

Metalation of Alkynes. 3. Kinetics of Acetoxythallation¹

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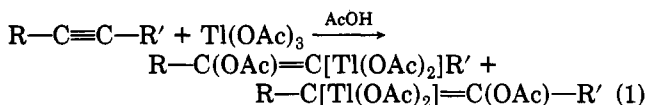
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The rates of $\text{Tl}(\text{OAc})_3$ addition to symmetrically and unsymmetrically substituted alkynes (4-octyne, 2-heptyne, 2-nonyne, 1,4-diacetoxy-2-butyne, methyl 2-octynoate, 1-phenylpropyne, 1-phenyl-1-pentyne, and methyl phenylpropynoate) were measured in acetic acid. The rate law is second-order, first order in both alkyne and thallium acetate. Activation parameters were determined for representative substrates. The kinetic data are in agreement with an associative process characterized by the electrophilic attack of thallium acetate at the triple bond. A quantitative comparison with acetoxymercuration shows that thallation is a slower reaction for all the alkynes investigated. Acetoxyplumbation of the same alkynes does not occur.

Mercuric acetate, thallium triacetate, and lead tetraacetate are isoelectronic metal ion derivatives, widely used as reagents in organic synthesis. The high level of interest resulted in extensive literature on the use and behavior of these reagents and in many reviews about their reactions with organic substrates.² However, comparisons of reactivity among these reagents are qualitative only,^{3,4} whereas quantitative data are a necessary support for any proposed mechanism.

Recently, we started to investigate the mechanism of the reaction between alkynes and mercuric acetate,^{5,6} obtaining the first quantitative data for acetoxymercuration.⁶ We now report on a kinetic investigation of the reaction between alkynes and thallium(III) acetate that leads to the corresponding (acetoxythallio)vinyl derivatives (eq 1).



No product from acetoxyplumbation reaction was isolated when the same alkynes were reacted with $\text{Pb}(\text{OAc})_4$.

Results and Discussion

The addition of thallium triacetate to alkynes in acetic acid occurs with yields from moderate to high at a temperature in the range 50–60 °C. The corresponding (acetoxythallio)vinyl acetates have been isolated and identified. The analyses resulted in agreement with that of the analogous compounds previously known.^{7,8}

Acetic acid was chosen as solvent, in order to allow a comparison with the acetoxymercuration reaction.⁶ Kinetic experiments were performed under pseudo-first-order conditions, spectrophotometrically and by gas chromatography, following the formation of the addition product or the disappearance of the substrate, respectively. Results in excellent agreement were obtained with the two methods. The reaction was generally followed up to 80–90%

conversion. With slow reacting substrates, the data corresponding to 50–70% of the addition reaction were considered, since subsequent processes were affecting the readings (see Experimental Section).

The acetoxythallation of alkynes follows a second-order rate law, first order in substrate and first order in $\text{Tl}(\text{OAc})_3$. The results are summarized in Table I. Experimental data for a typical kinetic run are reported in Table II.

Alkylacetylenes were more reactive than the aryl ones, and diphenylethyne did not react at all. Electron-withdrawing substituents such as the methoxycarbonyl and the acetoxy groups decreased the reactivity (Table I, entries 4, 5, and 8). The results are in agreement with the assumption that the electrophilic attack by a thallium(III) species is the rate-determining step, in a process analogous to oxythallation of alkenes.⁹

The previously obtained k_2 values for the acetoxymercuration of the same substrates⁶ are also reported in Table I for comparison, along with the ratio $k_{\text{Hg}(\text{OAc})_2}/k_{\text{Tl}(\text{OAc})_3}$ for all the investigated alkynes. The same trend is observed in both reactions, as it is better represented graphically (Figure 1). It is interesting to note that the ratio of reactivity increases from the least reactive alkynes toward the most reactive ones. Within the alkyne series, mercury(II) and thallium(III) acetates exhibit roughly the same selectivity (e.g. $k_{2\text{-heptyne}}/k_{1\text{-phenyl-1-pentyne}} = 1.2 \times 10^4$ for mercury and 1.6×10^4 for thallium), unlike previous results with alkenes, where it was observed that, under comparable conditions, $\text{Tl}(\text{III})$ is more selective than $\text{Hg}(\text{II})$.¹⁰

The effect of increasing the alkyl length in arylalkyl-alkynes is that of lowering the reactivity in both reactions ($k_{\text{PhC}\equiv\text{CCH}_3}/k_{\text{PhC}\equiv\text{CC}_3\text{H}_7} = 2.1$ in mercuration and 3.4 in thallation). This has generally been the case in the oxymercuration of alkenes and has been interpreted in terms of a larger role played by steric factors with respect to electronic ones.¹¹

Activation parameters were determined for selected substrates, with dialkyl, aryl alkyl, and electron-withdrawing substituents (Table III). Activation entropies for 2-heptyne and 1-phenylpropyne acetoxythallation are the same, within experimental error. In fact, the difference in the reactivity of these substrates results from differences in activation enthalpies. The presence of electron-with-

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Table I. Overall Second-Order Rate Constants for the Acetoxythallation of Alkynes at 25 °C and Comparison with Acetoxymercuration

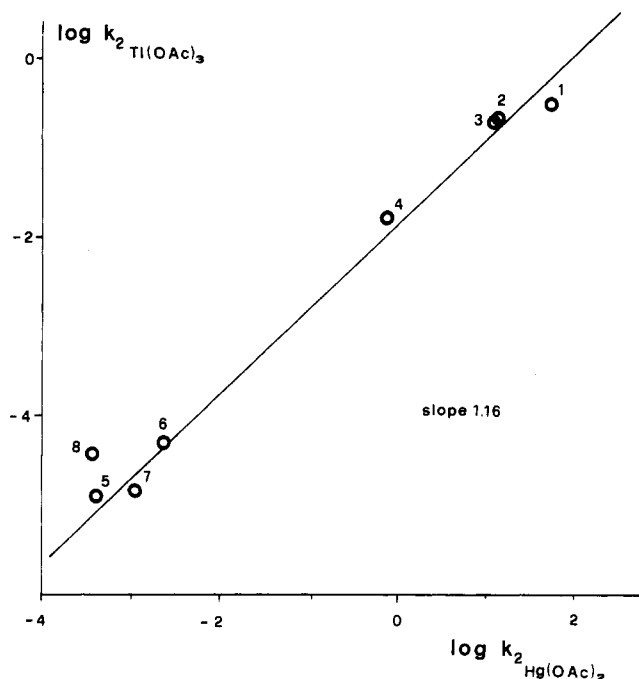
entry	alkyne	$k_2, \text{M}^{-1} \text{s}^{-1}$	$[\text{Tl}(\text{OAc})_3]/[\text{alkyne}]$	method ^a	$k_2(\text{Hg}(\text{OAc})_2), \text{M}^{-1} \text{s}^{-1}$	$k_2(\text{Hg}(\text{OAc})_2)/k_2(\text{Tl}(\text{OAc})_3)$
1	4-octyne	0.29 ± 0.01	14–15	A, B	53	183
2	2-heptyne	0.22 ± 0.01	13	B	13.1^b	128^c
3	2-nonyne	0.19 ± 0.01	16	B	11.7^b	62
4	1,4-diacetoxy-2-butyne	$(1.58 \pm 0.03) \times 10^{-2}$	12–13	A, B	0.72	46
5	methyl 2-octynoate	$(2.5 \pm 0.8) \times 10^{-5}$	10	A, B	3.9×10^{-4}	16
6	1-phenylpropyne	$(4.7 \pm 0.3) \times 10^{-5}$	0.3–77	B	2.3×10^{-3}	49
7	1-phenyl-1-pentyne	$(1.4 \pm 0.2) \times 10^{-5}$	12–34	A, B	1.1×10^{-3}	79
8	methyl phenylpropynoate	$(3.8 \pm 0.2) \times 10^{-5}$	10–30	A, B	3.7×10^{-4}	10

^aSee Experimental Section. ^bReference 6. ^cAt 16.1 °C.

Table II. Experimental Data for a Typical Kinetic Run: Reaction between 2-Heptyne and $\text{Tl}(\text{OAc})_3$ in AcOH at 25.0 °C^a

A_t	t, s	A_t	t, s
0.2359	12	0.2856	204
0.2458	36	0.2889	228
0.2544	60	0.2914	252
0.2619	84	0.2938	276
0.2681	108	0.2956	300
0.2735	132	0.2974	324
0.2783	156	0.2990	348
0.2822	180	0.3005	362

^a $[\text{Alkyne}] = 2.10 \times 10^{-3} \text{ M}$; $[\text{Tl}(\text{OAc})_3] = 3.20 \times 10^{-2} \text{ M}$; $A_\infty = 0.308$; $k_{\text{obsd}} = 6.20 \times 10^{-3} \text{ s}^{-1}$; correlation coefficient = 0.9998; reaction % followed = 90%; $k_2 = 0.19 \text{ M}^{-1} \text{ s}^{-1}$.

**Figure 1.** Reactivity comparison between $\text{Tl}(\text{OAc})_3$ and $\text{Hg}(\text{OAc})_2$ in the reaction with some substituted alkynes.

drawing groups in the alkyl chain also results in increase of activation enthalpy, as in 1,4-diacetoxy-2-butyne. Comparison of activation parameters between mercuration and thallation (Table III) for substrates common to both reactions shows that enthalpy is the factor producing the higher reactivity in mercuration. This effect is slightly reduced by the entropies that appear less negative in thallation. Negative entropies are consistent with a rate-determining associative process.

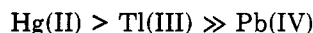
In view of similarities between acetoxymercuration and acetoxythallation of alkynes, the nature of the cationic intermediate in the rate-limiting step is likely to be the

same with both reagents, probably an unsymmetrically bridged cation.⁶ Bridged transition states and intermediates have also been suggested in the oxythallation of some alkenes.^{12,13}

In terms of alkyne reactivity, a comparison between rate constants for thallation and ionization potentials (I) (Table IV) shows some correlation. However, the trend is opposite to that expected, since increasing reactivity is observed with increasing ionization potentials. A similar trend was reported for the oxythallation of internal alkenes, whereas terminal olefins exhibited a linear correlation with ionization potentials, in agreement with the order of reactivity.⁹ We believe that looking at such correlations can be misleading at times, since IP's correspond to the overall energy state of the molecule and not necessarily to the specific site involved in the occurring reaction. Accordingly, the inverse correlation observed in our case may be just accidental.

When 4-octyne, 2-heptyne, 1,4-diacetoxy-2-butyne, and 1-phenylpropyne were treated with equivalent amounts of lead tetraacetate in acetic acid, no reaction occurred, even at high temperatures (80–100 °C) and prolonged reaction times.

Thus, the order of reactivity in this series of metal ion acetates is as follows:



It is interesting to compare this trend with some properties of the metal ions. The standard reduction potentials decrease from lead(IV) to mercury(II) ($E^\circ = 1.7, 1.25,$ and 0.85 for $\text{Pb(IV)}, \text{Tl(III)},$ and Hg(II) acetates, respectively³), in a direction opposite to the reactivity of the metal ions toward alkynes. Thus, the reaction is not charge-controlled.

Dissociation of an acetate group leads to a species, $\text{M}^+(\text{OAc})_{n-1}$, which should be more reactive than the neutral compound in the electrophilic attack to the triple bond. In fact, the values of $K_{\text{dissociation}}$ increase with the increasing reactivity of the metal ion ($K_{\text{dissociation}}$ in AcOH = 3.75×10^{-9} for $\text{Hg}(\text{OAc})_2$, 1.38×10^{-12} for $\text{Tl}(\text{OAc})_3$, and negligible for $\text{Pb}(\text{OAc})_4$ ³). However, the values are very small, so that other factors should be taken in account. Moreover, quantitative studies on the ring-opening reactions of cyclopropanes in AcOH showed that the electrophilic reagents are the neutral covalent species $\text{M}(\text{OAc})_n$ rather than cationic $\text{M}^+(\text{OAc})_{n-1}$.^{17,18}

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Table III. Activation Parameters for the Acetoxythallation of Some Alkynes and Comparison with Acetoxymercuration^a

alkyne	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	range of temp, °C	$\Delta H^\ddagger_{\text{Hg(OAc)}_2}$, kcal/mol	$\Delta S^\ddagger_{\text{Hg(OAc)}_2}$, eu
$\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3$	10.1 ± 0.8	$-(28 \pm 2.7)$	16.1–56.1		
$\text{AcOCH}_2\text{C}\equiv\text{CCH}_2\text{OAc}$	14.9 ± 0.4	$-(17 \pm 1.2)$	16.1–56.1	8.8 ± 0.6	$-(30 \pm 1.8)^b$
$\text{PhC}\equiv\text{CCH}_3$	15.1 ± 0.5	$-(27.5 \pm 0.2)$	25.0–68.0	11.5 ± 0.4^c	$-(33 \pm 2)^c$

^a Correlation coefficients 0.993–0.999. ^b Range of temperature 16.8–56.2 °C. ^c Reference 6.

Table IV. Reactivity of Alkyne Acetoxythallation Compared with Ionization Potentials

entry	alkyne	$\log k_2$	I , eV
1	4-octyne	-0.54	9.196 ^a
2	2-heptyne	-0.66	9.323 ^a
3	2-nonyne	-0.72	9.293 ^b
7	1-phenylpropyne	-4.33	8.47 ^{c,d}
8	1-phenyl-1-pentyne	-4.85	8.37 ^c

^a Reference 14. ^b Calculated according to ref 14. ^c Reference 15. ^d Reference 16.

The first event of the reaction process is probably displacement by the alkyne of a solvent molecule in the metal coordination sphere, followed by formation of a reactive cationic intermediate with release of an acetate group from the metal. On going from Hg(II) to Pb(IV), the coordination sphere of the metal is increasingly more populated by acetate groups than by solvent molecules. Therefore, it is progressively more difficult for a neutral unsaturated species to reach the metal ion at a suitable distance for a reactive interaction to occur. However, it can be doubtful whether the observed order of reactivity depends on such differences in coordination. In fact, these reagents have been found to undergo very fast exchange with the solvent,³ acetate groups moving rapidly between the coordination sphere and the medium. During this exchange, alkyne molecules might come in contact with a reactive ionic species, whether it is from mercury(II), thallium(III), or lead(IV). Therefore, the difference in reactivity, must depend more intrinsically on the nature of the metal ion.

It is quite remarkable that the observed rates of addition to alkynes vary accordingly to the energies of the empty frontier orbitals, as calculated by Klopman for the metal ions in aqueous solutions.¹⁹ In fact, the reagents are soft electrophiles, with softness decreasing and LUMO increasing from Hg(II) to Pb(IV) (-4.64 eV for Hg(II) and -3.37 eV for Tl(III)).

In qualitative terms, the reactivity seems to depend on the distance between the HOMO of the nucleophilic alkyne and the LUMO of the metal. The gap increases from mercury to thallium and is too large in the case of lead, so that the addition reaction is totally prevented.

It is interesting to compare our results with those reported by Strašák and Majer for the oxythallation of alkenes.²⁰ These authors found a good linear relationship between the logarithms of the reaction rate for a series of alkenes and the inverse of the LUMO–HOMO gap. The substrate selectivity, represented by ρ^* and decreasing in the order $\text{Cl}^+ > \text{Br}^+ > \text{Hg}^{2+} > \text{Tl}^{3+} > \text{Ag}^+$, for the corresponding electrophilic additions to alkenes, was also explained in terms of orbital interaction effects. Kinetic studies on the electrophilic aromatic substitution of benzene and toluene by mercury(II) and thallium(III) trifluoroacetates showed the mercury salt to be more reactive by the same order of magnitude we observed for the reaction toward alkynes.²¹

On the other hand, an inverse order of reactivity was observed for the ring opening of cyclopropanes; i.e., $\text{Tl}(\text{OAc})_3 > \text{Hg}(\text{OAc})_2$.¹⁷ Although a HOMO–LUMO interaction between a carbon–carbon bond of cyclopropane and the metal ion is still possible, the reactive process may involve either corner or edge attack by the electrophile and have different energy requirements than in the attack on unsaturated systems. The data were explained in terms of charge control of the reaction, according to the decrease of reduction potentials from Tl^{3+} to Hg^{2+} .

Therefore, there is evidence of significant orbital control in the interaction between these metal ions and unsaturated systems.

Experimental Section

Gas chromatographic analyses have been carried out with a Hewlett-Packard Model 5890A apparatus equipped with a 1.5 m 2% OV 101 Chromosorb GAW-DMCS column. ¹H NMR spectra have been recorded on a Bruker WP-80 and a Varian EM-360 spectrometer with CDCl_3 as solvent and Me_4Si as the internal standard.

Spectrophotometric measurements have been performed with thermostated Cary 219 and Varian DMS 90 spectrophotometers.

Microanalyses were obtained from Microanalysis Service of the CNR "Area di Ricerca" (Montelibretti, Roma).

Materials. 4-Octyne, diphenylethyne, thallium triacetate, lead tetraacetate, and acetic acid were commercially available reagent grade products and were used without further purification.

1-Phenylpropyne,²² 1-phenyl-1-pentyne,²³ methyl phenylpropynoate, methyl 2-octynoate, and 1,4-diacetoxy-2-butyne²⁴ were prepared according to literature methods or to an appropriate modification. All the synthesized alkynes were purified by distillation and checked for purity by gas chromatography ($\geq 98\%$).

Product Analysis. Acetoxythallation products were isolated according to the literature,^{7,8} by adding thallium triacetate in AcOH to an equivalent amount of the alkyne in the same solvent, at a temperature in the range 50–65 °C, depending on the substrate. After a reaction time ranging between 5 and 24 h, the solvent was removed under vacuum without overheating; the residue was treated with CH_2Cl_2 to dissolve the organometallic products, and unreacted $\text{Tl}(\text{OAc})_3$ was separated by filtration. The resulting solution was evaporated in vacuum leaving a sticky oil that was washed with hexane to remove unreacted alkyne or demetalated byproducts. Yields ranged between 47 and 87%. Crude reaction products were crystallized from boiling hexane to give white or yellow powders, which were characterized by ¹H NMR. Elemental analyses of stable compounds are in excellent agreement with calculated values.

¹H NMR spectra of previously known compounds were identical with those reported. Acetoxythallation products from the other alkynes gave spectra from which assignments of structure were made according to the values of $J(^{205}\text{Tl}-\text{H})$ coupling constants, as reported in the literature.^{7,8} The data are as follows.

From 4-Octyne. ¹H NMR: δ 0.91 (t, $J_{\text{H-H}} = 7$ Hz, 6 H, CH_3), 1.4–1.8 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.05 (s, 6 H, $\text{Tl}(\text{OAc})_2$), 2.12 (s, 3 H, OAc), 2.2 (d of t, $J_{\text{H-H}} = 7$ Hz, $J_{\text{Tl-H}} = 148$ Hz, 2 H, $\text{CH}_2\text{C}=\text{CTl}(\text{OAc})_2$), 2.34 (d of t, $J_{\text{H-H}} = 7$ Hz, $J_{\text{Tl-H}} = 1315$ Hz, 2 H, $\text{C}=\text{CCH}_2[\text{Tl}(\text{OAc})_2]$). The data are in agreement with the structure resulting from the product of anti addition: (*E*)- $\text{CH}_3\text{CH}_2\text{CH}_2(\text{AcO})\text{C}=\text{C}[\text{Tl}(\text{OAc})_2]\text{CH}_2\text{CH}_2\text{CH}_3$. Anal. Calcd for

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$C_{14}H_{23}O_6Ti$: C, 34.20; H, 4.71. Found: C, 33.72; H, 4.68. Melting point: 105–109 °C.

From 2-Heptyne. 1H NMR: δ 0.88 (m, 3 H, CH_3), 1.3 (m, 4 H, $(CH_2)_2$), 2.02 (s, 6 H, $Tl(OAc)_2$), 2.13 (s, 3 H, OAc), 1.93 (d of br s, $J_{Ti-H} = 989$ Hz, 3 H, $C=C(CH_3)Ti(OAc)_2$), 3.1 (left-hand triplet of a doublet approximately centered around δ 2.2; right-hand peak buried under the multiplet due to $(CH_2)_2$; $J_{H-H} = 7$ Hz, $J_{Ti-H} = 130$ –140 Hz, $CH_2C=CTl(OAc)_2$). Data are in agreement with the structure of $(E)-(AcO)_2Ti(CH_3)C=C(OAc)(CH_2)_3CH_3$ as the main reaction product. Anal. Calcd for $C_{13}H_{21}O_6Ti$: C, 32.69; H, 4.43. Found: C, 32.55; H, 4.54.

From 2-Nonyne. 1H NMR: δ 0.89 (m, 3 H, CH_3), 1.3 (m, 8 H, $(CH_2)_4$), 2.06 (s, 6 H, $Tl(OAc)_2$), 2.25 (s, 3 H, OAc), 1.98 (d of br s, $J_{Ti-H} = 979$ Hz, 3 H, $C=C(CH_3)Ti(OAc)_2$), 3.1 (left-hand broad peak of a doublet approximately centered around δ 2.2; right-hand peak buried under the multiplet due to CH_2 groups; $J_{Ti-H} = 130$ –140 Hz, $CH_2C=CTl(OAc)_2$). Data are in agreement with the structure of $(E)-(AcO)_2Ti(CH_3)C=C(OAc)(CH_2)_5CH_3$ as the main reaction product. Anal. Calcd for $C_{15}H_{25}O_6Ti$: C, 35.62; H, 4.98. Found: C, 35.81; H, 5.02. Melting point: 88–93 °C.

From 1,4-Diacetoxy-2-butyne. The oil obtained from the workup gave the following 1H NMR spectrum ($CDCl_3$): δ 2.00 (s, 3 H, $CH_3CO_2CH_2CH_2$), 2.13 (s, 3 H, $CH_3CO_2CH_2CO$), 2.73 (t, $J_{H-H} = 6.3$ Hz, 2 H, $CH_2CO_2CH_2CH_2$), 4.32 (t, $J_{H-H} = 6.2$ Hz, 2 H, $CH_3CO_2CH_2CH_2$), 4.64 (s, 2 H, $CH_3CO_2CH_2CO$). These data are consistent with the following structure: $CH_3CO_2CH_2COC-CH_2CH_2OCOCH_3$. The product (85 mg, 90% yield) was obtained from 80 mg of alkyne (0.47 mmol) and 210 mg (0.55 mmol) of $Tl(OAc)_3$. Ketones and other oxidation products are known to be obtained from demetalation of vinylthallium compounds.⁸ The adduct from 1,4-diacetoxy-2-butyne is therefore less stable than the adducts from the other alkynes and undergoes fast demetalation and rearrangements in the reaction conditions and during workup.

From Methyl 2-Octynoate. 1H NMR ($CDCl_3$): δ 0.85 (m, 3 H, CH_3), 1.2 (m, 6 H, $(CH_2)_3$), 2.02 and 2.03 (two s, $Tl(OAc)_2$), 2.10 and 2.20 (two s, OAc), 3.70 (s, 3 H, CO_2CH_3), 2.03 (d of t, $J_{H-H} = 7$ Hz, $J_{Ti-H} = 75$ Hz, $CH_2C=CTl(OAc)_2$), 5.01 (t of low intensity, $J_{H-H} = 6.5$ Hz). The spectrum is consistent with the presence of at least two adducts. The material obtained from the workup was an oil, and crystallizations attempted in order to separate the adducts were not successful. Anal. Calcd for $C_{15}H_{23}O_6Ti$: C, 33.63; H, 4.33. Found: C, 33.46; H, 4.38.

From Methyl Phenylpropynoate. 1H NMR ($CDCl_3$): δ 2.03 (s, 6 H, $Tl(OAc)_2$), 2.24, 2.35 and 2.39 (three s, 3 H, OAc), 3.75, 3.79, 4.00 (three s, 3 H, CO_2CH_3), 7.3–8.1 (complex signal, 5 H, aromatic protons). The spectrum of the white powder obtained shows the presence of three main products of addition.

Kinetic Measurements. Kinetic experiments have been carried out under pseudo-first-order conditions, with different methods.

(A) Known quantities in acetic acid of excess $Tl(OAc)_3$, the alkyne, and the appropriate internal standard were mixed in a thermostated reaction vessel. Samples (0.5 mL) of the reaction mixture were taken with a syringe at known times and added to 5 mL of water and 1 mL of CCl_4 in a separatory funnel. The organic phase was examined at the gas chromatograph immediately after separating and drying with anhydrous Na_2SO_4 . Blank experiments confirmed the reliability of the method. Linear alkanes of high purity, from C_{11} to C_{18} were used as internal standards. The disappearance of the substrate was followed with time, thallated species being not detectable by gas chromatography.

(B) Solutions at known concentration of the reactants were separately put in a silica cell with septum, allowed to reach 25 °C in the thermostated cell compartment of the spectrophotom-

eter, and mixed. The absorbance increase due to the formation of the product was followed with time at the appropriate wavelength. When infinity time absorbance was not available, due to the occurrence of subsequent reactions, the value was extrapolated, according to the Mangelsdorf's method.²⁵

The title of $Tl(OAc)_3$ solutions was checked by titration with standardized $Na_2S_2O_3$.²⁶

The data are reported in Table I as overall second-order rate constants. They are mean values of several runs carried out under conditions specified as follows (wavelengths and fractions of the reaction followed are given in parentheses).

4-Octyne: $C_3H_7C\equiv CC_3H_7$, 2.20×10^{-3} to 4.16×10^{-3} M; $Tl(OAc)_3$, 2.30×10^{-2} to 5.78×10^{-2} M (310 nm, 57–80%).

2-Heptyne: $CH_3(CH_2)_3C\equiv CCH_3$, 2.60×10^{-3} M; $Tl(OAc)_3$, 3.30×10^{-2} M (310 nm, 66–90%).

2-Nonyne: $CH_3(CH_2)_5C\equiv CCH_3$, 2.10×10^{-3} M; $Tl(OAc)_3$, 3.30×10^{-2} M (312 nm, 88–90%).

1,4-Diacetoxy-2-butyne: $AcOCH_2C\equiv CCH_2OAc$, 1.70×10^{-3} to 3.94×10^{-3} M; $Tl(OAc)_3$, 3.30×10^{-2} to 5.12×10^{-2} M (325 nm, 71–85%).

Methyl 2-octynoate: $C_6H_{11}C\equiv CCO_2CH_3$, 2.24×10^{-3} to 5.44×10^{-3} M; $Tl(OAc)_3$, 2.79×10^{-2} to 5.12×10^{-2} M (296, 325 nm, 88%).

1-Phenylpropyne: $PhC\equiv CCH_3$, 1.12×10^{-3} to 3.00×10^{-3} M; $Tl(OAc)_3$, 3.15×10^{-2} to 4.19×10^{-2} M (310, 325, 328 nm, 56–72%).

1-Phenyl-1-pentyne: $PhC\equiv CC_3H_7$, 1.90×10^{-3} to 2.84×10^{-3} M; $Tl(OAc)_3$, 3.15×10^{-2} to 5.12×10^{-2} M (310, 325, 328 nm, 56–98%).

Methyl phenylpropynoate: $PhC\equiv CCO_2CH_3$, 1.75×10^{-3} to 4.62×10^{-3} M; $Tl(OAc)_3$, 2.33×10^{-2} to 5.16×10^{-2} M (310, 325 nm, 56–61%).

Values for a typical run are given in Table II.

Activation Parameters. The rate measurements at various temperatures were duplicated. Good Arrhenius plots were obtained in all cases. The related data, in addition to the rate coefficients in Table I, are as follows (temperatures are given in parentheses).

2-Heptyne: $CH_3(CH_2)_3C\equiv CCH_3$, 2.60×10^{-3} M; $Tl(OAc)_3$, 3.30×10^{-2} M; k_2 ($M^{-1} s^{-1}$) = 0.102 (16.1 °C), 0.51 (40.0 °C), 0.95 (56.1 °C).

1,4-Diacetoxy-2-butyne: $AcOCH_2C\equiv CCH_2OAc$, 1.70×10^{-3} M; $Tl(OAc)_3$, 3.30×10^{-2} M; k_2 ($M^{-1} s^{-1}$) = 6.3×10^{-3} (16.1 °C), 5.0×10^{-2} (40.0 °C), 0.20 (56.1 °C); $AcOCH_2C\equiv CCH_2OAc$, 2.40×10^{-3} M; $Hg(OAc)_2$, 3.26×10^{-2} M; k_2 ($M^{-1} s^{-1}$) = 0.39 (16.8 °C), 1.24 (38.4 °C), 2.91 (56.2 °C).

1-Phenylpropyne: $PhC\equiv CCH_3$, 4.30×10^{-4} to 4.40×10^{-2} M; $Tl(OAc)_3$, 1.30×10^{-3} to 3.30×10^{-2} M; k_2 ($M^{-1} s^{-1}$) = 1.8×10^{-4} (40.0 °C), 1.7×10^{-3} (67.5 °C).

The results are reported in Table III.

Reaction with $Pb(OAc)_4$. Lead tetraacetate in acetic acid was added under nitrogen to equivalent amounts of alkynes (4-octyne, 1-phenylpropyne, 2-heptyne, and 1,4-diacetoxy-2-butyne) and heated at 80–100 °C for 48–96 h. After workup as described for acetoxythallation, no acetoxyplumbation product was isolated.

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Registry No. $PrC\equiv CPr$, 1942-45-6; $MeC\equiv CBu$, 1119-65-9; $MeC\equiv C(CH_2)_2Bu$, 19447-29-1; $AcOCH_2C\equiv CCH_2OAc$, 1573-17-7; $BuCH_2C\equiv CCO_2Me$, 111-12-6; $PhC\equiv CMe$, 673-32-5; $PhC\equiv CPr$, 4250-81-1; $PhC\equiv CCO_2Me$, 4891-38-7; $Tl(OAc)_3$, 2570-63-0.

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