64	115—117	37.1(37.2)	4.4(4.3)
H	CH_3	n-C_4H_9	20	2	60	118—119	38.2(38.6)	4.5(4.6)
H	CH_3	i-C_4H_9	25	15	58	102—103	39.0(38.6)	4.9(4.6)
H	i-C_3H_7	CH_3	20	24	60	124—125	39.8(39.7)	4.8(4.9)
H	i-C_3H_7	C_2H_5	25	24	74	91.5—93	38.7(41.0)[c]	4.8(5.2)
CH_3	CH_3	CH_3	20	0.5	70	134	35.6(35.6)	3.9(4.0)
CH_3	CH_3	C_2H_5	20	20	58	121—122	36.3(37.2)	4.1(4.3)

a) Based on Tl(III) salt charged. b) Reported,[2] 127.5—128 °C. c) After recrystallization four times from chloroform.

Table 2. Carboxylate absorption bands (in cm^{-1})[a] and J_{Tl-H} (in Hz) and δ (in ppm)[b,c] of I



I R^1	I R^2	I R^3	J_{Tl-H_B} (δ_B)	J_{Tl-H_C} (δ_C)	J_{Tl-H_A} (δ_A)	$J_{Tl-CH_3(R^1)}$ (δ)	$\nu_{asym}(CO_2)$		$\nu_{sym}(CO_2)$	
H	CH_3	CH_3	760 (3.07)	920 (3.17)	748 (4.58)	—	1600(s)	1525(s)	1422(s)	1390(s)
H	CH_3	C_2H_5	768 (3.08)	921 (3.11)	737 (4.82)	—				
H	CH_3	n-C_3H_7	768 (3.07)	929 (3.18)	751 (4.66)	—				
H	CH_3	i-C_3H_7	786 (3.07)	921 (3.19)	818 (4.85)	—				
H	CH_3	n-C_4H_9	774 (3.03)	934 (3.18)	757 (4.66)	—	1600(s)	1530(s)	1425(s)	1380(s)
H	CH_3	i-C_4H_9	772 (3.07)	917 (3.18)	828 (4.65)	—	1598(s)	1527(s)	1415(s)	1380(sh)
H	i-C_3H_7	CH_3	758 (3.05)	906 (3.13)	752 (4.60)	—	1586(s)	1505(s)	1415(m)	1392(m)
H	i-C_3H_7	C_2H_5	759 (3.03)	904 (3.13)	716 (4.70)	—				
CH_3	CH_3	CH_3	810 (3.23)	892 (3.20)	—	29 (1.76)	1608(s)	1530(s)	1424(s)	1375(s)
CH_3	CH_3	C_2H_5	822 (3.25)	890 (3.17)	—	29 (1.76)				

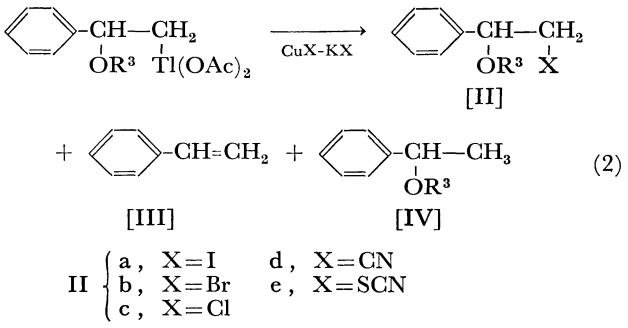
a) Paraffin and hexachlorobutadiene mulls. In methylthallium(III) diacetate, 1613(s), 1530(s), 1428(s), and 1375(s) cm^{-1} were the observed bands.[9b] b) $CDCl_3$ and CD_3OD solvent; TMS as the internal standard. c) In ethylthallium (III) diisobutyrate, $J_{Tl-CH_2\underline{CH_3}}$ of 1626 Hz and $J_{Tl-\underline{CH_2}}$ of 822 Hz were reported.[9a]

$J_{Tl-\alpha-H}$ is larger than $J_{Tl-\beta-H}$ and this was attributed to a possible geometric effect in rigid molecule.[12] Since the interaction between mercury and oxygen is proposed in the oxymercuration of cycloalkenols,[13] it may be possible to assume that in I thallium interacts with oxygen of alkoxy group to restrict free rotation of C_α–C_β bond in some extent. This may be one reason for the unexpected small value of J_{Tl-H_A} in I. Electronic absorption spectra (in EtOH) of I showed a maximum at 226 mμ, and ε of I (R^1=H, R^2=R^3=CH_3), I (R^1=H, R^2=CH_3, R^3=C_2H_5) and I (R^1=H, R^2=i-C_3H_7, R^3=CH_3) were 1.8×10^4, 1.4×10^4 and 2.1×10^4, respectively.

From β-methylstyrene no alkoxythallium(III) compounds were isolated using methanol and ethanol as solvents after stirring at 20 °C for 5 hr. Similarly, attempts to isolate oxythallium(III) compounds from cyclohexene were unsuccessful either with thallium(III) acetate in chloroform or chloroform–acetic acid (10 : 1) as solvents, or with thallium(III) trifluoro-

acetate in trifluoroacetic acid–*n*-pentane (1 : 5) as solvent at 15 °C.

Reaction of Alkoxythallium(III) Compounds of Styrene with Copper Salts. A mixture of I (R^1=H, R^2=CH_3) and the copper(I) salt and/or potassium salt was stirred for 5 hr under reflux in various organic solvents such as acetonitrile, 1,4-dioxane, THF, methanol, chloroform, and DMF. As a result thallium was replaced by halogen or pseudohalogen to afford II along with small amounts of styrene [III] and α-alkoxyethylbenzene [IV], acetonitrile being the solvent of choice for the preparation of II (Eq. (2)). Although in the cases of iodide and thiocyanate the reaction



(2)

proceeded with the potassium salt alone as reported by Mitani *et al.*[7] in thiocyanate case, the addition of the corresponding copper(I) salts was found to increase the yield of II in both cases. For chloride, bromide, and cyanide, however, a replacement of thallium by halogen or pseudohalogen scarcely occurred with the potassium salt alone, while II was obtained in good yield using the corresponding copper(I) salts. Interestingly, the addition of the potassium salt to the reaction system containing copper(I) salt caused a remarkable improvement in the yield of II. In contrast to the aryl carbon–Tl bond,[8] the alkyl carbon–Tl bond of I was cleaved usually by copper(I) salts, and not so readily by copper(II) salts.

From the reaction using I (R^1=H, R^2=R^3=CH_3), the by-products such as phenylacetaldehyde [V], α-methoxy-β-acetoxy- [VI], β-acetoxy-β-methoxy- [VII], and β,β-dimethoxyethylbenzenes[VIII] were sometimes obtained, the distribution and the amount of these depending on the reaction conditions. These compounds are obviously the decomposition products of I, because, for example, Kabbe[2] reported the formation of VIII by stirring I (R^1=H, R^2=R^3=CH_3) in methanol at 65 °C for 4 days (64% yield). We have also examined the decomposition of I (R^1=H, R^2=R^3 CH_3) in various solvents by refluxing for 5 hr (without any copper and/or potassium salts) and the results in acetonitrile, 1,4-dioxane and methanol were shown in Eq. (3) where the yields of III and V were less than 3%. Only a slight amount of the decomposition products was formed in DMF, THF, CH_2Cl_2, and CCl_4.

a. Iodination (Table 3). Although the reaction mixture was heterogeneous in acetonitrile because of the insolubility of copper(I) iodide, the good yield of IIa was obtained in this solvent. Small or trace amounts of III and IV were always detected as by-products. Though IIa was obtained using either po-

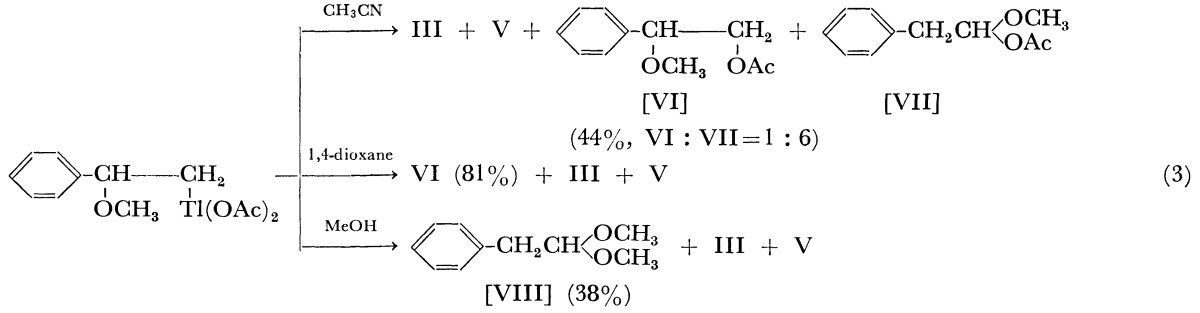


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Table 3. Results of iodination

Reaction time, 5 hr

I(R^1=H, R^2=CH_3) R^3 (5 mmol)	CuI (mmol)	KI (mmol)	Solvent (25 ml)	React. Temp. (°C)	Products (yield, %)[a]			Remarks
					IIa	III	IV	
CH_3	0	10	CH_3CN	81	64	trace	trace	V s. a.[b]
CH_3	10	0	CH_3CN	81	68	17	trace	V s. a.
CH_3	5	5	CH_3CN	81	71	5	trace	V s. a.
CH_3	5	10	CH_3CN	81	89	2	trace	V s. a.
C_2H_5	5	10	CH_3CN	81	82	trace	trace	V s. a.
n-C_3H_7	5	10	CH_3CN	81	73	2	trace	V s. a.
n-C_4H_9	5	10	CH_3CN	81	72	5	trace	V s. a.
CH_3	0	10	1,4-dioxane	101	21	trace	trace	VI 74
CH_3	10	0	1,4-dioxane	101	35	19	3	VI s. a.
CH_3	5	5	1,4-dioxane	101	44	15	4	VI s. a.
CH_3	5	10	1,4-dioxane	101	35	trace	26	VI 12
CH_3	5	5	THF	66	46	2	30	

a) Based on I. b) s. a.=a small amount (1—2%).

tassium iodide or copper(I) iodide alone, it was found that the reaction in the presence of both salts gave the best yield of IIa. The reaction of I with iodine or lithium iodide in acetonitrile gave only a trace amount of IIa.

b. Bromination and Chlorination (Table 4). In contrast to the iodination the reaction of I with potassium bromide alone gave only a small amount of IIb, while copper(I) bromide reacted with I to afford IIb in fairly good yield together with small amounts of III, IV, and bis(2-alkoxy-2-phenylethyl)thallium bromide, the disproportionation product of I (see Experimental). The yield of IIb was increased by the addition of potassium bromide as in the case of iodination. The addition of potassium chloride instead of the bromide also improved the yield of IIb and an additional formation of a small amount of IIc was observed in this case. Acetonitrile and methanol were revealed to be the solvent of choice, and 1,4-dioxane, DMF, and $CHCl_3$ could also be used as solvents, although the selectivity for IIb was low in the last three solvents. While it has been reported that methyl thallium diacetate reacted readily with aqueous solution of sodium chloride, bromide, or iodide to give the corresponding methyl halide,[9a] the reaction of I with potassium bromide in water at 20 °C or 100 °C for 1 hr afforded III, V, a trace amount of IIb, and thallium(I) bromide. The yields of III and V were 3% and 56% at 20 °C, and 2% and 31% at 100 °C respectively. This fact means that in water as solvent the decomposition of I to V and III is much faster than the formation of alkyl halide and that the nature of C–Tl bonds of I and methylthallium diacetate is different in some way. None of IIb was obtained from the reaction of I with copper(II) bromide in acetonitrile as solvent. The reaction of I with bromine in acetonitrile did not give any of IIb at 81 °C for 5 hr.

While only a slight amount of IIc was obtained from the reaction of I with potassium chloride in acetonitrile, the reaction proceeded smoothly in the presence of both copper(I) and potassium chlorides in the same solvent to afford IIc, III and IV. Here, the selectivity and also the yield of IIc were slightly lower than those of iodination and bromination. When the reaction of I with copper(I) chloride was carried out in the presence of potassium bromide, IIb and IIc were obtained, being the former predoninant. Bis(2-alkoxy-2-phenylethyl) thallium chloride was also obtained in a small amount as in the case of bromination and it became apparent that such disproportionated compounds could be formed in the presence of copper(I) halide and irrespective of the presence of potassium halide. Thus, bis-(2-methoxy-2-phenylethyl) thallium bromide and chloride were obtained in 15—20% yield by refluxing I (R^1=H, R^2=R^3=CH_3) and copper(I) bromide or chloride in acetonitrile respectively (see experimental part), and the disproportionation product[14] of I (R^1=H, R^2=CH_3, R^3=*n*-C_3H_7) was obtained in 10% yield

Table 4. Results of bromination and chlorination

I(R^1=H, R^2=CH_3) R^3 (5 mmol)	Cu salt (mmol)	K salt (mmol)	Solvent (25 ml)	React. temp. (°C)	React. time (hr)	Products (yield, %)[a] IIb	IIc	III	IV	Remarks
CH_3	0	KBr 10	CH_3CN	81	5	6	0	trace	0	V 24 VI 4
CH_3	CuBr 10	0	CH_3CN	81	1	29	0	5	trace	R_2TlBr[b] 20
CH_3	CuBr 10	KCl 10	CH_3CN	81	1	40	1	3	1	
CH_3	CuBr 10	0	CH_3CN	81	5	53	0	12	trace	R_2TlBr s. a.[c]
CH_3	CuBr 5	KBr 5	CH_3CN	81	5	69	0	4	4	R_2TlBr s. a.
CH_3	CuBr 10	KBr 10	CH_3CN	81	5	87	0	3	4	R_2TlBr s. a.
CH_3	CuBr 10	KBr 20	CH_3CN	81	5	83	0	4	4	R_2TlBr s. a.
C_2H_5	CuBr 10	KBr 10	CH_3CN	81	5	86	0	2	2	R_2TlBr s. a.
n-C_3H_7	CuBr 10	KBr 10	CH_3CN	81	5	79	0	3	4	R_2TlBr s. a.
n-C_4H_9	CuBr 10	KBr 10	CH_3CN	81	5	68	0	7	2	R_2TlBr s. a.
CH_3	CuBr 10	KBr 10	MeOH	56	5	84	0	2	0	VII 2 VIII trace
CH_3	CuBr 10	KBr 10	1,4-dioxane	101	5	38	0	36	trace	VI 20
CH_3	CuBr 10	KBr 10	DMF	80	5	54	0	10	trace	V 4
CH_3	CuBr 10	KBr 10	$CHCl_3$	61	5	72	0	9	6	VII 5
CH_3	CuBr 10	KBr 10	pyridine	117	5	0	0	2	0	
CH_3	0	KCl 10	CH_3CN	81	5	0	3	2	1	VI 4, VII 14 $RTlCl_2$ 15
CH_3	CuCl 10	0	CH_3CN	81	1	0	27	trace	1	R_2TlCl 15
CH_3	CuCl 10	KCl 10	CH_3CN	81	1	0	36	2	2	R_2TlCl 10
CH_3	CuCl 10	KBr 10	CH_3CN	81	1	27	12	3	2	
CH_3	CuCl 10	KCl 10	CH_3CN	81	5	0	59	18	7	R_2TlCl s. a.
C_2H_5	CuCl 10	KCl 20	CH_3CN	81	5	0	50	8	6	R_2TlCl s. a.
n-C_3H_7	CuCl 10	KCl 20	CH_3CN	81	5	0	60	9	6	R_2TlCl s. a.
n-C_4H_9	CuCl 10	KCl 20	CH_3CN	81	5	0	45	9	2	R_2TlCl s. a.

a) Based on I. b) R=$C_6H_5CH(OCH_3)CH_2$ c) s. a.=a small amount (2—8%).

Table 5. Results of cyanation and thiocyanation

Acetonitrile as solvent 25 ml; React. temp 81 °C; React. time 5 hr

I(R^1=H, R^2=CH_3) R^3 (5 mmol)	Cu salt (mmol)		K salt (mmol)		Products (yield, %)[a] IId	IIe	III	IV	Remarks
CH_3	0		KCN	10	0	0	trace	0	
CH_3	CuCN	10	0		74	0	6	trace	VII 14
CH_3	CuCN	10	KCN	10	3	0	trace	trace	V 6, VI 5, VII 14
CH_3	CuCN	10	KBr	10	86	0	5	4	IIb trace
CH_3	CuCN·C_5H_5N[b]	10	0		65	0	2	trace	VII 7
CH_3	CuBr	10	KCN	10	60	0	6	4	IIb 5
CH_3	K[Cu(CN)$_2$][c]	10	0		1	0	1	1	V 2, VII 3
C_2H_5	CuCN	10	KBr	10	74	0	7	10	IIb trace
n-C_3H_7	CuCN	10	KBr	10	68	0	3	11	IIb trace
n-C_4H_9	CuCN	10	KBr	10	62	0	3	6	IIb trace
CH_3	Cu(CN)$_2$	5	0		48	0	6	0	VII 16
CH_3	0		KSCN	10	0	72	trace	trace	
CH_3	CuSCN	10	0		0	44	3	9	VII 8
CH_3	CuSCN	5	KSCN	10	0	96	0	0	
CH_3	Cu(NCS)$_2$	10	0		0	23	0	trace	V 7, VII 26

a) Based on I. b) CuCN-pyridine (1 : 1) complex. c) CuCN-KCN (1 : 1) complex.

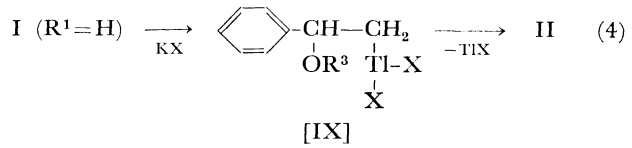
(after recrystallization from methanol) together with IIc (35%) and small amounts of III, IV, and VI by refluxing I (10 mmol) and copper(I) chloride (20 mmol) in acetonitrile for 5 hr. None of IIc was obtained from the reaction of I with copper(II) chloride in acetonitrile as solvent.

c. Cyanation and Thiocyanation (Table 5). I did not react with potassium cyanide to give IId, while a good yield of IId was obtained from the reaction of I with copper(I) cyanide in acetonitrile. In contrast to the halogenation described above, the addition of potassium cyanide to the reaction mixture of I and copper(I) cyanide lowered strongly the yield of IId. Instead of potassium cyanide, potassium bromide showed some effect for improving the yield of IId with a formation of only a trace amount of IIb. Small amounts of disproportionated organothallium(III) compounds were sometimes detected as in the case of halogenation. The reaction seemed to be strongly affected by the kind of solvent and almost no reaction was observed in other solvents such as pyridine, 1,4-dioxane, and methanol which were the good solvents for the reaction of arylthallium(III) compounds with copper cyanide.[8b] Copper(II) cyanide could also be used for this reaction, but the activity was inferior to copper(I) salt. No isonitrile compounds were detected in all cases.

For thiocyanation, I(R^1=H, R^2=R^3=CH_3) is known to react easily with potassium thiocyanate to give IIe.[7] We found that copper(I) thiocyanate also reacted with I to give IIe, the best yield of which was obtained in the presence of both of copper(I) and potassium thiocyanates. The reaction with copper(II) thiocyanate afforded IIe in a low yield together with considerable amounts of the decomposition products. None of isothiocyanate compounds were obtained in all cases.

d. Attempts of the Reactions of I with Copper(II) Fluoride and Some Other Metal Salts. The reaction of I (R^1=H, R^2=R^3=CH_3) with copper(II) fluoride dihydrate in dioxane at refluxing temperature gave only the decomposition products such as V and VI together with α-methoxyethylbenzene. Similarly none of fluorinated compounds were obtained from the reaction even in the presence of potassium fluoride in DMF or acetonitrile as solvents. No appreciable reaction of I was observed with copper(II) acetate or acetylacetonate. In acetonitrile as solvent mercury(II) and silver cyanides or iron(II) chloride hydrate did not react with I to give IId or IIc respectively.

e. Some Consideration on the Reaction Scheme of Halogenation and Pseudohalogenation. Although it has been known that no substitution of mercury by halogen or pseudohalogen occurs in the reaction of oxymercurated compounds of olefins with potassium iodide, cyanide, or thiocyanate,[15] thallium in I was readily substituted by iodide or thiocyanate to afford IIa or IIe as described above. As proposed by Mitani *et al.*,[7] this reaction may proceed through the exchange of the acetate ligand of I by group X giving very unstable alkylthallium(III) diiodide or dithiocyanate [IX] followed by an intramolecular migration of X to alkyl carbon (Eq. (4)). For chloride and bromide, IX seemed to be rather stable and did not give II readily. We will describe in a separate paper about the isolation of IX (X=Cl or Br).



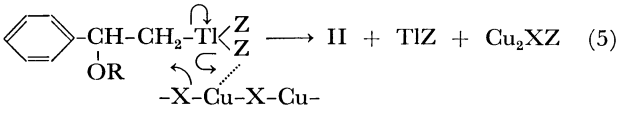
(4)

In connection to this observation, it should be noted here that mercury in the oxymercurated compound of olefins has been known to be substituted electrophilically by iodine or bromine molecule,[15] while no such reaction was observed with I as described above. These facts may be explained by the difference of the oxidation potential between Hg and Tl; namely a reductive

cleavage of carbon-metal bonds would be much easier in thallium compound than in mercury one and so a favorable nucleophilic attack on carbon can be expected for the former and a favorable electrophilic attack for the latter.

Next the reaction scheme of I with copper salts should be considered. In contrast to the reaction of arylthallium(III) salt with copper salts,[8] it is not necessary to use copper(II) salt in this case. This fact may be explained as follows. Since it has been stated[16] that Pd(II) aryls are more stable than Pd(II) alkyls and require stronger oxidants to decompose them, it seems reasonable to assume that Tl(III) alkyls do not require stronger oxidant compared to Tl(III) aryls if the latter is more stable than the former. In fact arylthallium(III) compounds were quite stable and did not give any appreciable amount of decomposition products under the conditions shown in Eq. (3) where I gave many products. The reason why I did not react with copper(II) salts in acetonitrile so readily is not certain at present but the choice of a suitable solvent may improve the yield of II. Thus, the reaction of I with copper(II) bromide in the presence of potassium bromide in pyridine at refluxing temperature for 1 hr gave a 20% yield of IIb, while IIc was obtained in 30—50% yield by the reaction using copper (II) chloride in pyridine or dioxane as solvent.

As to the halogenation and pseudohalogenation of I with copper(I) salts, first, the reaction does not appear to involve radicals because the reaction of I (5 mmol) with copper(I) and potassium bromides (both of 10 mmol) in the presence of acrylonitile (10 mmol) at 81 °C for 5 hr in acetonitrile as solvent under N_2 gave neither polyacrylonitrile nor alkylated acrylonitrile[17] even though an appreciable amount of IIb (53% yield) was still obtained. Second there is no evidence of the substitution of thallium with copper salt, because none of α-alkoxystyrene or acetophenone and copper metal was obtained which may be derived from alkylcopper compound if formed.[18] Third a free carbonium cation is not formed in the reaction because halogenation or pseudohalogenation occurred at the position where thallium was attached previously, and none of phenyl migrated compounds was detected in the products. Fourth there is a clear difference in product distributions between the reaction with potassium salt alone and that with copper(I) salt alone in polar acetonitrile solvent. This may suggest that direct attack of unionized copper(I) species is operative. Considering all these facts an ionic concerted intermolecular scheme shown in Eq. (5) seems to be most reasonable.



$$\longrightarrow \text{II} + \text{TlZ} + \text{Cu}_2\text{XZ} \quad (5)$$

Coordination of the ligand on Tl with copper (shown in dotted line) may be one of the driving forces of the reaction. In fact the reaction of I with copper(I) bromide in strong complexing solvent such as pyridine or *N,N*-tetramethylethylenediamine gave none of II at refluxing temperature for 5 hr, while IId was obtained in good yield (65%) in acetonitrile from the reaction of I with copper(I) cyanide–pyridine (1 : 1) complex where a coordination site of copper is still vacant.

As has been described above, the addition of potassium salt to the reaction mixture showed a remarkable effect for improving the yield of II. The reasons for this effect may be as follows. The solubility of copper(I) salt in solvents is increased by the coordination between potassium and copper salts, and the coordination makes Cu–X bond loosen and the attack of X on carbon easy. For example, 1.15 g out of 1.43 g (10 mmol) of copper(I) bromide or only 0.05 g out of 1.19 g (10 mmol) of potassium bromide was soluble in 25 ml of acetonitrile at 81 °C, while 1.51 g out of 2.62 g of a mixture of both bromides (each of 10 mmol) was soluble in the same amount of acetonitrile at 81 °C. It should be also noted that the deoxythallation of I to give styrene was prevented in the presence of potassium iodide, bromide, or thiocyanate. For cyanation with copper(I) cyanide, however, the addition of potassium cyanide prevented the formation of IId. This may be due to the formation of the unreactive coordination compound, $K[Cu(CN)_2]$, which is known to have a spiral polymeric structure in which each Cu atom is covalently bound to two carbon atoms and one nitrogen atom.[19] In fact the reaction of I with this compound prepared separately gave only 1% yield of IId in acetonitrile as solvent. When the reaction of I with copper(I) cyanide and potassium bromide was carried out in acetonitrile, IId was the main product and IIb was obtained only in a trace amount. In contrast to this, it may be interesting to note that the reaction of I with a mixture of copper(I) bromide and potassium cyanide in the same solvent, which was refluxed for 1 hr before the addition of I, gave a small amount of IIb and the main product was IId in this case. In connection to this the following observations are worth to refer. As shown in Table 4, the reaction of I with copper(I) bromide in the presence of potassium chloride gave almost IIb, while with copper(I) chloride and potassium bromide a mixture of IIc and IIb was obtained under similar conditions, the former being a minor product. These results can be explained by the consideration of the equilibrium shown in Eqs. (6) and (7) which are based on the HSAB principle;[20] *i.e.*, Cu^+ is soft acid and $CN^- > Br^- > Cl^-$ are soft bases with decreasing order of softness.

$$\text{CuCl} + \text{KBr} \rightleftarrows \text{CuBr} + \text{KCl} \quad (6)$$

$$\text{CuBr} + \text{KCN} \rightleftarrows \text{CuCN} + \text{KBr} \quad (7)$$

Although the precise nature of the formation of III and IV is uncertain at present, it is noteworthy to refer to the following facts. As to the formation of III, it is clear that the deoxythallation of I giving III was catalyzed by copper salt, because the amount of III formed is larger at the reactions in the presence of copper salt than at those without it. Halogen acid such as hydrogen chloride has been known to accelerate the deoxymercuration of alkoxymercurated compounds of olefins[21] and the elimination of the alkoxy group giving mercurinium ion followed by demercuration has been proposed as the reaction mechanism.[21] We

observed similar phenomena in I (R^1=H, R^2=R^3=CH_3) which gave 73% yield of III and 93% of Tl^{3+} salt by the reaction with hydrogen chloride (0.2 M) in an aqueous ethanol solvent under stirring at 20 °C for 2 hr. This fact suggests that similar reaction mechanism may be operative for the formation of III in Tl case as well. Copper salt may help the elimination of alkoxy group in the present reactions. In connection to the formation of IV, it is interesting to note that the action of water[22] or hydrogen iodide[23] on trialkylthallium split off the corresponding hydrocarbon RH and that the reaction of diorganothallium(III) carboxylate with tetramethyltin in methanol[24] gave also a hydrocarbon. This protodethallation can be explained by an electrophilic substitution on carbon by hydrogen. The action of water, which may exist in solvent or metal salts, on I might give IV by similar reaction scheme, but more work should be necessary to discuss it.

Experimental

The IR spectra were taken with Hitachi EPI-S2 and Perkin-Elmer 521 spectrometers in paraffin and hexachlorobutadiene mulls. The UV and visible spectra were taken with Hitachi EPS-2U spectrometer using ethanol as solvent. The NMR spectra were recorded by a Varian A-60 spectrometer in $CDCl_3$ or CD_3OD as solvents, using TMS as the internal standard. The glc analyses were carried out on Shimadzu 5APTF and 4BMPF apparatus, using PEG 6000 (25%)-Chromosorb W (3m) and Apiezon L (30%)-Celite (1 and 3m) columns (N_2 as the carrier gas).

Materials. All the organic materials except the alkoxythallium(III) compounds of olefins were purified before use by distillation, while commercially available copper and and potassium salts and other inorganic materials were used without further purification. $Cu(NCS)_2$ was prepared by the reported method from $CuSO_4 \cdot 5H_2O$ and KSCN.[25] Copper(I) cyanide-pyridine (1 : 1) complex was prepared by the same method reported previously.[8a] $K[Cu(CN)_2]$[26] was prepared by stirring 77 mmol of KCN and 39 mmol of CuCN in 20 ml of water at 20 °C for 2 hr, collecting white crystals (3.3 g) precipitated after evaporating the reaction mixture to 5 ml, washing with a small amount of water and drying over silica gel; yield 54% (Found: C, 15.66; N, 18.68%. Calcd for C_2N_2KCu: C, 15.53; N, 18.11%). Thallium(III) acetate and isobutyrate were prepared by stirring thallium(III) oxide in acetic acid and isobutyric acid at 65 °C for 20 hr and at 90 °C for 2 hr respectively, collecting white amorphous crystals formed after cooling, and drying over CaO.

Preparation of Alkoxythallium(III) Compounds of Olefins, I. The following example of I (R^1=R^2=R^3=CH_3) shows a typical experimental procedure. To a yellow-orange homogeneous solution of thallium(III) acetate (19.4 g, 0.05 mol) in methanol (50 ml), α-methylstyrene (11.8 g, 0.1 mol) was added drop by drop at 15—20 °C. The mixture was stirred at 20 °C for 30 min during which period the color of the homogeneous solution turned to colorless. The mixture was added by 200 ml of petroleum ether (30—70 °C), stored in an ice-box at −10 °C for 2 hr. The white precipitates of I (R^1=R^2=R^3=CH_3) (16.0 g, 70% yield) thus formed were collected by filtration and were recrystallized from benzene. I is very soluble in pyridine, DMF, DMSO, carbon disulfide, methanol, acetic acid, and dichloromethane, soluble in acetone, acetonitrile, dioxane, nitromethane, chloroform, dichloroethane, ethanol, ethyl acetate, diglyme, THF, and sparingly soluble in ether, benzene, petroleum ether (30—70 °C), carbon tetrachloride, and water. NMR spectral data of I except those of methine and methylene protons shown in Table 2 are as follows: δ 2.0 (s, 6H, $OCOCH_3$) when R^2 is methyl; 1.23 (d, 12H, J_{H-H}=7 Hz, $-COCH(CH_3)_2$) and 2.57 (septet, 2H, J_{H-H}=7 Hz, $OCOCH(CH_3)_2$) when R^2 is isopropyl; some peaks due to respective alkoxy group; 6.9—7.7 (m, 5H, phenyl).

Decomposition of I (R^1=H, R^2=R^3=CH_3) in Dioxane. A mixture of I (4.58 g, 10 mmol) and dioxane (50 ml) was stirred for 5 hr at 100 °C. The precipitates thus formed (TlOAc: 1.53 g, 5.8 mmol) were filtered off after cooling and the filtrate was added by 200 ml of water and extracted with *n*-hexane. Glc analysis of a part of the extract using ethyl cinnamate as the internal standard showed that the products were VI (81%) and slight amounts of III and V. After drying over Na_2SO_4, the extract was distilled to give 1.0 g (52% yield) of VI; bp 103—110 °C/8 mmHg. NMR δ 2.07 (s, 3H, $OCOCH_3$), 3.30 (s. 3H, OCH_3), 4.12—4.48 (m, 3H, $>CHCH_2-$), 7.35 (s, 5H, phenyl). Found: C, 67.99; H, 7.43%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

Decomposition of I (R^1=H, R^2=R^3=CH_3) in Acetonitrile. After I (4.58 g, 10 mmol) was stirred in acetonitrile (50 ml) for 5 hr at 80 °C, the reaction mixture was worked up as described above. Glc analysis of the extract showed that the products were III (1.5%), VI (6%) and VII (38%). Distillation of the extract gave a mixture of VI and VII (VI : VII=1 : 3.5; 0.3 g); bp 65—76 °C/5 mmHg. NMR of VII, δ 2.00 (s, 3H, $OCOCH_3$), 2.93 (d, 2H, J_{H-H}=5.5 Hz, $-CH_2-$), 3.33 (s, 3H, OCH_3), 5.81 (t, 1H, J_{H-H}=5.5 Hz, $-CH\langle$), 7.17 (s, 5H, phenyl). Analysis of the mixture of VI and VII; Found: C, 67.78; H, 7.40. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

Formation of Bis(2-methoxy-2-phenylethyl)thallium Bromide and Chloride. A pale green heterogeneous mixture of I (R^1=H, R^2=R^3=CH_3) (2.29 g, 5 mmol) and copper(I) bromide (1.43 g, 10 mmol) in acetonitrile (25 ml) was stirred at 81 °C for 1 hr during which period the colour of the solution turned to deep green. After the reaction mixture was cooled down, the pale yellow precipitates (1.59 g, IR inactive) thus formed were filtered off and water (200 ml) was added to the filtrate to afford 0.40 g of white solids which were revealed to be bis(2-methoxy-2-phenylethyl)thallium bromide. Recrystallization from acetonitrile gave 0.27 g of pure white needle crystals (19.5% yield based on I). IR; 1088 (s)cm^{-1} (ν_{C-O}); mp>300 °C. Found: C, 38.82; H, 4.02%. Calcd for $C_{18}H_{22}O_2BrTl$: C, 38.98; H, 4.00%.

The same procedure using copper(I) chloride gave white amorphous solid of bis(2-methoxy-2-phenylethyl)thallium chloride (0.19 g after recrystallization from acetonitrile; 14.9 % yield based on I). IR; 1090 (s)cm^{-1} (ν_{C-O}); mp, slowly decomposed over 205 °C. Found: C, 42.02; H, 4.42%. Calcd for $C_{18}H_{22}O_2ClTl$ C, 42.38; H, 4.35%.

Reaction of I with Copper Salts. The following example shows a typical experimental procedure.

Reaction of I(R^1=H, R^2=R^3=CH_3) with Copper(I) Cyanide in the Presence of Potassium Bromide. A white heterogeneous solution of I (2.29 g, 5 mmol), copper(I) cyanide (0.89 g, 10 mmol), and potassium bromide (1.19 g, 10 mmol) in acetonitrile (25 ml) was stirred at 81 °C for 5 hr during which period the blue precipitates came out gradually. The reaction mixture was worked up as in the case of the decomposition of I in dioxane and glc analysis of the benzene extract showed that the products were IId (R^3=CH_3) (86%), III (4%), IV (R^3=CH_3) (4%) and a trace amount of IIb. Distillation of the extract gave 0.76 g of pure IId; bp 109—

110 °C/5 mmHg. IR; 2250 (ν_{CN}) 1106 (ν_{C-O}), 760 and 703 (phenyl) cm^{-1}. NMR: δ 2.70 (d, 2H, J=6 Hz), 3.29 (s, 3H), 4.44 (t, 1H, J=6 Hz), 7.36 (s, 5H). All the other cyano compounds were isolated by distillation respectively, and explained reasonably by IR and NMR spectra. IId (R^3=C_2H_5), bp 140—142 °C/18 mmHg. IId (R^3=n-C_3H_7), bp 120—122 °C/6 mmHg. IId (R^3=n-C_4H_9), bp 139—140 °C/9 mmHg. Some spectroscopic data and boiling point of other II are as follows. IIa (R^3=CH_3), bp 105—108 °C/6 mmHg (lit,[27] bp 107—108 °C/5 mmHg). IIa (R^3=C_2H_5), bp 110—112 °C/6 mmHg [lit,[28] bp 142—144 °C/14 mmHg]. IIa (R^3=n-C_3H_7), bp 121—122 °C/6 mmHg, IR: 1110 (ν_{C-O}), 760 (phenyl), 700 (phenyl) and 580 (ν_{C-I}) cm^{-1}. NMR: δ 0.73 (t, 3H, J=7 Hz), 1.60 (m, 2H, J=7 Hz), 3.31 (d, 2H, J=6 Hz), 3.32 (t, 2H, J=7 Hz), 4.38 (t, 1H, J=6 Hz) and 7.32 (s, 5H). Found: C, 41.09; H, 4.24%. Calcd for $C_9H_{11}OI$: C, 41.24; H, 4.23%. IIa (R^3=n-C_4H_9), bp 124—125 °C/5 mmHg. IIb (R^3=CH_3), bp 98—99 °C/7.5 mmHg (lit,[29] bp 117—118 °C/15 mmHg), IR 1115 (ν_{C-O}), 760 (phenyl), 700 (phenyl) an 600 (ν_{C-Br}) cm^{-1}, NMR: δ 3.29 (s, 3H), 3.47 (d, 1H J=5.5 Hz), 3.48 (d, 1H, J=7 Hz), 4.37 (q, 1H, J=7 Hz and 5.5 Hz) and 7.33 (s, 5H). IIb (R^3=C_2H_5), bp 90—91 °C/4 mmHg (lit,[30] bp 78 °C/2 mmHg). IIb (R^3=n-C_3H_7), bp 96—98 °C/3.5 mmHg (lit,[29] bp 146—148 °C/27 mmHg). IIb (R^3=n-C_4H_9), bp 112—113 °C/4 mmHg (lit,[29] bp 165—166 °C/32 mmHg). IIc (R^3=CH_3), bp 79—82 °C/4 mmHg, (lit,[31] bp 92—93 °C/8 mmHg), IR, 1115 (ν_{C-O}), 756 (phenyl), 725 (ν_{C-Cl}) and 700 (phenyl) cm^{-1}. NMR: δ 3.32 (s, 3H), 3.62 (d, 1H, J=6 Hz), 3.64 (d, 1H, J=7 Hz), 4.37 (q, 1H, J=7 Hz and 6 Hz) and 7.37 (s, 5H). Found: C, 63.79; H, 6.72%. Calcd for $C_9H_{11}OCl$: C, 63.35; H, 6.50%. IIc (R^3=C_2H_5), bp 86—88 °C/5 mmHg (lit,[31] bp 101—103 °C/8 mmHg). IIc (R^3=n-C_3H_7), bp 88—91 °C/4 mmHg (lit,[31] bp 111—112 °C/8 mmHg). IIc (R^3=n-C_4H_9), bp 98—101 °C/4 mmHg (lit,[31] bp 122—125 °C/8 mmHg). IIe (R^3=CH_3), bp 146—147 °C/9 mmHg, IR, 2150 (ν_{SCN}), 1105 (ν_{C-O}), 770 and 700 (phenyl) cm^{-1}. NMR: δ 3.17 (d, 1H, J=6 Hz), 3.18 (d, 1H, J=7 Hz), 3.27 (s, 3H), 4.41 (q. 1H, J=7 Hz and 6 Hz) and 7.33 (s. 5H).

Authentic Samples for Glc Analysis. IV and IIc were prepared by the reported method[32] from styrene, copper(II) chloride and alcohols. α-Methoxyethylbenzene (IV, R^3=CH_3) was also prepared by alkaline $NaBH_4$ reduction of α-methoxy-β-acetoxymercuriethylbenzene: bp 71—72 °C/23 mmHg; NMR δ 1.42 (d, 3H, J=6.5 Hz), 3.20 (s. 3H), 4.28 (q, 1H, J=6.5 Hz) and 7.30 (s, 5H). VIII was prepared by refluxing 5 mmol of I (R^1=H, R^2=R^3=CH_3) for 5 hr in methanol (25 ml) containing 5 mmol of BF_3 etherate; yield 92%, bp 103—108 °C/28 mmHg, NMR δ 2.90 (d. 2H), 3.33 (s, 6H), 4.55 (t, 1H) and 7.28 (s, 5H). All of IIa were also obtained in pure state from the reaction of styrene with copper(II) chloride and potassium iodide in alcohols (at refluxing temperature for 2—3 hr).[33]

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