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Metalation of Alkynes. 4. The Methoxymercuration Reaction

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Methoxymercuration of symmetrically and unsymmetrically substituted alkynes (4-octyne, 2-heptyne, 2-nonyne, 1,4-dimethoxy-2-butyne, 1,4-diacetoxy-2-butyne, methyl 2-octynoate, methyl phenylpropynoate, 1-phenylpropyne, 1-phenyl-1-pentyne, diphenylethyne) was investigated. The corresponding α-mercurated enol ethers were generally isolated and characterized, except for 4-octyne, 2-heptyne, and 2-nonyne, which yielded α-acetoxymercurio ketones. Methoxymercuration was investigated kinetically. The rate law is second order, first order in both alkyne and mercuric acetate. Arylalkynes are less reactive than alkyl derivatives and the reaction rate is decreased by electron-withdrawing substituents. Activation parameters were determined for selected substrates. The kinetic data are in agreement with an electrophilic associative rate-determining step. Product analysis results suggest the formation of a cationic intermediate, the nature of which may vary from an unsymmetrically bridged species to an open carbocation, depending on the substrate.

Alkenylmercurials are receiving a renewed interest, since they can be stereoselectively transformed into butadienes, in the presence of palladium complexes[1] and rhodium complexes under catalytic conditions.[2] Moreover, carbonylation of alkenylmercurials is an important route to symmetrical vinyl ketones[3] or to unsaturated esters.[4] Recently, synthesis of 1,4-dienes via vinylpalladation[5] and of methoxy-substituted alkenes, from catalytic and oxidative methoxymercuration of terminal alkynes,[6] were reported.

[(Acetoxymercurio)vinyl]acetates are easily prepared by treating alkynes with mercuric acetate in acetic acid as the solvent[7,8] and regiochemistry,[7] stereochemistry,[8] and kinetics[9] were reported. On the contrary, the analogous (acetoxymercurio)vinyl ethers are reported not to form directly[10] and may be obtained by transmetalation reaction only.[11]

The results from the reaction of alkynes with catalytic amounts of mercuric acetate[12] prompted us to exploit the possibility of preparing mercurated vinyl ethers directly from alkynes and mercuric acetate, at least in some favorable cases.

We report on investigation of the reaction and kinetics of some alkynes with mercuric acetate in methanol as the solvent.

Results and Discussion

A series of disubstituted alkynes (dialkyl, arylalkyl, and diaryl) was made to react with equimolar or excess mercuric acetate in methanol solution, at room temperature. The products from the reactions were isolated and identified. Since direct identification was not always unambiguous and elemental analysis is generally not feasible (due to a tendency of the products to decompose and in some instances to coprecipitation of the inorganic mercury species[13]), reductive demercuration was used as an additional tool. However, particular care has to be taken when demercuration is performed with these derivatives, further transformations being possible when the workup does not follow the addition of sodium borohydride immediately (e.g., enol ethers convert into ketones).

In the case of the aryl derivatives, the products from addition were isolated (eq 1), with yields ranging between 44 and 95% (see Experimental Section), with the regio- and stereochemistry depending on the substrate.

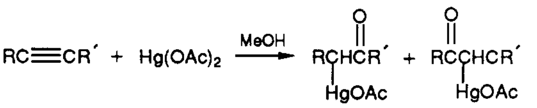
$$\mathrm{ArC{\equiv}CR + Hg(OAc)_2 \xrightarrow{MeOH} ArC(OMe){=}C(HgOAc)R + ArC(HgOAc){=}C(OMe)R} \qquad (1)$$

In the case of diphenylethyne, the two geometric isomers of structure $\mathrm{PhC(OMe){=}C(HgOAc)Ph}$ were obtained in a 95% total yield after 24 h. The relative ratio was calculated from integration of the peaks from the methoxy groups in the NMR spectrum and was found to be 3:1. When the reaction was carried out by with a 3-fold excess of mercuric acetate for 4 h, the products were isolated in a 74% yield, with the same ratio of stereoisomers. These experiments indicate that the reaction is quantitative and the products are obtained under kinetic control, no equilibration being observed given the appropriate time.

The formation of both stereoisomers is in agreement with either an open carbocation as the intermediate or a competitive syn and anti attack on an unsymmetrically bridged cationic species.

The products obtained from diphenylethyne, 1-phenylpropyne, and 1-phenyl-1-pentyne represent the first series of α-(acetoxymercurio)-β-methoxyvinyl derivatives prepared by a direct method. According to Larock, there is only one case in which a vinyl mercurial has been isolated from alkoxymercuration of alkynes;[11] this case involved a peculiar substrate, containing in the skeleton the alcohol functionality, at the right distance to give a stable cycle.[14]

Dialkylalkynes showed a different behavior, yielding α-acetoxymercurio ketones (eq 2).



$$\mathrm{RC{\equiv}CR' + Hg(OAc)_2 \xrightarrow{MeOH} R\underset{HgOAc}{C}H\overset{O}{\overset{\|}{C}}R' + R\overset{O}{\overset{\|}{C}}\underset{HgOAc}{C}HR'} \qquad (2)$$

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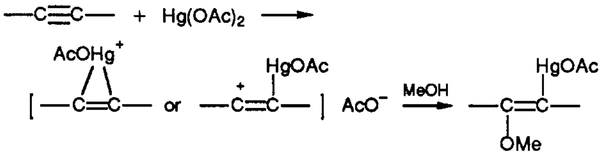
Table I. Overall Second-Order Rate Constants for the Methoxymercuration of Some Alkynes at 25 °C

entry	alkyne	k_2, M^{-1} s^{-1}	$\frac{[Hg(OAc)_2]}{[alkyne]}$	% reactn followed	method
1	4-octyne	0.487 ± 0.0008	10–31	69–99	GC
		0.49 ± 0.03	25	66–88	UV
2	2-heptyne	1.22 ± 0.03	12	96–98	GC
		1.22 ± 0.17	20	58–99	UV
3	2-nonyne	1.02 ± 0.02	12	90–93	GC
		0.99 ± 0.05	14	57–98	UV
4	1,4-dimethoxy-2-butyne	$(1.9 \pm 0.2) \times 10^{-3}$	16–26	91–95	UV
5	1,4-diacetoxy-2-butyne	0.15 ± 0.01	11–12	86–95	UV
6	methyl 2-octynoate	$(3.7 \pm 0.2) \times 10^{-3}$	54–179	69–92	UV
7	methyl phenylpropynoate	$(1.24 \pm 0.06) \times 10^{-2}$	10–32	64–92	UV
8	1-phenylpropyne	$(2.8 \pm 0.4) \times 10^{-2}$	0.0335–915	42–95	UV
9	1-phenyl-1-pentyne	$(3.7 \pm 0.5) \times 10^{-2}$	10–98	66–96	UV
10	diphenylethyne	$(3.3 \pm 0.3) \times 10^{-2}$	10–75	89–99	UV,GC

5-(Acetoxymercurio)-4-octanone was isolated from 4-octyne with yields up to 99%, 2-(acetoxymercurio)-3-nonanone and 3-(acetoxymercurio)-2-nonanone were obtained from 2-nonyne, in a 3:1 ratio and 73% overall yield, and 2-(acetoxymercurio)-3-heptanone and 3-(acetoxymercurio)-2-heptanone were formed from 2-heptyne, with an 88.5% total yield and a 2.5:1 ratio.

This result is interesting in itself, since it is known that it is difficult to obtain α-mercurated carbonyl compounds, especially from the aqueous mercuration of alkynes.[11a] Reductive demercuration by $NaBH_4$ gave the corresponding 3-nonanone (77%) as well as 2-nonanone (23%), and 3-heptanone (71%) as well as 2-heptanone (29%), from the mixture of mercurated products.

The results concerning the product regiochemistry of differently substituted alkynes and the product stereochemistry of the symmetrically substituted ones can be discussed in terms of the nature of the reaction intermediate, which, in principle, can be either a bridged species or an open carbocation (eq 3).



(3)

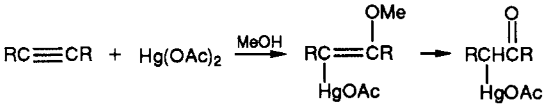
In fact, the (methoxycarbonyl)-substituted alkynes exhibit a definite pattern in terms of regiochemistry of the reaction. The strongly electron-withdrawing substituent plays a role in directing the electrophilic reagent, a single regioisomer of structure $RC(O)CH_2CO_2Me$ ($R = C_5H_{11}$, Ph) being formed from methyl 2-octynoate and methyl phenylpropynoate after prolonged treatment with $NaBH_4$. In both cases, the oxygenated functional group—that comes from the nucleophilic attack by the solvent on the cationic intermediate—is remote from the methoxycarbonyl group; apparently, the intermediate has a carbocation character with the (partial) positive charge far from the electron-attracting substituent.

This may be the case for the arylalkylalkynes as well. When reductive demercuration of the reaction products was performed under conditions chosen in order to obtain ketones (see Experimental Section), only $PhCOCH_2CH_3$ formed from 1-phenylpropyne. This result is in agreement with the formation of an open carbocation as the intermediate, bearing the positive charge on the carbon adjacent to the phenyl group. However, the presence of a longer alkyl chain in 1-phenyl-1-pentyne resulted in formation of both regioisomers. After reductive demercuration, 84% $PhCOCH_2C_3H_7$ and 16% $PhCH_2COC_3H_7$ were obtained. We suggest that the stronger electron-releasing ability of the propyl group stabilizes a (partial) positive charge on the carbon atom β to the phenyl group, resulting in the formation of the second regioisomer. In this case too, the reaction has proceeded through either an unsymmetrically bridged species or two different open cationic species.

Also in the case of the dialkylalkynes (2-heptyne and 2-nonyne), the formation of two products, 3-heptanone (71%) and 3-nonanone (77%) being the major regioisomers after treatment with $NaBH_4$, suggests that both types of intermediates are possible.

As to the stereochemistry, both *E* and *Z* stereoisomers were obtained from methyl phenylpropynoate and 1-phenylpropyne, besides diphenylethyne. It was not possible to make an unambiguous attribution of the configuration of each stereoisomer, because no coupling constant is available, and the only difference is the fragmentation pattern in the mass spectra of the demercurated species. Nevertheless, the occurrence of syn addition is significant in that it indicates that the symmetrically bridged mercurinium ion may be ruled out.

The reaction, kinetically investigated, follows a second-order rate law, first order in alkyne and first order in mercuric acetate. Kinetic experiments were performed under pseudo-first-order conditions, generally using an excess of the mercurating agent, either following the disappearance of the alkyne by gas chromatography or the formation of the product by electronic spectroscopy. The use of both techniques was very useful with dialkylalkynes. At first, results from gas chromatographic and UV experiments gave quite different results for the second-order rate coefficients. As a matter of fact, the reaction followed in the UV region was the subsequent transformation from the mercurated enol ether to the mercurated ketone, actually isolated (eq 4). A careful inspection of the absorbance values at the early stages of the reaction revealed the occurrence of two processes. By using a UV diode array spectrophotometer in the range 220–350 nm, it was possible to obtain second-order rate constants for the methoxymercuration reaction in excellent agreement with those evaluated from GC measurements (see Table I).



$$RC{\equiv}CR + Hg(OAc)_2 \xrightarrow{MeOH} \underset{HgOAc}{RC}{=}\overset{OMe}{CR} \rightarrow \underset{HgOAc}{RCH}\overset{O}{\overset{\|}{C}}R \qquad (4)$$

No problem of this kind was observed with the other substrates. However, special care was necessary with diphenylethyne, the addition product from which underwent subsequent reaction, partially superimposed with the first one. Therefore, the absorbance value at infinity time had to be extrapolated.

Alkyl-substituted alkynes (Table I, entries 1–3) were more reactive than alkynes with an aryl substituent (Table I, entries 7–10), with the same reactivity pattern as ob-

Table II. Comparison between Acetoxymercuration[9] and Methoxymercuration Second-Order Rates

entry	alkyne	k_{MeOH}/k_{AcOH}
1	$C_3H_7C{\equiv}CC_3H_7$	0.009
3	$CH_3C{\equiv}C(CH_2)_5CH_3$	0.09
4	$MeOCH_2C{\equiv}CCH_2OMe$	0.04
5	$AcOCH_2C{\equiv}CCH_2OAc$	0.21
6	$CH_3(CH_2)_4C{\equiv}CCO_2Me$	9.5
7	$PhC{\equiv}CCO_2Me$	33.5
9	$PhC{\equiv}CC_3H_7$	33.6
10	$PhC{\equiv}CPh$	1031

Table III. Activation Parameters for Arylalkyne Methoxymercuration

alkyne	$\Delta H^{\neq}$, kcal/mol	$\Delta S^{\neq}$, eu	corrltn coeff	temp range, °C
$PhC{\equiv}CCH_3$	6.5 ± 0.4	−44 ± 1	0.995	25.0–45.1
$PhC{\equiv}CC_3H_7$	5.4 ± 0.6	−47 ± 2	0.985	25.0–45.1
$PhC{\equiv}CPh$	5.0 ± 0.2	−48.4 ± 0.5	0.998	20.0–49.9

served in acetoxymercuration.[9] However, the substrate selectivity of the reaction in methanol is much lower than that in acetic acid:

$$\begin{aligned} k_{4\text{-octyne}}/k_{PhC{\equiv}CPh} &= 15 \text{ in MeOH} \\ &= 1600 \text{ in AcOH} \end{aligned}$$

Considering the rate constant values for the reaction in methanol, this result stems from both a diminished reactivity of alkylalkynes (4-octyne, $k_{MeOH}/k_{AcOH} = 0.01$) and an increased reactivity of arylalkynes ($PhC{\equiv}CPh$, $k_{MeOH}/k_{AcOH} \simeq 1000$; Table II).

The different reactivity of alkylalkynes may be explained with the different nucleophilicity of the two solvents, methanol being more nucleophilic,[15] thus reducing the electrophilicity of the mercurated reagent.

A different explanation is necessary for arylalkynes. The reactivity of acetoxymetalation appeared to be related to the distance between the HOMO of the alkyne and the LUMO of the metal ion.[16] Thus, the low reactivity of arylalkynes in acetic acid was explained in terms of higher HOMO–LUMO distance than in the alkylalkynes, because of resonance stabilization of the ground state in the aromatic substrates.[9] Apparently, in methanol the transition state is earlier than in acetic acid, resembling more the reactants, and therefore loosing less resonance stability. This hypothesis is confirmed by the low values of activation enthalpy (Table III; $PhC{\equiv}CPh$, $\Delta H^{\neq} = 5.0$ kcal/mol in MeOH, 13.9 kcal/mol in AcOH[9]). Activation entropies have large negative values, in agreement with an ordered transition state, as expected from a cationic species, surrounded by nucleophilic solvent molecules.

With electron-withdrawing substituents (Table I, entries 4–6), the reactivity decreased, as expected for an electrophilic rate-determining step.

In conclusion, methoxymercuration of alkynes is an electrophilic addition that is likely to proceed through a cationic intermediate, the nature of which may vary from an unsummetrically bridged species to an open carbocation, depending on the substrate. In favorable cases, it allows isolation of mercurated enol ethers or α-mercurated ketones.

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.

Gas–mass spectrometry analyses have been performed with a Hewlett-Packard 5970B system, equipped with a Hewlett-Packard 5890 gas chromatograph.

^1H NMR spectra have been recorded on a Bruker WP-80 spectrometer with $CDCl_3$ as the solvent and Me_4Si as the internal standard.

Thermostatted Cary 219, Cary 210, and HP 8452 diode array spectrophotometers have been used for spectroscopic measurements.

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

Materials. Mercuric acetate, 4-octyne, 1-phenylpropyne, and diphenylethyne were commercially available reagent grade products and were used without further purification, after checking for their purity. 1,4-Dimethoxy-2-butyne, 1,4-diacetoxy-2-butyne, 1-phenyl-1-pentyne, 2-heptyne, 2-nonyne, methyl 3-phenylpropynoate, and methyl 2-octynoate were prepared and purified as previously reported.[9] All the synthesized alkynes were purified by distillation and checked for purity by gas chromatography (≥98%).

Product Analysis. General Procedure. Equimolar amounts of alkyne and mercuric acetate in methanol were reacted at room temperature under a nitrogen atmosphere. After a time dependent on the substrate disappearance, as monitored by GC (for example, a 0.4 M solution of 2-heptyne reacted in 7 h, a 0.4 M solution of 1-phenylpropyne reacted in 24 h), any solid formed was removed by filtration through Celite and the solvent was completely evaporated off from the filtrate, under vacuum and without heating. Generally, a white or pale yellowish oily residue remained that was dissolved with dichloromethane and filtered (Celite aid) from unreacted $Hg(OAc)_2$. The residue, from evaporation of dichloromethane under vacuum, was washed twice or three times with pentane or hexane to remove any alkyne remaining even when the mercurated compound was somewhat soluble in hydrocarbons. The product thus obtained was dried thoroughly under vacuum and examined by NMR spectrometry. When possible, elemental analysis was performed.

The identification was confirmed by reductive demercuration (with aqueous $NaBH_4/OH^-$[17]) and gas chromatography/mass spectrometry technique. In some instances iododemercuration was performed with an iodine solution in dichloromethane.[13]

The results were as follows.

From 4-Octyne. 5-(Acetoxymercurio)-4-octanone was isolated after being washed with hexane, in a 73% yield (crude product, 81%). When 4-octyne was reacted with a 5-fold excess of mercuric acetate, the same product was obtained quantitatively (yield 99%). ^1H NMR ($CDCl_3$) δ: 3.5 (m, -C(O)C*H*HgOAc-), 2.6 (t, 2 H, -C*H*$_2$C(O)-), 1.95 (s, 3 H, HgOAc), 1.70–1.2 (complex, 6 H, three -C*H*$_2$-), 0.96 and 0.88 (two triplets partly superimposed, 6 H, C*H*$_3$). ^{13}C NMR ($CDCl_3$) δ: 209.44 (-C(O)-), 176.85, (HgOC(O)CH$_3$).

Reductive demercuration yielded 4-octanone [GC/MS: m/z, 128 (M^+) (M_r 128.21), 113 ($M^+ - Me$), 99 ($M^+ - Et$), 85 ($M^+ - Pr$)]; if the workup does not follow the addition of $NaBH_4$ immediately, 4-octanol is also produced [GC/MS: m/z 129 ($M^+ - 1$), 112 ($M^+ - H_2O$)]. Iododemercuration gave 5-iodo-4-octanone [GC/MS: m/z 254 (M^+) (M_r 254.11), 225 ($M^+ - Et$), 127 ($M^+ - I$)].

From 2-Heptyne. 2-(Acetoxymercurio)-3-heptanone [^1H NMR ($CDCl_3$) δ: 2.6 (t, -C(O)C*H*$_2$), 1.4 (d, C*H*$_3$CH(HgOAc)-, superimposed to the signals of the methylene group). ^{13}C NMR ($CDCl_3$) δ: 210.4, (-C(O)-)] was obtained as the main product, together with 3-(acetoxymercurio)-2-heptanone [^1H NMR ($CDCl_3$) δ: 2.29 (s, C*H*$_3$C(O)). ^{13}C NMR ($CDCl_3$) δ: 207.7 (-C(O)-). Signals common to both compounds: ^1H NMR 3.5 (m, C(O)C*H*(HgOAc)-), 1.94 (s, 3 H, HgOAc), 1.6–1.2 (m, 4 H, -C*H*$_2$C*H*$_2$), 0.95–0.75 (m, 3 H, -CH$_2$C*H*$_3$); ^{13}C NMR δ 176.8, HgO*C*(O)CH$_3$] in an overall 88.5% yield, after washing with hexane (yield of crude product, 97%).

Reductive demercuration produced 29% 2-heptanone [GC/MS: m/z 114 (M^+) (M_r 114.18), 99 ($M^+ - Me$), 85 ($M^+ - Et$)] and 71% 3-heptanone [GC/MS: m/z 114 (M^+), 85 ($M^+ - Et$, base peak)].

From 2-Nonyne. 2-(Acetoxymercurio)-3-nonanone [^1H NMR ($CDCl_3$) δ: 2.6 (t, -C(O)C*H*$_2$-), 1.4 (d, C*H*$_3$CH(HgOAc), superim-

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(15) See, e.g.; Floris, B.; Illuminati, G. *Coord. Chem. Rev.* **1975**, *16*, 107.

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posed to the signals of the methylene groups). ^{13}C NMR (CDCl$_3$) δ: 210.6 (-C(O)-)] and 3-(acetoxymercurio)-2-nonanone [^{1}H NMR (CDCl$_3$) δ: 2.32 (s, C*H*$_3$C(O)). ^{13}C NMR (CDCl$_3$) δ: 207.6 (-C(O)-). Signals common to both compounds: ^{1}H NMR δ 3.55–3.45 (complex, (-C(O)C*H*(HgOAc)), 1.91 (s, 3 H, HgOAc), 1.6–1.4 (complex), -C(O)CH$_2$C*H*$_2$- and -CH(HgOAc)C*H*$_2$-), 1.3–1.1 (m, 6 H, -(C*H*$_2$)$_3$-), 0.77 (t, 3 H, C*H*$_3$); ^{13}C NMR δ 176.8 (HgO*C*(O)CH$_3$)] were formed, in a global 73% yield (crude product, 81%).

From reductive demercuration, 77% 3-nonanone [GC/MS: *m/z* 142 (M$^+$) (M_r 142.24), 113 (M$^+$ – Et, base peak), 99 (M$^+$ – Pr), 85 (M$^+$ – Bu)] and 23% 2-nonanone were obtained [GC/MS: *m/z* 142 (M$^+$), 127 (M$^+$ – Me), 113 (M$^+$ – Et), 99 (M$^+$ – Pr), 85 (M$^+$ – Bu)].

From 1,4-Dimethoxy-2-butyne. In the course of the reaction, metallic mercury formed; the species isolated after the usual workup were not directly identifiable [^{1}H NMR (CDCl$_3$) δ 2.05 (s, HgOAc, several signals in the OCH$_3$ zone)]. Reductive demercuration gave 32.5% 1,2,4-trimethoxy-2-butene, CH$_3$OCH$_2$CH═C(OCH$_3$)CH$_2$OCH$_3$ [GC/MS: *m/z* 146 (M$^+$) (M_r 146.18), 101 (M$^+$ – CH$_2$OCH$_3$, base peak)] and 61% 1,4-dimethoxy-2-butanone, CH$_3$OCH$_2$CH$_2$COCH$_2$OCH$_3$ [GC/MS: *m/z* 132 (M$^+$) (M_r, 132.16), 87 (M$^+$ – CH$_2$OCH$_3$, base peak), together with 6.5% of some oligomerization products (GC/MS: *m/z* 380 and 426).

From 1,4-Diacetoxy-2-butyne. The reaction of 1,4-diacetoxy-2-butyne (255 mg, 1.5 mmol) with equimolar mercuric acetate gave abundant white precipitate, which could not be redissolved and therefore allowed no direct identification. On standing, it decomposed releasing metallic mercury. From the workup of the solution, only 67 mg were recovered, containing 1,4-diacetoxy-2-(acetoxymercurio)-3-methoxy-2-butene, AcOCH$_2$C(HgOAc)═C(OCH$_3$)CH$_2$OAc [43%; ^{1}H NMR (CDCl$_3$) δ 4.69 (s, 2 H, AcOC*H*$_2$C(HgOAc)═), 4.14 (s, 2 H, AcOC*H*$_2$C(OMe)═), 3.21 (s, 3 H, OC*H*$_3$), 2.08 (s, 6 H, C*H*$_3$CO$_2$-), and 2.02 (s, 3 H, HgOAc)], and demercurated vinyl ethers, i.e., *cis*- and *trans*-1,4-diacetoxy-2-methoxy-2-butene (57%; ^{1}H NMR δ 5.45 and 5.88, -CH═).

Reductive demercuration performed on the white solid yielded a single product, 1,4-diacetoxy-2-methoxy-2-butene (GC/MS: *m/z* 203.25 (M$^+$+1) M_r 202.21).

From Methyl 2-Octynoate. With this substrate also, a white precipitate formed that did not dissolve in chloroform and could not be identified directly. The white solid has a carbon and hydrogen content lower than expected (Calcd for C$_{12}$H$_{20}$O$_5$Hg: C, 32.40, H, 4.53. Found: C, 27.28, H, 3.56), probably because some inorganic mercury coprecipitated.[13] However, after treatment with sodium borohydride, a single product was obtained and identified as the vinyl ether. GC/MS: *m/z* 186 (M$^+$) (M_r 186.25), 171 (M$^+$ – Me), 155 (M$^+$ – OMe), 111 (M$^+$ – CH$_2$CO$_2$CH$_3$). The solution contained mostly unreacted alkyne and less than 2% vinyl ether, as indicated by analysis of the products from reductive demercuration. Under iododemercuration conditions, methyl 3-oxooctanoate was obtained, as identified by mass spectrometry. GC/MS: *m/z* 171 (M$^+$) (M_r 172.22), 99 (M$^+$ – CH$_2$CO$_2$CH$_3$), 71 (M$^+$ – C$_5$H$_{11}$).

From Methyl Phenylpropynoate. Methyl 2-(acetoxymercurio)-3-methoxy-3-phenylpropenoate was isolated in a 73% yield (crude product, 80.5%). ^{1}H NMR (CDCl$_3$): δ 7.9–7.2 (m, 5 H, Ph), 3.74 and 3.71 (two s, CO$_2$C*H*$_3$), 3.5 and 3.2 (s, 3 H, OC*H*$_3$), 1.90 (s, 3 H, HgOAc). The intensity of CO$_2$C*H*$_3$ signals is lower than expected for a 1:1 addition product; the data are consistent with the formation of two isomers. ^{13}C NMR (CDCl$_3$) δ: 176.8 (HgO*C*(O)CH$_3$), 197.7 (CO$_2$CH$_3$).

From treatment with sodium borohydride and immediate workup, the two stereoisomers of methyl 3-methoxy-3-phenylpropenoate, A [40%; GC/MS *m/z* 192 (M$^+$) (M_r 192.12), 191 (M$^+$ – 1), 161 (M$^+$ – OCH$_3$, base peak), 177 (M$^+$ – CH$_3$), 133 (M$^+$ – OC(O)CH$_3$), 115 (M$^+$ – Ph)] and B [60%; GC/MS *m/z* 193 (M$^+$ + 1), 161 (M$^+$ – OCH$_3$), 151, 105 (PhCO$^+$). When the reaction time is prolonged to 30 min, methyl 3-oxo-3-phenylpropanoate was isolated [GC/MS: *m/z* 178 (M$^+$) (M_r 178.19), 147 (M$^+$ – OCH$_3$), 105 (PhCO$^+$)].

From 1-Phenylpropyne. 2-(Acetoxymercurio)-1-methoxy-1-phenylpropene (44%) was isolated (crude product 79%) as a ca. 1:1 mixture of *E* and *Z* isomers [^{1}H NMR (CDCl$_3$) δ: 7.7–7.3 complex, 5 H, Ph), 3.41 (s), and 3.39 (s, 3 H altogether, OC*H*$_3$), 1.98 (s, 3 H, HgOAc), and 1.08 and 1.06 (two s, C*H*$_3$). ^{13}C NMR (CDCl$_3$) δ: 176.10 (HgO*C*(O)CH$_3$)]. Reductive demercuration with workup performed 30 min after NaBH$_4$ addition gave 1-phenyl-1-propanone [^{1}H NMR (CDCl$_3$) δ: 7.9–8.0 and 7.4–7.6 (5 H, Ph), 3.0 (q, 2 H, C*H*$_2$CH$_3$), and 1.24 (t, 3 H, CH$_2$C*H*$_3$). GC/MS: *m/z* 134 (M$^+$) (M_r 134.18), 105 (M$^+$ – Et)], whereas immediate analysis revealed the presence of 42% 1-phenyl-1-propanone together with the two stereoisomeric vinyl ethers, 1-methoxy-1-phenylpropene, A [50%; GC/MS *m/z* 151 (M$^+$ + 3 H), 133 (M$^+$ – Me), 117 (M$^+$ - OMe), 105 (PhCHMe$^+$ or PhCO$^+$)] and B [8%; GC/MS *m/z* 151 (M$^+$ + 3 H), 133 (M$^+$ – Me), 121 (PhC(OMe)H$^+$), 105 (PhCHMe$^+$), 91 (PhCH$_2$$^+$)].

From 1-Phenyl-1-pentyne. Vinyl ether (80%) was obtained (crude product 95%) from the reaction between 1-phenyl-1-pentyne and equimolar mercuric acetate [^{1}H NMR (CDCl$_3$) δ: 7.6–7.1 (m, 5 H, Ph), 3.24 and 3.12 (two s (1:1.6), OC*H*$_3$), 1.94 (s, HgOAc), 2.5–2.0 (m, 2 H, ═CCH$_2$-), 1.6–1.1 (m, 2 H, ═CCH$_2$C*H*$_2$CH$_3$), 0.905 and 0.795 (two t, 3 H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 176.67, HgO*C*(O)CH$_3$]. Prolonged reductive demercuration (30 min) gave 84% 1-phenyl-1-pentanone [GC/MS: *m/z* 162 (M$^+$) (M_r 162.23), 105 (PhCO$^+$), 120 (PhCOCH$_2$$^+$ + H), 77 (Ph$^+$)] and 16% 1-phenyl-2-pentanone [GC/MS: *m/z* 162 (M$^+$), 91 (PhCH$_2$$^+$), 71 (CH$_3CH_2CH_2CO^+$, base peak)]. Demercuration stopped immediately after NaBH$_4$ addition produced 77% 1-methoxy-1-phenyl-1-pentene [GC/MS: *m/z* 177 (M$^+$ + 1) (M_r 176.26), 151, 133 (M$^+$ – Pr), 121 (PhC(OMe)H$^+$), 105 (PhCO$^+$)] and 23% 2-methoxy-1-phenyl-1-pentene [GC/MS: *m/z* 176 (M$^+$), 147 (M$^+$ – Et, base peak), 133 (M$^+$ – Pr), 91 (PhCH$_2$$^+$)].

From Diphenylethyne. The two stereoisomers of 1-(acetoxymercurio)-2-methoxy-1,2-diphenylethene were isolated in a 95% total yield and 3:1 relative ratio, after 24 h. A 74% yield and the same stereoisomeric ratio were obtained after 4 h and a 3-fold excess of mercuric acetate (0.64 g of diphenylethyne, 3.6 mmol, and 3.96 g of mercuric acetate, 12.4 mmol). Anal. Calcd for C$_{17}$H$_{16}$O$_3$Hg: C, 43.54, H, 3.44. Found: C, 43.63, H, 3.10. ^{1}H NMR (CDCl$_3$) δ: 7.8–6.9 (m, 10 H, aromatic protons), 3.52 and 3.44 (two s, 3 H altogether, OC*H*$_3$), 2.03 (s, 3 H, HgOAc).

1-Iodo-2-methoxy-1,2-diphenylethene was obtained from iododemercuration reaction [GC/MS: *m/z* 336 (M$^+$) (M_r 336.18)], whereas 1-methoxy-1,2-diphenylethene was isolated from reductive demercuration [GC/MS: *m/z* 210 (M$^+$) (M_r 210.27), 105 (PhCO$^+$, base peak)], together with some amount of 1,2-diphenylethanone [GC/MS: *m/z* 196 (M$^+$) (M_r 196.25), 105 (PhCO$^+$, base peak)], when workup is delayed 30 min after the addition of NaBH$_4$.

Kinetic Measurements. Kinetic experiments have been carried out under pseudo-first-order conditions, following with time either the alkyne disappearance (by gas chromatography, with internal standard) or the product formation (by UV spectroscopy).

(a) Gas Chromatographic Method. Solutions at known concentration of the reactants and the appropriate internal standard in methanol were mixed in a thermostatted reaction vessel. Samples (0.5 mL) of the reaction mixture, taken at known times, were examined at the gas chromatograph, after quenching the reaction with water, extracting with dichloromethane, and drying over anhydrous sodium sulfate. The reliability of the method was checked with blank experiments. Linear alkanes of high purity, from C10 to C18, were used as internal standards. All the kinetics were at least duplicated and the reactions gave good first-order linear plots up to 99% reaction.

(b) UV Method. Solutions at known concentrations of alkyne in methanol and mercuric acetate in the same solvent were separately put in the two parts of a silica cell with septum and allowed to reach the desired temperature in the thermostatted cell compartment of the spectrophotometer. After mixing, the absorbance increase due to the reaction was followed with time, at the appropriate wavelength. With fast reacting alkynes, the entire spectrum range was recorded by using the HP 8452 diode array spectrophotometer. Rate coefficients computed at different wavelengths were in good agreement. When infinity time absorbance was not available, due to the occurrence of subsequent reactions, the value was extrapolated by the Mangelsdorf's method.[18] When available, experimental and extrapolated infinity time absorbance were in excellent agreement.

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Table IV. Experimental Data for a Typical Kinetic Run: Reaction between 1-Phenylpropyne and $Hg(OAc)_2$ in MeOH at 25.0 °C[a]

A_t	t, min	A_t	t, min
0.1195	0	0.8052	24
0.2950	3	0.8427	27
0.4193	6	0.8762	30
0.5145	9	0.9058	33
0.5919	12	0.9321	36
0.6568	15	0.9556	39
0.7134	18	0.9769	42
0.7620	21	0.9964	45

[a] [alkyne] = 3.12×10^{-4} M; [$Hg(OAc)_2$] = 2.85×10^{-2} M; $A_\infty = 1.084$; $k_{obs} = 8.8 \times 10^{-2}$ s^{-1}; correlation coefficient = 0.999; reaction % followed = 91%; $k_2 = 2.9 \times 10^{-2}$ s^{-1} M^{-1}.

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

4-Octyne ($C_3H_7C\equiv CC_3H_7$): 2.11×10^{-3} to 4.97×10^{-3} M; $Hg(OAc)_2$, 3.28×10^{-2} to 0.155 M (262, 266, 268, 270, 296, 300, 304, 306 nm).

2-Heptyne ($CH_3C\equiv C(CH_2)_3CH_3$): 2.60×10^{-3} to 4.66×10^{-3} M; $Hg(OAc)_2$, 2.67×10^{-2} to 5.22×10^{-2} M (258, 262, 266, 268, 290, 296, 300, 306, 310 nm).

2-Nonyne ($CH_3C\equiv C(CH_2)_5CH_3$): 2.31×10^{-3} to 3.76×10^{-3} M, $Hg(OAc)_2$, 2.67×10^{-2} to 5.22×10^{-2} M (290, 296, 300, 310, 316 nm).

1,4-Dimethoxy-2-butyne ($MeOCH_2C\equiv CCH_2OMe$): 1.75×10^{-3} M; $Hg(OAc)_2$, 2.86×10^{-2} to 4.60×10^{-2} M (290 nm).

1,4-Diacetoxy-2-butyne ($AcOCH_2C\equiv CCH_2OAc$): 1.75×10^{-3} to 4.10×10^{-3} M; $Hg(OAc)_2$, 2.1×10^{-2} to 4.6×10^{-2} M (290 nm).

Methyl 2-octynoate ($CH_3(CH_2)_4C\equiv CCO_2CH_3$): 8.08×10^{-4} to 4.81×10^{-3} M; $Hg(OAc)_2$, 4.35×10^{-2} to 0.145 M (310, 325 nm).

Methyl 3-phenylpropynoate ($PhC\equiv CCO_2CH_3$): 7.89×10^{-4} M; $Hg(OAc)_2$, 5.03×10^{-3} to 2.51×10^{-2} M (300, 310 nm).

1-Phenylpropyne ($PhC\equiv CCH_3$): 2.50×10^{-5} to 8.50×10^{-2} M; $Hg(OAc)_2$, 1.15×10^{-2} to 0.115 M (300, 310 nm).

1-Phenyl-1-pentyne ($PhC\equiv CC_3H_7$): 4.70×10^{-4} to 4.70×10^{-3} M; $Hg(OAc)_2$, 1.15×10^{-2} to 0.115 M (289, 310 nm).

Diphenylethyne ($PhC\equiv CPh$): 7.29×10^{-5} to 7.29×10^{-3} M; $Hg(OAc)_2$, 2.55×10^{-3} to 0.128 M (310, 316 mn).

Values for a typical run are given in Table IV.

Activation Parameters. The kinetic experiments at different temperatures were duplicated. The related data are as follows (temperatures given in parentheses).

1-Phenylpropyne ($PhC\equiv CCH_3$): 1.29×10^{-3} M; $Hg(OAc)_2$, 2.21×10^{-2} to 0.135 M; k_2 (M^{-1} s^{-1}) = 3.17×10^{-2} (30.0 °C), 3.95×10^{-2} (35.0 °C), 5.00×10^{-2} (40.0 °C), 5.72×10^{-2} (44.9 °C), 5.82×10^{-2} (45.1 °C).

1-Phenyl-1-pentyne ($PhC\equiv CC_3H_7$): 1.70×10^{-3} M; $Hg(OAc)_2$, 2.67×10^{-2} M; k_2 (M^{-1}s^{-1}) = 4.71×10^{-2} (35.0 °C), 5.94×10^{-2} (40.0 °C), 6.53×10^{-2} (44.9 °C), 7.17×10^{-2} (45.1 °C).

Diphenylethyne ($PhC\equiv CPh$): 1.59×10^{-2} M; $Hg(OAc)_2$, 4.98×10^{-2} to 9.97×10^{-2} M; k_2 (M^{-1}s^{-1}) = 3.00×10^{-2} (20.0 °C), 4.09×10^{-2} (30.0 °C), 4.55×10^{-2} (34.8 °C), 5.49×10^{-2} (40.0 °C), 6.45×10^{-2} (44.9 °C), 7.32×10^{-2} (49.9 °C).

The second-order rate coefficients, together with the values at 25 °C (Table I), yielded good Arrhenius plots. Activation parameters are in Table III.

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Registry No. [$Hg(OAc)_2$], 1600-27-7; $CH_3(CH_2)_2C\equiv C(CH_2)_2CH_3$, 1942-45-6; $CH_3C\equiv C(CH_2)_3CH_3$, 1119-65-9; $CH_3C\equiv C(CH_2)_5CH_3$, 19447-29-1; $CH_3OCH_2C\equiv CCH_2OCH_3$, 16356-02-8; $AcOOCH_2C\equiv CCH_2OAc$, 1573-17-7; $CH_3OC(O)C\equiv C(CH_2)_5CH_3$, 111-12-6; $CH_3OC(O)C\equiv CPh$, 4891-38-7; $PhC\equiv CCH_3$, 673-32-5; $PhC\equiv C(CH_2)_2CH_3$, 4250-81-1; $PhC\equiv CPh$, 501-65-5; $CH_3(CH_2)_2C(O)CH(HgOAc)(CH_2)_2CH_3$, 122948-91-8; $CH_3CH(HgOAc)C(O)(CH_2)_3CH_3$, 122948-92-9; $CH_3C(O)CH(HgOAc)(CH_2)_3CH_3$, 122948-93-0; $CH_3CH(HgOAc)C(O)(CH_2)_5CH_3$, 122948-94-1; $CH_3C(O)CH(HgOAc)(CH_2)_5CH_3$, 122948-95-2; $AcOCH{=}C(HgOAc)CH(OCH_3)CH_2OAc$, 122948-96-3; $CH_3OC(O)C(HgOAc){=}C(OCH_3)(CH_2)_4CH_3$, 122948-97-4; $CH_3OC(O)C(HgOAc){=}C(OCH_3)Ph$, 122948-98-5; (*E*)-$CH_3C(HgOAc){=}C(OCH_3)Ph$, 122948-99-6; (*Z*)-$CH_3C(HgOAc){=}C(OCH_3)Ph$, 122949-00-2; (*E*)-$PhC(HgOAc){=}C(OCH_3)Ph$, 122949-02-4; (*Z*)-$PhC(HgOAc){=}C(OCH_3)Ph$, 122949-01-3; $CH_3(CH_2)_2C(O)(CH_2)_3CH_3$, 589-63-9; $CH_3(CH_2)_2CH(OH)(CH_2)_3CH_3$, 589-62-8; $CH_3(CH_2)_2C(O)CH(I)(CH_2)_2CH_3$, 122949-03-5; $CH_3C(O)(CH_2)_4CH_3$, 110-43-0; $CH_3CH_2C(O)(CH_2)_3CH_3$, 106-35-4; $CH_3CH_2C(O)(CH_2)_5CH_3$, 925-78-0; $CH_3C(O)(CH_2)_6CH_3$, 821-55-6; $CH_3OCH_2CH{=}C(OCH_3)CH_2OCH_3$, 122949-04-6; $CH_3O(CH_2)_2C(O)CH_2OCH_3$, 25680-86-8; (*Z*)-$AcOCH_2C(OCH_3){=}CHCH_2OAc$, 122949-05-7; (*E*)-$AcOCH_2C(OCH_3){=}CHCH_2OAc$, 122949-06-8; $CH_3OC(O)CH_2C(O)(CH_2)_4CH_3$, 22348-95-4; (*E*)-$CH_3OC(O)CH{=}C(OCH_3)Ph$, 60456-20-4; (*Z*)-$CH_3OC(I)CH{=}C(OCH_3)Ph$, 40203-51-8; $PhC(O)CH_2CH_3$, 93-55-0; (*E*)-$PhC(OCH_3){=}CHCH_3$, 4541-69-9; (*Z*)-$PhC(OCH_3){=}CHCH_3$, 4518-65-4; $PhC(OCH_3){=}C(HgOAc)(CH_2)_2CH_3$, 122949-07-9; $PhC(O)(CH_2)_3CH_3$, 1009-14-9; $PhCH(I)CH(OCH_3)Ph$, 122949-08-0; $PhC(OCH_3){=}CHPh$, 79341-79-0; $CH_3OC(I)CH_2C(O)Ph$, 614-27-7.

Photochemistry of Fluorinated Aryl Azides in Toluene Solution and in Frozen Polycrystals

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Several fluorinated triplet aryl nitrenes have been generated in low-temperature polycrystals by photolysis of the corresponding azides. Upon extended photolysis at −196 °C the nitrenes abstract hydrogen from frozen toluene to give anilino–benzyl radical pairs, which subsequently combine to give CH insertion products. The radical pairs and the triplet nitrenes have been detected by EPR. In toluene solution, the major reaction products are tar, the corresponding fluorinated anilines, and azo compounds.

The photochemical reactions of aryl azides have been studied for several years. These reactions have gained considerable attention due to their utility in heterocyclic synthesis,[1] in the production of photoimaging devices,[2] and in the biochemical method of photoaffinity labeling (PAL).[3] In a PAL experiment, an analogue of a natural

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