Acetoxythallation of Acetylenes and the Proto- and Halogenodethallation of the Products

Sakae UEMURA, Hideyuki TARA, Masaya OKANO, and Katsuhiko ICHIKAWA*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

**Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606*

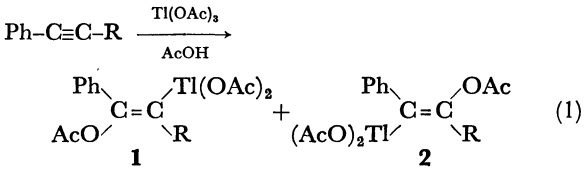
(Received March 29, 1974)

The *trans* acetoxythallation of alkylphenylacetylene with $Tl(OAc)_3$ proceeds in acetic acid at 50—75 °C for 1—3 hr to give a mixture of two isomeric vinylthallium(III) compounds in 54—79% yields, 2-acetoxy-1-alkyl-2-phenyl- and 2-acetoxy-2-alkyl-1-phenylvinylthallium(III) diacetates [$C_6H_5C(OAc)=C(R)-Tl(OAc)_2$ (**1**) and $C_6H_5C(Tl(OAc)_2)=C(OAc)R$ (**2**), where R=Me, Et, *n*-Pr, and *n*-Bu]. Protodethallation of **1** and **2** in refluxing acetic acid occurs with retention of configuration to afford $C_6H_5C(OAc)=C(R)H$ (**3**) and $C_6H_5CH=C(OAc)R$ (**4**), respectively. The reaction of **1** and **2** with $NaBH_4$ in protic solvents at pH 6—7 also gives **3** and **4** with retention of configuration, where the hydrogen for replacement of thallium group comes almost completely (>98%) from the solvent. **1** and **2** are relatively stable to water and dilute HCl, while they readily give ketones in alkaline condition. Halogeno-, cyano-, and thiocyanodethallations of **1** is conducted by reactions with the corresponding copper(II) or (I) salts in acetonitrile to give $C_6H_5C(OAc)=C(R)X$ (X=I, Br, Cl, CN, and SCN) with retention of configuration. Bromodethallation of **1**(R=CH_3) by bromine gives $C_6H_5C(OAc)=C(CH_3)Br$ stereospecifically in pyridine (retention), while α,α-dibromopropiophenone is obtained in CS_2 and acetonitrile.

Oxymercuration and oxythallation of olefins give stable β-alkoxyalkylmercury and β-alkoxyalkylthallium compounds, respectively.[1,2] Oxymercuration of acetylenes affords the β-alkoxyvinylmercury compounds.[3] Although the reaction pathways through oxythallation of acetylenes were postulated in the hydration[4] and oxidation[5] reactions of acetylenes with thallium(III) salts, there has been no report on the successful isolation of oxythallated compounds (the oxythallates) of acetylenes by direct reaction between acetylenes and thallium (III) salts. Recently, Uemura *et al.*[6] and Sharma and Fellers[7] succeeded independently in isolating the oxythallates from alkylphenylacetylenes and dialkylacetylenes, respectively. The thallium group of oxythallates of olefins was replaced by halogens and pseudohalogens by use of the corresponding copper salts[8] and by hydrogen in the reduction with $NaBH_4$ in protic solvents.[9] Arylthallium compounds reacted similarly with such reagents to give aryl halides[10] and pseudohalides.[11] It seems worthwhile examining how the vinylic C–Tl bond of the oxythallates of acetylenes acts towards these reagents in order to compare the nature of the various kinds of C–Tl bonds. We report herewith on the preparation of the oxythallates of alkylphenylacetylenes and also the results of some reactions of the isolated vinylthallium compounds with acetic acid, $NaBH_4$, alkali, halogens, and copper halides, cyanide and thiocyanate.

Results and Discussion

Preparation of Acetoxythallated Compounds of Alkylphenylacetylenes, 1 and 2. Methyl-, ethyl-, *n*-propyl-, and *n*-butyl-phenylacetylenes reacted with $Tl(OAc)_3$ in acetic acid at 50—75 °C for 1—3 hr to give an isomeric mixture of 2-acetoxy-1-alkyl-2-phenylvinylthallium diacetate (**1**) and 2-acetoxy-2-alkyl-1-phenylvinylthallium diacetate (**2**) in 54—79% yield as in the following. The yield of products decreased with an increase in the bulkiness of the alkyl group. The isomer ratios (**1**:**2**) determined by treatment with $NaBH_4$ were 2.8—



(1)

2.5 for Me, 1.9—1.8 for Et, *n*-Pr, and *n*-Bu. A mixture of **1** and **2** was isolated as white amorphous solids, stable in air and soluble in polar solvents, which were recrystallized from alcohols, acetone, CCl_4, 1,2-dichloroethane and benzene. Separation of each isomer was achieved by careful recrystallization from suitable solvents such as methanol, ethanol or diethyl ether. Each of the isomers **1** (R=Me), **1** (R=Et), and **2** (R=Et) was separated in a pure form, but it was not possible to separate either of **1** or **2** having the *n*-propyl or *n*-butyl group. The reaction conditions for the preparation of **1** and **2**, isolated yields, isomer ratios of **1** to **2**, melting points, and analytical data are summarized in Table 1.

The IR spectra (paraffin and hexachlorobutadiene mulls) of **1** and **2** showed strong absorption bands at 1760 and 1640 cm^{-1} due to vinyl ester group, $\nu_{C=O}$ and $\nu_{C=C}$ respectively, together with many bands in the acetate region [1600 (sh), 1560 (s), 1515 (s), 1420 (s, broad), and 1365 (m) cm^{-1}] which can be assigned to both the bridging and non-bridging acetate groups as has been discussed in the cases of aryl- and alkylthallium diacetates.[8,12]

Assignment of the structures of **1** and **2** was best carried out by NMR spectra (in CD_3OD). Coupling constants between Tl and the protons of the methyl or methylene group at allylic position in **1** were 976—1316 Hz, while those in **2** were 116—142 Hz. The values are quite reasonable considering the results reported by Maher and Evans in various organothallium compounds.[13] The aromatic ring protons were coupled with Tl in **2**, J_{Tl-o-H} and J_{Tl-m-H} being 126 and 64 Hz respectively, in contrast to the nearly singlet peak in **1**, showing that Tl was attached to the carbon α and β to phenyl group in **2** and **1**

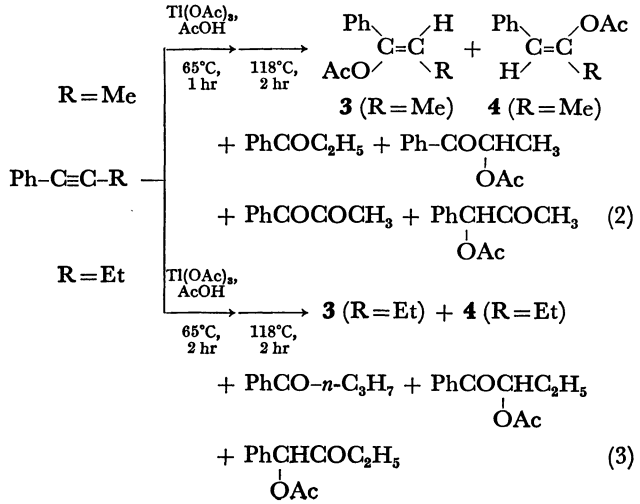
TABLE 1. ACETOXYTHALLATION OF ALKYLPHENYLACETYLENES

Ph-C≡C-R R (mmol)	Tl-$(OAc)_3$ (mmol)	AcOH (ml)	Temp. (°C)	Time (hr)	Products, Yield (%)[a] 1+2	Ratio[b] 1/2	mp(d) (°C)	Analysis Found (Calcd) C	H
CH_3 20	10	10	65	1	75 (89)	2.5	**1** 169—171	36.28 (36.20)	3.40 (3.44)
CH_3 10	5	5	60	2	79 (87)	2.8	**1+2** 135—141	35.95 (36.20)	3.40 (3.44)
C_2H_5 20	10	10	65	2	70 (85)	1.8	**1** 133—135	37.75 (37.56)	3.72 (3.74)
							2 133—134	37.30 (37.56)	3.72 (3.74)
C_2H_5 20	10	10	60	3	71 (85)	1.8	**1+2** 104—114		
n-C_3H_7 20	10	10	65	3	66 (85)	1.9	**1+2** 120—126	38.73 (38.84)	4.23 (4.03)
n-C_4H_9 20	10	10	65	3	54 (73)	1.9	**1+2** 95—105	39.70 (40.06)	4.31 (4.30)

a) Based on $Tl(OAc)_3$ charged. Yields in parentheses were based on $Tl(OAc)_3$ consumed. b) Determined by hydrogenolysis with $NaBH_4$ in methanol.

respectively. The methyl protons of acetoxy group appeared as a doublet (J=13 Hz). This can be attributed to long-range coupling with Tl ($^6J_{Tl-H}$= 3.0 Hz was reported[14]) or through-space coupling with Tl. Since the coupling constant of 142 Hz (J_{Tl-CH_3}) in **2** (R=Me) agrees with that of 144 Hz between Tl on C_3 and methyl protons on C_2 in the 2-acetoxy-3-diacetoxythallium-*trans*-2-butene[7] where acetoxy (on C_2) and thallium (on C_3) are in *trans* position, we may assign the structure of **2** to the *trans*-acetoxythallate. From the NMR data and the structure of **2**, it seems reasonable to assign the structure of **1** as another *trans*-acetoxythallate. We also confirmed this configuration by protolysis and hydrogenolysis of **1**. Structures of **1** and **2** suggest that acetoxythallation proceeded completely in a *trans* fashion at least in the case of alkylphenylacetylenes. In contrast, Sharma and Fellers[7] obtained a mixture of *trans*- and *cis*-acetoxythallates from dimethylacetylene, but they observed at the same time the formation of only the *trans*-isomer from diethylacetylene. The bulkiness of substituent on acetylenes seems to affect the mode of addition of thallium(III) salt to triple bond.

When the reaction mixture was refluxed for 2 hr in acetic acid after being kept at 65 °C for 1 hr, none of **1** and **2** was isolated, various organic products being obtained instead. Thus, from methylphenylacetylene, a mixture of 1-acetoxy-*trans*-1-phenylpropene [**3**(R=Me)], 2-acetoxy-*trans*-1-phenylpropene [**4**(R=Me)],



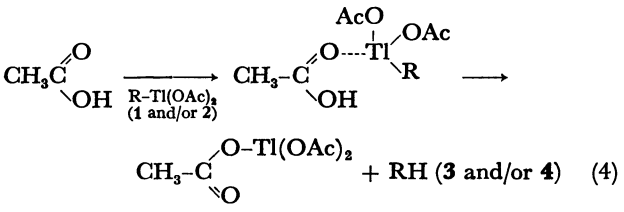
propiophenone, α-acetoxypropiophenone, 1-phenyl-1,2-propanedione, and 1-acetoxy-1-phenylacetone was obtained as shown below, **3** and **4** being the main products. Similarly, 1-acetoxy-*trans*-1-phenylbutene [**3**(R=Et)], 2-acetoxy-*trans*-1-phenylbutene [**4**(R=Et)], butyrophenone, acetoxybutyrophenone and 1-acetoxy-1-phenyl-2-butanone were the identified products from the reaction of ethylphenylacetylene. Here, **3** and **4** may be formed by protolysis of the intermediate acetoxythallates **1** and **2** by the solvent, while products other than **3** and **4** were found to be formed by the subsequent oxidation reaction of **3** and **4** with $Tl(OAc)_3$. In these reactions all of $Tl(OAc)_3$ was reduced to the thallium(I) salt, due partly to the oxidation of **3** and **4** and partly because of that of acetic acid solvent.[15]

From *t*-butylphenylacetylene (R=*t*-Bu) and diphenylacetylene (R=Ph), none of **1** and **2** was isolated by being stirred at 65 °C for 1—3 hr, and even under more drastic reaction conditions (at refluxing temperature for 4—24 hr) acetylenes were recovered almost quantitatively together with small amounts of the oxidation products. Several attempts to isolate **1** and **2** (or the methoxythallates) from the reaction of methylphenyl- or ethylphenylacetylenes with $Tl(OAc)_3$ in methanol solvent were unsuccessful under stirring at 25 °C for 5 hr, acetylenes being recovered in all cases. At refluxing temperature for 4 hr only the oxidation product, methyl 2-phenylpropionate,[16] was obtained in 50% yield from methylphenylacetylene as in the case of the reaction with $Tl(NO_3)_3$.[5]

Protodethallation of 1 and 2 by Acetic Acid. In order to confirm the possibility that various organic products (Eqs. (2) and (3)) were formed *via* the acetoxythallates of acetylenes, **1** or a mixture of **1** and **2** was heated in refluxing acetic acid for 2 hr. It was found that **1**(R=Me) gave **3**(R=Me) as the main product together with propiophenone, α-acetoxypropiophenone, and 1-phenyl-1,2-propanedione, while a mixture of **1**(R=Me) and **2**(R=Me) afforded **4**(R=Me) and 1-acetoxy-1-phenylacetone in addition to the four products. All the products were the same as those obtained directly from methylphenylacetylene. Similarly, a mixture of **1**(R=Et) and **2**(R=Et) gave the same products as those in Eq. (3), **3**(R=Et) and **4**(R=Et) being the main products. All the products other than **3** and **4** were formed by oxidation of **3** and **4** with $Tl(OAc)_3$; for example, **3**(R=Me) gave α-acetoxypropiophenone

as the main product together with small amounts of propiophenone and 1-phenyl-1,2-propanedione. A mixture of **3**(R=Me) and **4**(R=Me) afforded the above three compounds and 1-acetoxy-1-phenylacetone. A report was given on the α-acetoxylation and α,α-diacetoxylation (sometimes isolated as α-diketone) of ketones with $Tl(OAc)_3$ in acetic acid.[17] It was confirmed that propiophenone, butyrophenone, and phenylacetone reacted with $Tl(OAc)_3$ to give α-acetoxylated compounds and α-diketones (see Experimental). We might conclude that protolysis of **1** and **2** with acetic acid gives **3** and **4** followed by their subsequent oxidation with regenerated $Tl(OAc)_3$, and consequently that all the various products shown in Eqs. (2) and (3) were formed *via* acetoxythallation of acetylenes. The fact that *trans*-acetoxythallates gave exclusively **3** and **4** (where phenyl and alkyl are in *trans*-position) without formation of the *cis*-isomers indicates protodethallation to be completely stereospecific. In addition to the fact that proto- or halodemetallation and metal-metal exchange reaction of vinyl metal compounds (such metals as Hg, Sb, Sn, Li, and B) proceed electrophilically with retention of configuration,[18] deuteriodeboronation of vinylboron compounds by deuterioacetic acid[19] and also protolysis of vinylcopper compounds[20] proceed with complete retention of configuration. The results of protodethallation support the conclusion that acetoxythallation of alkylphenylacetylenes to form **1** and **2** proceeds completely in a *trans* fashion.

In contrast to facile protodethallation in acetic acid, **1** and **2** are stable in water and in aqueous HCl. For example, **1**(R=Me) gave **3**(R=Me) (5% yield), propiophenone (2%), α-acetoxypropiophenone (3%) together with methylphenylacetylene (4%) as the products only after refluxing for 3 hr. When **1**(R=Me) was treated with aqueous ethanol containing HCl (*ca.* 0.5 M) at 20 °C for 3 hr, hardly any reaction occurred. The almost quantitative protodethallation in acetic acid and the stability toward water and aqueous HCl seem to be a characteristic feature of the acetoxythallates of acetylenes. The alkoxythallates of olefins were solvolyzed with acetic acid and water to give oxidation products of olefins and no protodethallated compounds, while deoxythallation affording starting olefins occurred easily with aqueous ethanolic HCl.[8] It should be noted[21] that protolysis of various organoboranes proceeded smoothly by carboxylic acids with retention of configuration, but not by strong mineral acids, and that the unique effectiveness of carboxylic acids is attributed to the capability of boron of coordinating at the oxygen of the carbonyl group. We might assume that protolysis of vinylthallium compounds proceeds similarly to give **3** and/or **4** with



(4)

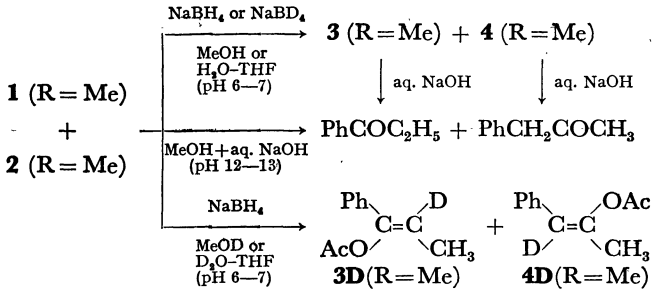
retention of configuration according to the following scheme, namely through coordination of thallium with the oxygen of the carbonyl group, and regenerated $Tl(OAc)_3$.

Table 2. Reaction of **1** and **2** with $NaBH_4$ in protic solvents at 0 °C for 1 hr

Tl compounds (mmol)			$NaBH_4$ (mmol)	Solvents (ml)	pH	Products and yield (%)[a]						
1 (R=Me)	**2**	**1**/**2** [b]				Methylphenylacetylene	**3**	**4** (R=Me)	**3D**	**4D**	Propiophenone	Phenylacetone
1	3	—	1.5	CH_3OH(20)	6— 7	3	85	0	—	—	trace	0
1	3	—	0.75	CH_3OH(20)	6— 7	3	69	0	—	—	trace	0
1+**2**	7.5	2.8	5	CH_3OH(40)	6— 7	3	66	24	—	—	trace	0
1+**2**	3.5	2.8	0.35	CH_3OH(30)	6— 7	3	18	8	—	—	trace	0
1	2	—	1	THF(20)+H_2O(20)	6— 7	4	84	0	—	—	trace	0
1+**2**	2	0.8	1	THF(10)+H_2O(10)	6— 7	4	42	53	—	—	trace	trace
1	3	—	0.75	CH_3OH(15)+3M-NaOH(5)	12—13	trace	trace	0	—	—	87[c]	0
1+**2**	2	0.8	0.5	CH_3OH(15)+3M-NaOH(5)	12—13	4	0	0	—	—	41	50
1	2	—	0	CH_3OH(15)+3M-NaOH(5)	12—13	trace	0	0	—	—	100	0
1+**2**	2	0.8	0	CH_3OH(15)+3M-NaOH(5)	12—13	3	0	0	—	—	41	12
1	5	—	2.5	CH_3OD(20)	6— 7	5	2	0	85	0	trace	0
1+**2**	5	0.8	2.5	THF(10)+D_2O(10)[d]	6— 7	3	1	1	39	47	trace	0
1	5	—	$NaBD_4$ 2.5	CH_3OH(20)	6— 7	2	90	0	<1	0	trace	0

a) Based on Tl compounds charged. b) Determined by NMR. c) 1-Phenylpropanol was obtained in 5% yield. d) React. Temp., 5 °C.

Hydrogenolysis of 1 and 2 by the Reaction with $NaBH_4$ in Protic Solvents. Hydrodemercuration of the oxymercurials of olefins by alkaline $NaBH_4$ reduction affording alcohols, ethers and amines *etc.* has been a current topic in the field of oxymetallation (solvomercuration-demercuration).[22,23] Oxymercuration of acetylenes and subsequent demercuration (*in situ*) by $NaBH_4$ gave ketones in an alkaline condition,[24] and enol acetates, enol ethers, and amines in a neutral condition.[25] The alkoxythallates of styrene were reduced by methanolic $NaBH_4$ especially in an alkaline condition to give styrene, α-alkoxyethylbenzenes and dialkylthallium salts, where styrene (the deoxythallation product) was the main product.[9] The hydrogen for replacement of thallium came from the solvent in contrast to the reduction of the oxymercurials of olefins where the hydrogen of $NaBH_4$ was used for hydrodemercuration.[23] In order to see how the thallium group of the oxythallates of acetylenes is replaced by hydrogen in the reaction with $NaBH_4$, **1** or a mixture of **1** and **2** was treated with $NaBH_4$ in various solvents such as methanol, aqueous methanol and aqueous THF at 0 °C for 1 hr. Some typical results are summarized in Table 2. In a neutral or slightly acidic condition (pH 6—7), **3**(R=Me) was obtained from **1**(R=Me) in a good yield together with a small amount of methylphenylacetylene (the deoxythallation product). Similarly a mixture of **1**(R=Me) and **2**(R=Me) was reduced to a mixture of **3**(R=Me) and **4**(R=Me) in methanol in more than 90% yield as shown in the following.

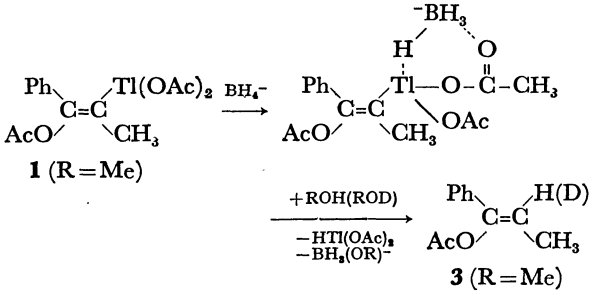


(5)

Since an isomer ratio of the products **3**(R=Me) and **4**(R=Me) was nearly the same as that of **1**(R=Me)/**2**(R=Me) determined by NMR, this reduction method was used for determining the ratios of **1** to **2** in the mixtures of the crude acetoxythallates of acetylenes (Table 1). In an alkaline condition (pH 12—13), **1**(R=Me) and a mixture of **1**(R=Me) and **2**(R=Me) afforded propiophenone and a mixture of propiophenone and phenylacetone, respectively, almost quantitatively. It was confirmed that **3**(R=Me) and **4**(R=Me) were readily hydrolyzed in this alkaline condition to propiophenone and phenylacetone respectively. It was also revealed that both **1**(R=Me) and **2**(R=Me) reacted with aqueous alkali to give the corresponding ketone even in the absence of $NaBH_4$ (Eq. (5)), the only difference being that the yield of **4** was lower in the absence of $NaBH_4$ than that in its presence. It is conceivable that **1** and **2** were solvolyzed in the reaction without $NaBH_4$ to the corresponding α-thallated ketones followed by hydrodethallation to give propiophenone and phenylacetone. Thus in the alkaline $NaBH_4$ reduction of **1** and **2**, both reaction routes would be operative.

When the reaction was carried out with $NaBD_4$ in methanol, hardly any deuterium incorporation was observed in the products, while the reaction with $NaBH_4$ in deuterated solvent such as MeOD or D_2O nearly completely gave the deuterated products, 1-acetoxy-2-deuterio-*trans*-1-phenylpropene (**3D**) and 2-acetoxy-1-deuterio-*trans*-1-phenylpropene (**4D**) (Eq. (5)). This shows that the hydrogen for replacement of thallium group came almost completely from the solvent and not from $NaBH_4$ as in the case of the reduction of the alkoxythallates of styrene.[9] In the reduction of arylthallium bis(trifluoroacetates) with $NaBH_4$ in ethanol, Herbert[26] pointed out that 2—8% of the hydrogen for replacement of thallium group to afford aromatic hydrocarbons came from $NaBH_4$. In the case of the reduction of the oxythallates of olefins and acetylenes, however, we could obtain only a small amount (at most 2% by NMR) of the deuterated products from the reaction with $NaBD_4$ in methanol.

The following facts should be noted when considering the reaction scheme of the reduction in a neutral condition: The reaction proceeded completely stereospecifically with retention of configuration. The reaction with the use of $BF_3(MeOH)_2$ or $B(OCH_3)_3$ instead of $NaBH_4$ gave none of **3** and **4**. Although the hydrogen for replacement of the thallium group came from the solvent, $NaBH_4$ was necessary as a reactant and not as a catalyst. The alkaline $NaBH_4$ reduction of oxymercurials of olefins proceeds *via* formation of an organomercuric hydride (RHgH) which undergoes homolytic dissociation to produce R· and ·HgH radicals, and the hydrogen for replacement of mercury arises from $NaBH_4$ and not from the solvent.[23] If a similar reaction scheme is operative in the reduction of the acetoxythallates of acetylenes and the intermediate organothallium hydride gives the vinyl radicals, they should give a mixture of *cis*- and *trans*-isomers since the vinyl radicals interconvert rapidly and give the isomeric mixtures.[27] For example, the reaction of *trans*-chlorovinylmercury (II) chloride with iodine in DMSO gave completely *trans*-1-chloro-2-iodoethylene by S_E1 mechanism, while a similar reaction gave a mixture of *trans*- and *cis*-isomers (50:50) in CCl_4 or benzene under an irradiation of light by a free-radical



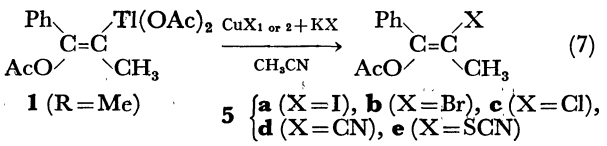
$$HTl(OAc)_2 \longrightarrow HOAc + TlOAc$$

$$1 + BH_3(OR)^- \xrightarrow{-HTl(OAc)_2} 3 + BH_2(OR)_2^-$$

$$\xrightarrow{1} 3 + BH(OR)_3^- \qquad (6)$$

mechanism.[28] Thus the radical reaction scheme may be excluded in our case. Considering the stereochemistry of the product we could assume that the reduction proceeds *via* an electrophilic substitution of thallium in vinylthallium compound by hydrogen or deuterium of the solvent, since the electrophilic substitution of metal in vinylmetal compounds by halogens, proton and metals proceed in almost all cases with retention of configuration, as shown in the scheme (6). This scheme shows why deuterium came from the solvent and not from $NaBD_4$. The borohydride might turn to oxyborohydride such as $B(OR)_4^-$ or $BH(OR)_3^-$. There is a possibility that $BH(OR)_3^-$ species becomes unreactive since the yields of **3** and/or **4** did not exceed 75% (based on $NaBH_4$ charged) in the reactions using a quarter or less mole of $NaBH_4$ and 1 mol of **1** and/or **2**. For example, the reaction of **1** (3 mmol) with $NaBH_4$ (0.75 mmol, 3 mmol equivalent H) gave 2.07 mmol of **3**, and the reaction with **1**+**2** (3.5 mmol) and $NaBH_4$ (0.35 mmol, 1.5 mmol equivalent H) gave 0.91 mmol of a mixture of **3** and **4** (Table 2). The result can be explained by assuming that three out of four hydrogens of BH_4^- were effective for reduction. We have observed similar phenomena in the $NaBH_4$ reduction of the alkoxythallates of styrene.[29]

Reaction of 1(R=Me) with Copper Salts and Halogens. Halogeno-, cyano-, and thiocyanodethallations proceed in the reactions of the arylthallium compounds[10,11] or the alkoxythallates of styrene[8] with copper halides, cyanides, and thiocyanates and in some case with iodine, bromine and potassium salts. In order to investigate whether a similar reaction occurs with the acetoxythallate of acetylene which has vinyl carbon–thallium bond, **1**(R=Me) was treated with copper(II) and (I) salts in various organic solvents. As shown in the following scheme thallium was replaced by iodide, bromide, chloride, cyanide and thiocyanate to give **5**, acetonitrile being chosen as the solvent.



(7)

Typical results are summarized in Table 3. Each of the products **5a**—**e** was found by glc and NMR to be uncontaminated with its geometrical isomer. **5a** and **5b** were identical with the products obtained by the reaction of **1** with molecular iodine (in CH_3OH) and bromine (in pyridine), where electrophilic substitution with retention of the configuration is the most plausible reaction scheme if we take into consideration the results of iodination[28] of vinylmercury compound in polar solvent and those of bromination of vinylmercuric bromide in pyridine.[30] We might thus conclude that all the products **5a**—**e** have the same configuration as that of the starting acetoxythallates of alkylphenylacetylenes.

Iododethallation proceeded with copper(I) iodide. Other reactions occurred with copper(II) salts in contrast to the case of the alkoxythallates of styrene having an alkyl carbon–thallium bond, where copper(I) salts were more effective for halogeno- and pseudohalogenodethallations. Although the reaction of **1**(R=Me) with KI afforded **5a** in a good yield, none of **5** was obtained by the use of other potassium salts. Satisfactory results were obtained for bromodethallation by copper salt by the reaction with $CuBr_2$ in the presence of KBr in acetonitrile. Other solvents such as dioxane, DMF, and methanol were also used for bromodethallation, but the yields of **5b** were low. There is a possibility that bromodethallation occurs with free bromine liberated by autodecomposition of $CuBr_2$ into Cu_2Br_2.[31] The result of the separate reaction of **1**(R=Me) with bromine in acetonitrile which gave α,α-dibromopropiophenone (**6**) and none of **5b**, however, excluded the above possibility and showed that $CuBr_2$ itself was

Table 3. Halodethallation of **1** with copper salts

1 (R=Me) (mmol)	Cu salt (mmol)	K salt (mmol)	Solvent (20 ml)	Temp. (°C)	Time (hr)	Products and yields (%) Methylphenylacetylene	**5**	
2		0 KI 8	CH_3CN	80	2	trace	**a**	74
2	CuI 4	0	CH_3CN	80	2	4	**a**	40[b]
2	CuI 4	KI 8	CH_3CN	80	2	5	**a**	58
2	$CuBr_2$ 4	0	CH_3CN	80	2	3	**b**	20
2	$CuBr_2$ 4	KBr 8	CH_3CN	80	2	trace	**b**	50
2	$CuBr_2$ 4	KBr 8	CH_3CN	20	24	trace	**b**	19
2	$CuBr_2$ 4	KBr 8	Dioxane	100	2	3	**b**	40
2	$CuBr_2$ 4	KBr 8	DMF	153	2	2	**b**	21[b]
2	$CuBr_2$ 4	KBr 8	CH_3OH	65	2	3	**b**	14
2	$CuBr_2$ 4	KBr 8	$CHCl_3$	61	2	0	**b**	2
2	CuBr 4	KBr 8	CH_3CN	80	2	6	**b**	1
2	$CuCl_2$ 4	KCl 8	CH_3CN	80	2	trace	**c**	11
2	CuCl 4	KCl 8	CH_3CN	80	2	trace	**c**	1
2	$Cu(CN)_2$ 4	0	CH_3CN	80	2	trace	**d**	15
2	CuCN 4	0	CH_3CN	80	2	trace	**d**	3
2	$Cu(NCS)_2$ 4	KSCN 8	CH_3CN	80	2	trace	**e**	8
2	CuSCN 4	KSCN 8	CH_3CN	80	2	trace	**e**	trace

a) Based on **1** (R=Me) charged. b) **3** (R=Me) was obtained in 7% yield.

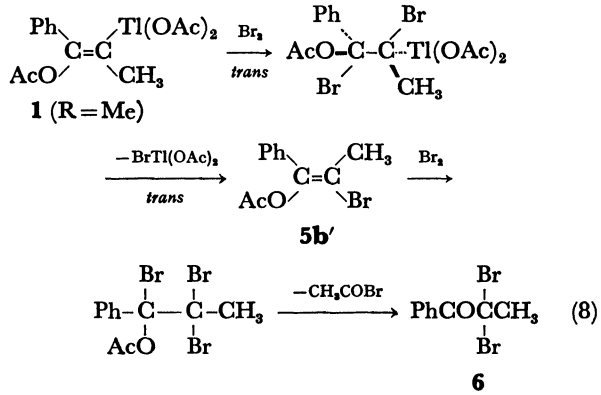
TABLE 4. HALODETHALLATION OF 1 WITH IODINE AND BROMINE

1 (R=Me) (mmol)	X_2 (mmol)	Solvent (20 ml)	Temp. (°C)	Time (hr)	Products and Yields (%)[a]		
					Methylphenylacetylene	5	6
2	I_2 4	CH_3OH	65	3	0	**a** 61	—
10	Br_2 20	Pyridine[b]	20	2	0	**b** 78	0
2	Br_2 4	CH_3CN	20	2	trace	0	82
2	Br_2 4	CH_3OH	20	2	1	**b** 23 **b′** 30	37
2	Br_2 4	CS_2	20	2	1	0	99
2	Br_2 2	CS_2	0	0.5	5	0	41
5b 2	Br_2 2	CH_3CN	20	2	0	**b**<1	>99

a) Based on **1** (R=Me) charged. b) 50 ml.

a reactant in the reaction with **1**. When a mixture of **1**(R=Me) and **2**(R=Me) was treated with $CuBr_2$, a mixture of **5b** and 2-acetoxy-1-bromo-*trans*-1-phenylpropene was obtained as expected. Other reactions such as chloro-, cyano-, and thiocyanodethallations proceeded with the corresponding copper(II) salts, but the yields of the products **5c—e** were low under the reaction conditions shown in Table 3.

In order to prepare an authentic sample of **5**, **1**(R=Me) was treated with iodine and bromine in suitable solvents. **1**(R=Me) reacted with iodine in methanol to give **5a**, while a mixture of **5b**, **6**, and another product (**5b′**, the isomer of **5b**; see Experimental) was obtained by the reaction with bromine. Only **5b** was obtained in pyridine in a good yield, while only **6** was obtained in carbon disulfide just as in the case of acetonitrile. The results of the reaction of **1** with halogens are summarized in Table 4. Since the alkoxythallates of styrene did not react with iodine and bromine,[8] the results show another example of the difference of reactivity between alkyl C–Tl and vinyl C–Tl bonds. The product in the reaction of **1**(R=Me) with bromine depends on the solvent which is in line with the reaction of vinylmercuric bromide.[30] In carbon disulfide, acetonitrile and methanol, the *trans*-addition of bromine to the double bond followed by *trans*-debromothallation may be operative in giving **5b′** which then reacts with another mole of bromine to afford **6**, as shown in the following.



In pyridine, the coordination of pyridine to thallium may activate the C–Tl bond towards the electrophilic attack by bromine. We confirmed that **5b** reacts very easily with bromine in carbon disulfide and acetonitrile to give **6**, while in pyridine the reaction does not proceed under the reaction conditions where halodethallation by halogen was carried out.

Experimental

The IR spectra were taken with Hitachi EPI-S2 and JASCO IR-S spectrometers in paraffin and hexachlorobutadiene mulls. The NMR spectra were recorded with a Varian A-60 spectrometer in $CDCl_3$, CCl_4, or CD_3OD as solvents, using TMS as an internal standard. Glc analyses were carried out on Shimadzu 5APTF and 4BMPF apparatus, using PEG 6000(25%)-Chromosorb W (3m), Apiezon L (30%)-Celite (1m), DEGS(25%)-Shimalite (1m), and EGSS-X(30%)-Chromosorb W (1m) columns (N_2 as carrier gas).

Materials. The following alkylphenylacetylenes were prepared from sodium phenylacetylide and *p*-toluenesulfonic acid alkyl ester:[32] methylphenylacetylene, bp 76—77 °C/18 mmHg (lit,[33] bp 185 °C); ethylphenylacetylene, bp 88—89 °C/16 mmHg (lit,[33] bp 201—203 °C); *n*-propylphenylacetylene, bp 97—104 °C/17 mmHg (lit,[33] bp 102—103 °C/18.5 mmHg); *n*-butylphenylacetylene, bp 82—86 °C/2.5 mmHg (lit,[33] bp 119—121 °C/18 mmHg). *t*-Butylphenylacetylene was prepared from phenylacetylene, ethyl magnesium bromide, and *t*-butyl bromide,[34] bp 92—97 °C/19 mmHg (bp 94—95 °C/18 mmHg). Diphenylacetylene was prepared by the alkaline dehydrobromination of stilbene dibromide;[35] mp 60—61 °C (lit,[35] mp 60—61 °C). Other organic materials were purified before use by distillation. Commercial inorganic materials were used without further purification. $Cu(NCS)_2$ was prepared from $CuSO_4 \cdot 5H_2O$ and KSCN.[36] $Tl(OAc)_3$ was prepared by stirring Tl_2O_3 in acetic acid at 65 °C for 24 hr. All the deuterium compounds, $NaBD_4$ (98%, Merck), CH_3OD (99%, CEA) and D_2O (99.8%, CEA) were used without purification.

Preparation of Acetoxythallates of Acetylenes, 1 and 2. The following preparation of **1**(R=Me) and **2**(R=Me) shows a typical procedure. To a slightly heterogeneous solution of $Tl(OAc)_3$ (3.81 g, 10 mmol) in acetic acid (10 ml) was added methylphenylacetylene (2.3 g, 20 mmol) drop by drop at 65 °C under stirring to give a pale-green solution. When the mixture was kept at 65 °C for 1 hr the color of the solution turned dark green. The solution was cooled down and acetic acid was evaporated off at room temperature with a rotary evaporator. The white solids obtained were purified by dissolution into $CHCl_3$ to remove the insoluble unreacted $Tl(OAc)_3$ (0.63 g), and then by washing with *n*-hexane after evaporation of $CHCl_3$ to remove the unreacted methylphenylacetylene and small amounts of the oxidation products to give a crude mixture of **1**(R=Me) and **2**(R=Me) (3.7 g; 75 and 89% yields based on $Tl(OAc)_3$ charged and consumed respectively); **1**/**2**=2.5 (by NMR), mp 135—

145 °C. The mixture was recrystallized from ethanol–*n*-hexane (1:1) mixed solvent and analyzed. **1**(R=Me) (1.0 g) was separated by recrystallization twice from ethanol, several attempts to isolate **2**(R=Me) being unsuccessful. NMR (CD_3OD) of **1**(R=Me) δ 1.85 [s, 6H, $Tl(OCOCH_3)_2$], 2.15 (d, 3H, $\equiv C-CH_3$, $J_{^{205}Tl-H}$=986 Hz, $J_{^{203}Tl-H}$=976 Hz), 2.18 (d, 3H, acetoxy, J_{Tl-H}=13 Hz), 7.40 (s, 5H, phenyl). NMR (CD_3OD) of **2**(R=Me) determined from a mixture of **1** and **2** is as follows: δ 1.83 (d, 3H, acetoxy, J_{Tl-H}=13 Hz), 1.85 [s, 6H, $Tl(OCOCH_3)_2$], 2.30 (d, 3H, J_{Tl-H}=142 Hz), 7.2—7.3 (m, 5H, phenyl, J_{Tl-o-H}=125.5 Hz, J_{Tl-m-H}=64 Hz).

The reaction with ethylphenylacetylene gave an oily product on evaporation of acetic acid. After unreacted $Tl(OAc)_3$ was removed with $CHCl_3$, it was solidified by being left to stand in *n*-hexane for two days or by decantation with *n*-hexane several times to give 3.6 g of a mixture of **1**(R=Et) and **2**(R=Et). This was recrystallized from either CCl_4, benzene, acetone or ethanol–*n*-hexane. Extraction with ether afforded 0.4 g of pure **1**(R=Et). NMR (CD_3OD) of **1**(R=Et) δ 1.15 (m, 3H, $C\underline{H}_3CH_2-$, J_{H-H}=7 Hz, J_{Tl-H}=20 Hz), 1.87 [s, 6H, $Tl(OCOCH_3)_2$], 2.17 (d, 3H, acetoxy, J_{Tl-H}=13 Hz), 2.66 (m, 2H, $CH_3C\underline{H}_2-$, J_{H-H}=7 Hz, J_{Tl-H}=1299 Hz), 7.40 (s, 5H, phenyl). Recrystallization from methanol gave 0.24 g of pure **2**(R=Et) as white needles. NMR (CD_3OD) of **2**(R=Et) δ 1.34 (t, 3H, $C\underline{H}_3CH_2-$, J_{H-H}=7 Hz), 1.85 (d, 3H, acetoxy, J_{Tl-H}=13 Hz), 1.90 [s, 6H, $Tl(OCOCH_3)_2$], 2.68 (m, 2H, $CH_3C\underline{H}_2-$, J_{H-H}=7 Hz, J_{Tl-H}=116 Hz), 7.2—7.3 [m, 5H, phenyl, J_{Tl-o-H}=126 Hz, J_{Tl-m-H}=64 Hz).

3.5 g and 2.9 g of a mixture of **1** and **2** were similarly obtained from *n*-propylphenylacetylene and *n*-butylphenylacetylene, respectively. The products from *n*-butylphenylacetylene, also oily at first, were treated as in the case of ethylphenylacetylene in order to solidify the products. They were recrystallized from either acetone or 1,2-dichloroethane and analyzed. Several attempts to separate each product were unsuccessful. NMR (CD_3OD) spectra of the mixture could be analyzed. $J_{Tl-H(-CH_2-C=)}$ was 1311 and 1316 Hz in **1**(R=*n*-Pr) and **1**(R=*n*-Bu) respectively, couplings of *o*- and *m*-hydrogen of phenyl group with thallium being also observed in **2**(R=*n*-Pr) and **2**(R=*n*-Bu).

All the reactions could be carried out at 50—75 °C without affecting either the ratio or the yield of **1** and **2**. A larger scale reaction (about 10 times) also gave satisfactory results.

Reaction of Methyl- and Ethylphenylacetylenes with $Tl(OAc)_3$. To an acetic acid (10 ml) solution of $Tl(OAc)_3$ (1.9 g, 5 mmol) was added methylphenylacetylene (1.16 g, 10 mmol) at 65 °C and the resulting pale-green solution was kept for 1 hr and then refluxed for 2 hr when the color of the homogeneous solution turned to orange and then to red. After being cooled down to room temperature, aqueous NaCl was added to the solution and the precipitated TlCl was filtered off. The filtrate was extracted with benzene and the extract was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. The extract was concentrated to *ca.* 5 ml with a rotary evaporator and analyzed by glc with ethyl cinnamate as an internal standard. The products were propiophenone (7%), 1-phenyl-1,2-propanedione (13%), **3**(R=Me) (78%), **4**(R=Me) (29%), α-acetoxypropiophenone (7%), and 1-acetoxy-1-phenylacetone (6%). The last two compounds were not separated by glc, their yields being determined by NMR. The yields were calculated on the basis of $Tl(OAc)_3$ charged. The yields of the above products in another experiment were 5, 12, 67, 25, 7, and 6%, respectively.

A similar treatment of ethylphenylacetylene gave a mixture of the following products; butyrophenone (6%), **3**(R=Et) (44%), **4**(R=Et) (24%), α-acetoxybutyrophenone (4%), 1-acetoxy-1-phenyl-2-butanone (**3**) and an unidentified compound (<3%).

Reaction of 3(R=Me) and 4(R=Me) with $Tl(OAc)_3$. A mixture of **3**(R=Me) (0.53 g, 3 mmol), $Tl(OAc)_3$ (1.91 g, 5 mmol), and acetic acid (20 ml) was refluxed for 2 hr, 75% of Tl^{3+} salt being consumed (iodometrically). The reaction mixture was treated as described above. Glc analysis showed the presence of unreacted **3**(R=Me) (0.26 mmol), 1-phenyl-1,2-propanedione [0.08 mmol, 3% yield based on **3**(R=Me) charged], propiophenone (0.13 mmol, 4%) and α-acetoxypropiophenone (1.84 mmol, 61%). A similar reaction of a mixture of **3**(R=Me) and **4**(R=Me) (0.53 g, 3 mmol, **3**/**4**=3.0) with $Tl(OAc)_3$ (1.15 g, 3 mmol) in acetic acid (20 ml) gave propiophenone (0.18 mmol, 6%), 1-phenyl-1,2-propanedione (0.21 mmol, 7%), α-acetoxypropiophenone (0.66 mmol, 22%), 1-acetoxy-1-phenylacetone (0.51 mmol, 17%) together with unreacted 1.08 mmol of **3**(R=Me) and 0.09 mmol of **4**(R=Me).

Reaction of Propiophenone, Butyrophenone, and Phenylacetone with $Tl(OAc)_3$. The reaction of propiophenone (1.34 g, 10 mmol) with $Tl(OAc)_3$ (3.81 g, 10 mmol) in acetic acid (30 ml) under reflux for 2 hr gave 1-phenyl-1,2-propanedione (3% yield) and α-acetoxypropiophenone[17] (50% yield, bp 140—145 °C/16 mmHg) as products. A similar reaction using butyrophenone afforded α-acetoxybutyrophenone (23%) and small amounts of unidentified products. Distillation gave pure α-acetoxybutyrophenone; bp 110—115 °C/3 mmHg, IR 1738 and 1695 ($\nu_{C=O}$) cm^{-1}. NMR ($CDCl_3$) δ 1.00 (t, 3H, J_{H-H}=7 Hz, CH_3-), 1.6—2.2 (m, 2H, $-CH_2-$), 2.13 (s, 3H, acetoxy), 5.82 (m, 1H, $-CH-$), 7.2—7.7 (m, 3H, phenyl), 7.8—8.2 (m, 2H, phenyl). Similarly, 1-acetoxy-1-phenylacetone (74%) and 1-phenyl-1,2-propanedione (4%) were obtained from the reaction of phenylacetone. Distillation gave pure 1-acetoxy-1-phenylacetone; bp 140—147 °C/17 mmHg. IR 1740 ($\nu_{C=O}$), 1228 (ν_{C-O}) cm^{-1}. NMR (CCl_4) δ 2.02 (s, 3H, CH_3-), 2.10 (s, 3H, acetoxy), 5.85 (s, 1H, methine), 7.35 (s, 5H, phenyl). Found: C, 69.28; H, 6.45%. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%.

Protodethallation of a Mixture of 1 and 2 by Acetic Acid. A mixture of **1**(R=Me) and **2**(R=Me) (1.5 g, 3 mmol, **1**/**2**=2.6) was dissolved in 20 ml acetic acid and the resulting slightly yellow homogeneous solution was refluxed for 2 hr to give a red solution. After being cooled down to room temperature, the reaction mixture was treated as described above and analyzed by glc. The products were methylphenylacetylene (1% yield), propiophenone (8%), 1-phenyl-1,2-propanedione (7%), **3**(R=Me) (46%), **4**(R=Me) (6%), α-acetoxypropiophenone (13%), and 1-acetoxy-1-phenylacetone (12%). A similar treatment of a mixture of **1**(R=Et) and **2**(R=Et) (**1**/**2**=1.6) gave the following products; ethylphenylacetylene (1%), butyrophenone (12%), **3**(R=Et) (39%), **4**(R=Et) (17%), α-acetoxybutyrophenone (6%), and 1-acetoxy-1-phenyl-2-butanone (5%).

Reaction of 1 and 2 with $NaBH_4$ in Protic Solvents. To a methanol (20 ml) solution containing 1.50 g (3.0 mmol) of **1**(R=Me) was added solid $NaBH_4$ (0.06 g, 1.5 mmol) in several portions, the temperature being kept at 0—4 °C. The mixture was then stirred for 1 hr at 0 °C. After the addition of aqueous NaCl and filtration of the resulting TlCl, the filtrate was extracted with benzene, and the extract was treated as described above. Glc analysis showed the presence of 0.09 mmol of methylphenylacetylene and 2.55 mmol (85%) of **3**(R=Me). The retention time of glc and the NMR spectrum of **3**(R=Me) were consistent with those of the sample prepared by the method reported by Fahey and Lee[37] but different from those of its isomer, 1-acetoxy-*cis*-1-phenylpropene.[37] NMR (CCl_4) δ 1.65 (d, 3H, $CH_3-C=$,

J_{H-H}=7 Hz), 2.16 (s, 3H, acetoxy), 5.75 (q, 1H, =CH, J_{H-H}=7 Hz), 7.0—7.4 (m, 5H, phenyl). A mixture of **1**(R=Me) and **2**(R=Me) (3.7 g, 7.5 mmol) gave a mixture of methylphenylacetylene (0.22 mmol), **3**(R=Me) (4.95 mmol), and **4**(R=Me) (1.80 mmol) by a similar treatment. Distillation gave 0.91 g (5.2 mmol) of a mixture of **3**(R=Me) and **4**(R=Me) (**3**/**4**=3.0), bp 122—130 °C/19.5 mmHg. NMR (CCl_4) of **4**(R=Me) was consistent with that reported by House *et al.*,[38] δ 2.03 (d, 3H, CH_3-C=, J_{H-H}=1 Hz), 2.06 (s, 3H, acetoxy), 5.83 (q, 1H, H-C=, J_{H-H}=1 Hz). 7.0—7.4 (m, 5H, phenyl). Analysis of a mixture of **3** and **4**. Found: C, 75.09; H, 7.02%. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%.

The reaction of **1** (R=Me) with $NaBH_4$ in CH_3OD solvent gave 1-acetoxy-2-deuterio-*trans*-1-phenylpropene; bp 125—129 °C/22 mmHg. NMR (CCl_4) δ 1.64 (s, 3H, CH_3-C=), 2.17 (s, 3H, acetoxy), 7.1—7.4 (m, 5H, phenyl). Found: C, 74.65; H, 6.98%. Calcd for $C_{11}H_{13}O_2$: C, 74.55; H, 7.39%. A mixture of **1** (R=Me) and **2** (R=Me) was reduced by $NaBH_4$ in THF-D_2O (1: 1) solvent at 5 °C for 1 hr to give 1-acetoxy-2-deuterio-*trans*-1-phenylpropene and 2-acetoxy-1-deuterio-*trans*-1-phenylpropene as the products. NMR (CCl_4) of the latter compound, δ 2.04 (s, 3H, CH_3-C=), 2.06 (s, 3H, acetoxy), 7.1—7.4 (m, 5H, phenyl).

The products obtained by a similar treatment in methanol with other oxythallates are as follows. A mixture of **3** (R=Et) and **4** (R=Et) (84% yield by glc, **3**/**4**=1.8); 63% yield by distillation, bp 132—135 °C/19.5 mmHg. **3** (R=Et) was prepared by refluxing butyrophenone in acetic anhydride in the presence of *p*-toluenesulfonic acid, bp 107—108 °C/5 mm Hg. NMR (CCl_4) δ 1.05 (t, 3H, $C\underline{H}_3CH_2$-, J_{H-H}=7 Hz), 1.8—2.3 (m, 2H, $CH_3C\underline{H}_2$-), 2.15 (s, 3H, acetoxy), 5.67 (t, 1H, =CH, J_{H-H}=7 Hz), 7.1—7.4 (m, 5H, phenyl). NMR (CCl_4) of **4** (R=Et) determined from a mixture of **3** (R=Et) and **4** (R=Et) is as follows: δ 1.13 (t, 3H, $C\underline{H}_3CH_2$-, J_{H-H}=7 Hz), 2.07 (s, 3H, acetoxy), 2.27 (q, 2H, $CH_3C\underline{H}_2$-, J_{H-H}=7 Hz), 5.85 (t, 1H, =CH, J_{H-H}=1 Hz), 7.1—7.4 (m, 5H, phenyl). A mixture of **3** (R=*n*-Pr) and **4** (R=*n*-Pr): 67% yield by distillation, bp 142—146 °C/19.5 mmHg. Found: C, 76.28; H, 8.17%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90% A mixture of **3** (R=*n*-Bu) and **4** (R=*n*-Bu): 59% yield by distillation, bp 153—156 °C/17.5 mmHg. Found: C, 77.42; H, 8.67%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

Reaction of 1(R=Me) and 2(R=Me) with NaOH. To a methanol (15 ml) solution of **1** (R=Me) (2 mmol) was added aqueous 3M-NaOH (5 ml) drop by drop, the temperature being kept at 0 °C. After the mixture was stirred for 1 hr at 0 °C, the precipitated Tl_2O_3 was filtered off and the filtrate was treated as usual. Glc analysis showed the formation of a trace amount of methylphenylacetylene and 2 mmol (100% yield) of propiophenone. A similar treatment of a mixture of **1**(R=Me) and **2**(R=Me) (2 mmol, **1**/**2**=0.8) gave methylphenylacetylene (0.05 mmol), propiophenone (0.82 mmol), and phenylacetone (0.23 mmol) as the products.

Reaction of 1(R=Me) with Copper Salts. The following shows a typical procedure. A yellowish green heterogeneous mixture of **1**(R=Me) (1.0 g, 2 mmol), CuI (0.76 g, 4 mmol), and KI (1.3 g, 8 mmol) in acetonitrile (20 ml) was stirred for 2 hr under refluxing temperature. After the reaction mixture had been cooled the dark-yellow precipitates were filtered. The filtrate was added to water and extracted with diethyl ether. Glc analysis of the ether extract using cumene and benzophenone as internal standards showed the presence of 0.1 mmol of methylphenylacetylene and 1.16 mmol (58% yield) of **5a**. Bp 114—116 °C/4 mmHg. NMR (CCl_4) δ 2.04 (s, 3H, acetoxy), 2.47 (s, 3H, CH_3-C=), 7.1—7.6 (m, 5H, phenyl). Found: C, 43.41; H, 3.60%. Calcd for $C_{11}H_{11}O_2I$: C, 43.73; H, 3.67%.

Characterization of other products is as follows. **5b**: bp 97—103 °C/3 mmHg. IR 1768 ($\nu_{C=O}$), 1200 (ν_{C-O}) cm^{-1}. NMR (CCl_4) δ 2.04 (s, 3H, acetoxy), 2.30 (s, 3H, CH_3C=), 7.2—7.6 (m, 5H, phenyl). Found: C, 52.07; H, 4.33%. Calcd for $C_{11}H_{11}O_2Br$: C, 51.79; H, 4.35%. It was revealed by NMR that there was an unidentified compound together with **5b** and **6** in the products obtained by the reaction of **1**(R=Me) with bromine in methanol at 20 °C for 2 hr. We may assign this compound as a geometrical isomer of **5b** [**5b'** (phenyl and methyl groups are on the same side)]; NMR (CCl_4) δ 2.09 (s, 3H, acetoxy), 2.33 (s, 3H, CH_3C=). 2-Acetoxy-1-bromo-*trans*-1-phenylpropene (**5b''**): The reaction of a mixture of **1**(R=Me) and **2**(R=Me) (5.0 g, 10 mmol, **1**/**2**=0.8) with $CuBr_2$ (4.5 g, 20 mmol) and KBr (4.8 g, 40 mmol) in acetonitrile (50 ml) under reflux for 2 hr gave **5b** and **5b''** as products (**5b**/**5b''**=1.13). Distillation gave a mixture of **5b** and **5b''**; 0.91 g (36% yield, **5b**/**5b''**=0.93), bp 95—105 °C/3 mmHg. NMR (CCl_4) of **5b''**, δ 1.81 (s, 3H, CH_3C=), 2.20 (s, 3H, acetoxy), 7.1—7.6 (m, 5H, phenyl). Analysis of a mixture of **5b** and **5b''**. Found: C, 52.22; H, 4.34%. **5c**: IR 1765 ($\nu_{C=O}$), 1200 (ν_{C-O}) cm^{-1}. NMR (CCl_4) δ 2.08 (s, 3H), 2.12 (s, 3H), 7.1—7.6 (m, 5H). Mass spectrum (*m/e*) 210 (M^+). **5d**: IR 2020 (ν_{CN}), 1775 ($\nu_{C=O}$), 1185 (ν_{C-O}) cm^{-1}. Mass spectrum (*m/e*) 201 (M^+). NMR (CCl_4) δ 1.93 (s, 3H, acetoxy), 2.19 (s, 3H, CH_3C=), 7.2—7.8 (m, 5H, phenyl). **5e**: IR 2150 (ν_{SCN}), 1765 ($\nu_{C=O}$), 1192 (ν_{C-O}) cm^{-1}. Mass spectrum (*m/e*) 233 (M^+). NMR (CCl_4) δ 2.11 (s, 3H, acetoxy), 2.22 (s, 3H, CH_3C=), 7.3 (s, 5H, phenyl). **6**: To a solution of **1**(R=Me) (1.0 g, 2 mmol) in CS_2 (15 ml) was added bromine (0.64 g, 4 mmol) in CS_2 (5 ml) drop by drop at 20 °C and the resulting red solution was stirred for 2 hr when the color turned pale orange. Glc analysis revealed the presence of a small amount of methylphenylacetylene and 1.98 mmol (99% yield) of **6**. Distillation gave 0.2 g (34% yield) of pure **6**; bp 100—104 °C/3.5 mmHg. IR 1682 ($\nu_{C=O}$) cm^{-1}. Mass spectrum (*m/e*) 290 (M^+), 292 (M^++2), 294 (M^++4). NMR (CCl_4) δ 2.72 (s, 3H, CH_3-), 7.2—7.6 [m, 3H, phenyl (*m*- and *p*-H)], 8.2—8.5 [m, 2H, phenyl (*o*-H)].

References

1) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

2) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

3) a) A. E. Borisov, V. D. Vil'chevskaya, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **90**, 383 (1953); *Chem. Abstr.*, **48**, 4434 (1954). b) A. N. Nesmeyanov, A.E. Borisov, I. S. Savel'eva, and M. A. Osipova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1961**, 1249; *Chem. Abstr.*, **56**, 1469 (1962). c) G. Drefahl, G. Heublein, and A. Wintzer, *Angew. Chem.*, **70**, 166 (1958).

4) a) S. Uemura, R. Kitoh, K. Fujita, and K. Ichikawa, This Bulletin, **40**, 1499 (1967). b) K. Ichikawa and S. Uemura, *Yuki Gosei Kagaku Kyokai Shi*, **29**, 400 (1971).

5) A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, and R. L. Robey, *J. Amer. Chem. Soc.*, **95**, 1296 (1973).

6) S. Uemura, K. Sohma, H. Tara, and M. Okano, *Chem. Lett.*, **1973**, 545.

7) R. Sharma and N. H. Fellers, *J. Organometal. Chem.*, **49**, C69 (1973).

8) S. Uemura, K. Zushi, A. Tabata, A. Toshimitsu, and M. Okano, This Bulletin, **47**, 920 (1974).

9) S. Uemura, A. Tabata, and M. Okano, *Chem. Commun.*, **1972**, 517.

10) S. Uemura, Y. Ikeda, and K. Ichikawa, *Tetrahedron*, **28**, 5499 (1972).

11) a) S. Uemura, Y. Ikeda, and K. Ichikawa, *ibid.*, **28**, 3025 (1972). b) S. Uemura, S. Uchida, M. Okano, and K. Ichikawa, This Bulletin, **46**, 3254 (1973).
12) a) H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, **10**, 211 (1967). b) H. Kurosawa and R. Okawara, *ibid.*, **19**, 253 (1969). c) A. G. Lee, *ibid.*, **22**, 537 (1970).
13) J. P. Maher and D. F. Evans, *J. Chem. Soc.*, **1965**, 637.
14) A. T. T. Hsieh and G. Wilkinson, *J. Chem. Soc. Dalton*, **1973**, 867.
15) For the reduction of $Tl(OAc)_3$ by acetic acid, see for example; A. South, Jr. and R. J. Ouellete, *J. Amer. Chem. Soc.*, **90**, 7064 (1968). E. C. Taylor, H. W. Altland, G. McGillivray, and A. McKillop, *Tetrahedron Lett.*, **1970**, 5285.
16) Bp 102 °C/27 mmHg. NMR ($CDCl_3$) δ 1.50 (d, 3H, $C\underline{H}_3CH$–), 3.65 (s, 3H, $COOCH_3$), 3.73 (q, 1H, $CH_3C\underline{H}$–), 7.25—7.35 (m, 5H, phenyl). Found: C, 72.85; H, 7.57%.
17) S. Uemura, T. Nakano, and K. Ichikawa, *Nippon Kagaku Zasshi*, **88**, 1111 (1967).
18) See, for example, O. A. Reutov and I. P. Beletskaya, "Reaction Mechanisms of Organometallic Compounds," North-Holland, Amsterdam (1968), Chap. 1—4.
19) J. R. Blackborow, *J. Chem. Soc. Perkin II*, **1973**, 1989. Protonolysis of vinylboron compound by acetic acid has been reported to proceed with retention of configuration by H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **81**, 1512 (1959).
20) J. Klein and R. Levene, *J. Chem. Soc. Perkin II*, **1973**, 1971.
21) H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca (1972), p. 313—317.
22) For example, a) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **95**, 8665 (1973) and references therein. b) References cited in Ref. 25.
23) a) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966). b) D. J. Pasto and J. Gontarz, *ibid.*, **91**, 719 (1969). c) G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970). d) G. A. Gray and W. R. Jackson, *ibid.*, **91**, 6205 (1969). e) G. A. Gray, W. R. Jackson, and V. M. A. Chambers, *J. Chem. Soc., C*, **1971**, 200. f) V. M. A. Chambers, W. R. Jackson, and G. W. Young, *Chem. Commun.*, **1970**, 1275; *J. Chem. Soc., C*, **1971**, 2075.
24) G. Chandra, D. Devaprabhakara, and M. S. Muthana, *Curr. Sci.*, **40**, 400 (1971).
25) P. F. Hudrlik and A. M. Hudrlik, *J. Org. Chem.*, **38**, 4254 (1973).
26) R. B. Herbert, *Tetrahedron Lett.*, **1973**, 1375.
27) O. Simamura, "Topics in Stereochemistry," Vol. 4, ed. by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York, N.Y. (1969), p. 21.
28) I. P. Beletskaya, V. I. Karpov, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **161**, 586 (1965); See also Ref. 18, p. 201—206.
29) S. Uemura, A. Tabata, and M. Okano, unpublished data.
30) C. P. Casey, G. M. Whitesides, and J. Kurth, *J. Org. Chem.*, **38**, 3406 (1973).
31) J. C. Barnes and D. N. Hume, *Inorg. Chem.*, **2**, 444 (1963).
32) J. R. Johnson, A. M. Schwartz, and T. L. Jacobs, *J. Amer. Chem. Soc.*, **60**, 1882 (1938).
33) M. T. Bogert and D. Davidson, *ibid.*, **54**, 334 (1932).
34) A. Mortreux and M. Blanchard, *Bull. Soc. Chim. Fr.*, **1970**, 4035.
35) L. I. Smith and M. M. Falkof, "Organic Syntheses," Coll. Vol. III, p. 350 (1955).
36) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, **36**, 3095 (1971).
37) R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966).
38) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).