

Metalation of Alkynes. Part 2. Behaviour of Alkynes with Mercury(II) Acetate in Methanol: a Systematic Reinvestigation.^{1,†}

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The reactions of a series of alkynes with mercury(II) acetate, both in equimolar and catalytic amounts, were investigated in methanol. Hex-1-yne, oct-1-yne, oct-4-yne, 1,4-diacetoxybut-2-yne, methyl oct-2-ynoate, methyl 3-phenylpropynoate, oct-2-ynoic acid, phenylpropynoic acid, oct-1-yn-3-ol, 1-ethynylcyclohexanol, 1-ethynylcyclohexylamine, phenylethyne, diphenylethyne, and ethynylferrocene were the examined substrates. The non-mercuriated products from the reaction were the corresponding vinyl ether, dialkoxyalkane, and ketone, isolated under preparative conditions. The presence of 0.1% toluene-*p*-sulphonic acid increased the reactivity. The reactions of oct-1-yne and oct-4-yne were studied in detail by following with time the formation of the products under a variety of conditions, and a mechanistic scheme was drawn. For comparison, styrene, *trans*-oct-4-ene, and *trans*- β -methylstyrene were treated with 5 mol % mercury(II) acetate. The reaction of alkenes was found to be non-catalytic.

The addition of water to alkynes, catalysed by mercuric salts and mineral acids, with formation of ketones, has been known for many years² and has produced several patents, in particular for the manufacture of acetaldehyde from acetylene.³ The reaction is still of interest and new reagents, such as Nafion-H/Hg^{II}^{4,5} or phenylmercuric hydroxide⁶ have been used.

The addition of carboxylic acids and alcohols to alkynes for the synthesis of enol derivatives⁷ is also an important reaction which has been less extensively studied. Recent investigation of the regio- and stereo-chemistry of acetoxy-mercuriation^{8,9} as well as kinetic studies¹⁰ have been reported. In general enol ethers are obtained from treatment of alkynes with alcohols in basic media.^{11,12} With respect to the reaction in the presence of mercuric species, information is scarce.

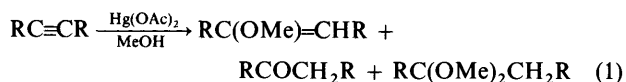
Between 1923 and 1938 Hennion and Nieuwland¹³ studied the reaction of HgO and boron trifluoride-diethyl ether, and later Nazarov and his co-workers presented results for investigations on vinylalkynes and alkynyl alcohols.¹⁴ Further literature reports are scattered¹⁵⁻¹⁸ but, nevertheless, the accepted mechanism is based on such results.¹⁹ A systematic investigation of the reaction might allow a better understanding of the mechanism, in view also of the importance of vinylmercurials in organic synthesis.^{20,21} Therefore, we decided to reinvestigate the reaction of alkynes with mercury(II) acetate in methanol, particularly regarding the results obtained with ethynylferrocene and phenylethyne;²² these have allowed us to draw a mechanistic scheme within which most of the species have been isolated.

Results and Discussion

The reaction of alkynes with mercury(II) acetate in methanol at 53 °C gave non-mercuriated products with yields from good to excellent. A 20:1 ratio of alkyne to the mercuric species allowed conversion into the corresponding ketone and/or dialkoxyalkane within a few days. With slow reacting alkynes, the reaction became feasible by addition of a small amount of toluene-*p*-sulphonic acid (TsOH) (0.1%). The latter compound accelerates the process with all the substrates.

The results are reported in Table 1. In some cases (Entries 7 and 10), the enol ether was isolated as the main product, but

its formation was observed at early stages of the reaction for almost all the investigated substrates (Table 2). In the case of terminal and alkylalkynes, only the ketone and the dialkoxyalkane were isolated, the vinyl ether being too unstable under the conditions of product separation (*i.e.* distillation or column chromatography). Thus, the reaction between alkynes and mercury(II) acetate in methanol may be formulated according to equation (1).



The conversion was possible also with a 100:1 ratio between the alkyne and mercury(II) acetate. Under these conditions, the reaction slowed down and the addition of 0.1% TsOH again had an accelerating effect (see Table 3 and 4).

Apparently, the process leading to the products is quite complex, as already shown with ethynylferrocene.²² In order to understand the factors affecting the reaction, two substrates oct-1-yne and oct-4-yne were studied and the course of the reaction followed by gas chromatography; only non-mercuriated species are detected. A variety of initial conditions were used and the results are reported in Figures 1-6.

Alkynes react with mercury(II) acetate in methanol *via* a complex pathway, that involves, in a first step, the electrophilic addition of the mercury(II) species to the π -bond, followed by the nucleophilic attack on the cationic intermediate by the solvent. Mercuriated vinyl derivatives have previously been isolated from the reaction of alkynes in acetic acid⁷⁻⁹ and postulated for the reaction in methanol.¹⁹

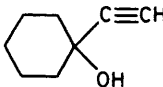
The 1-acetoxymercurio-2-methoxyvinyl species undergoes protodemercuration—a well known reaction of vinylmercurials²³—to give the enol ether, which is the first organic species detected. (This is particularly evident for a 1:1 ratio of the reactants, Figures 1 and 4.)

The protodemercuration step is a crucial one, because it restores the Hg(II) species, thus allowing catalytic behaviour. It explains also, the effect of traces of toluene-*p*-sulphonic acid, which accelerates the overall conversion, probably by facilitating the protodemercuration step. The accelerating effect of TsOH is particularly evident with aryl alkynes, whose mercuriated adducts are apparently more stable than those of alkyl alkynes.

Under comparable conditions [concentration, temperature,

† Part 1, ref. 10.

Table 1. Product composition from the reaction of alkynes with mercury(II) acetate in methanol at 53 °C

Entry	Substrate	5 mol % mercury(II) acetate						1 mol % mercury(II) acetate					
		Reaction t/h	% Unchanged alkyne	% Vinyl ether	% Ketone	% Dialkoxy-alkane	Overall yield %	Reaction t/h	% Unchanged alkyne	% Vinyl ether	% Ketone	% Dialkoxy-alkane	Overall yield %
1 ^a	Me(CH ₂) ₃ C≡CH	24	— ^c	—	17.5	4.4	21.9 ^d						
1 ^b		27	23.6	—	27.7	3.1	30.8 ^e						
2 ^a	Me(CH ₂) ₅ C≡CH	48	—	0.8	5.2	53.6	59.6 ^d	24	—	—	14.7	67.2	81.9 ^d
2 ^b		72	—	—	—	85.4	85.4 ^e						
3 ^a	Me(CH ₂) ₂ C≡C(CH ₂) ₂ Me	72	—	0.9	81.9	1.2	84.0 ^d	45	— ^c	—	4.5	5.4	9.9 ^d
4 ^a	Me(CH ₂) ₄ CH(OH)C≡CH							24	—	—	—	18.0	18.0 ^{f,g}
4 ^b		24	0.4	—	—	84.0	84.0 ^f						
5 ^a	AcOCH ₂ C≡CCH ₂ OAc	120	64.4	—	14.7	16.1	30.8 ^f						
6 ^a	Me(CH ₂) ₄ C≡CCO ₂ H ^h	24	—	8.2 ⁱ	45.7 ⁱ	9.6 ^k	63.5 ^d						
6 ^b		24	—	—	4.5 ⁱ	33.0 ^k	37.5 ^d						
7 ^a	Me(CH ₂) ₄ C≡CCO ₂ Me	72	—	69.3	—	24.8	94.1 ^f						
8 ^a	PhC≡CH	72	—	—	11.4	69.0	71.4 ^d	72	—	14.9	5.5	30.6	51.0 ^d
9 ^a	PhC≡CCO ₂ H ^h	24	—	—	71.2 ^l	8.4 ^m	79.6 ^d	72	57.0 ⁿ	—	31.9 ^l	1.7 ^m	33.6 ^d
9 ^b		24	37.2 ⁿ	—	39.0 ^l	1.7 ^m	40.7 ^d	72	50.1 ⁿ	—	5.2 ^l	14.3 ^m	19.5 ^d
10 ^a	PhC≡CCO ₂ Me	72	—	73.5	—	18.8	92.3 ^f						
11 ^a	PhC≡CPh	48	—	14.6	44.9	13.9	73.4 ^o	72	—	12.3	24.2	58.8	95.3 ^f
12 ^a	FcC≡CH	168	—	—	94.0	—	94.0 ^o						
12 ^b		120	—	—	70.0	—	70.0 ^o						
13 ^a		96	—	—	72.0	13.6	85.6 ^o						

^a With 0.1% TsOH. ^b Without TsOH. ^c Distilled with the solvent. ^d On the basis of distilled product. ^e Species separated by distillation. ^f On the basis of crude product. ^g Considerable amounts of unidentified species with high molecular mass. ^h Decarboxylates. ⁱ 2-Methoxyhept-2-ene. ^j Heptan-2-one. ^k 2,2-Dimethoxyheptane. ^l Acetophenone. ^m 1,1-Dimethoxy-1-phenylethene. ⁿ Phenylethyne. ^o Species separated by column chromatography.

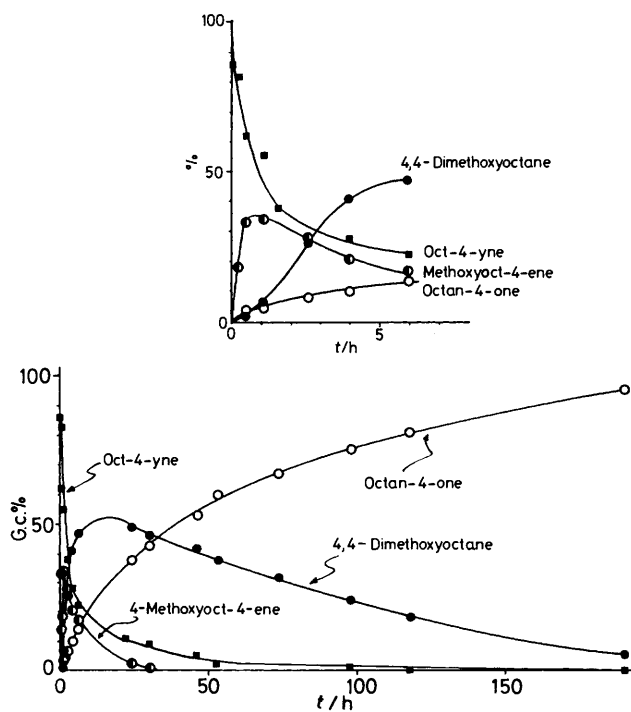


Figure 1. Gas chromatographic percentages for the reaction between oct-4-yne and mercury(II) acetate (1:1) in methanol at 50 °C

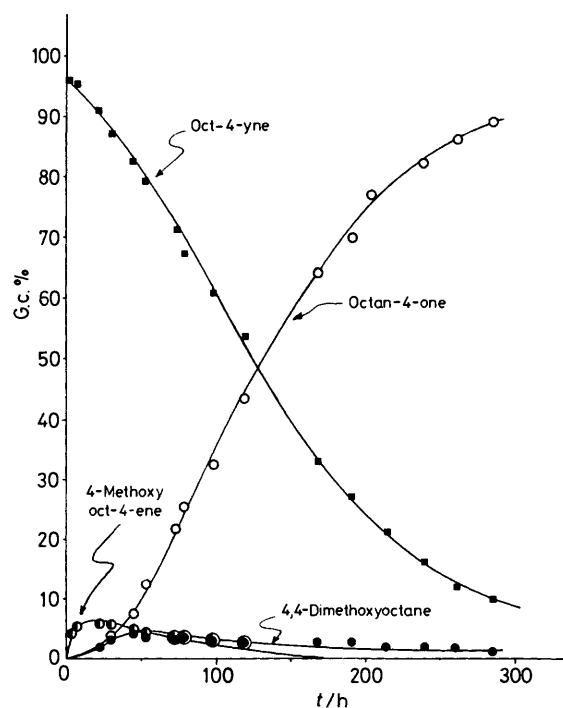


Figure 2. Gas chromatographic percentages for the reaction between oct-4-yne and mercury(II) acetate (20:1) in methanol at 50 °C

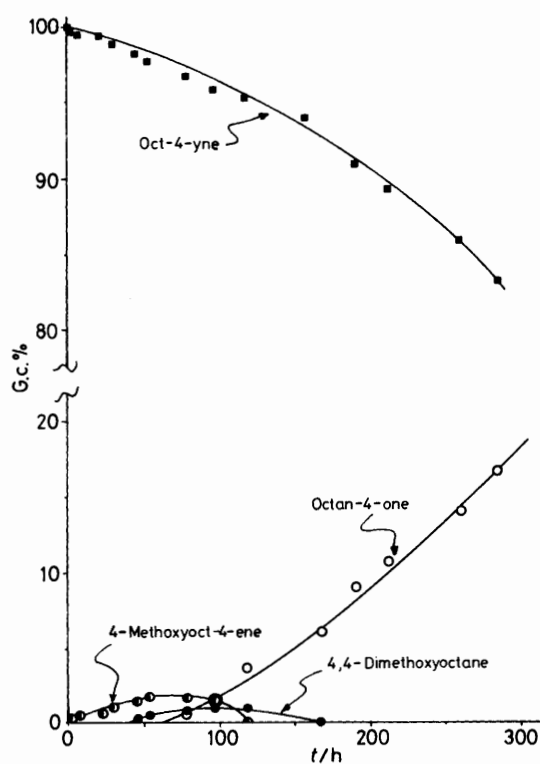
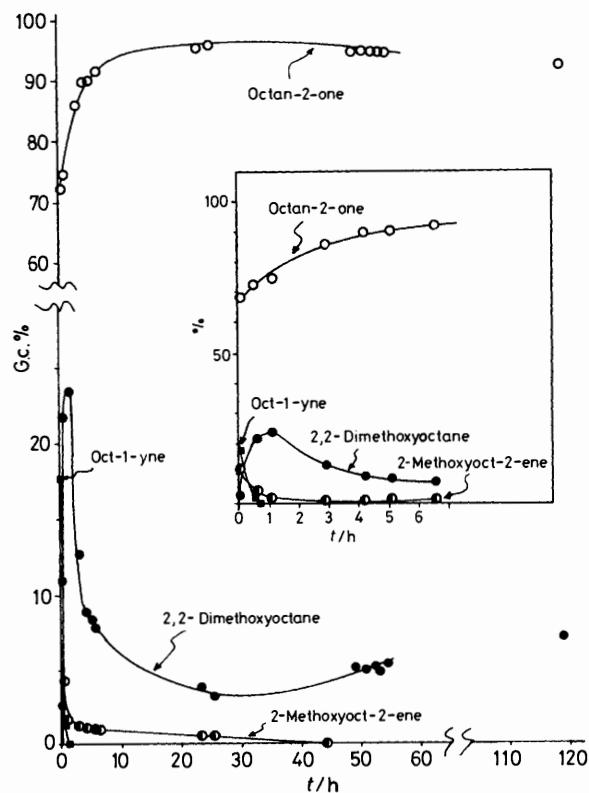
and percentage of mercury(II) acetate] oct-1-yne disappears more rapidly than oct-4-yne (see Figures 3 and 6, and 2 and 5), thus indicating a higher reactivity of the former substrate. It is

noteworthy that with the 1:1 ratio oct-1-yne disappears almost immediately after mixing the reactants (Figure 4), while oct-4-yne is consumed more slowly (Figure 1). This fact is due to the

Table 3. Gas chromatographic percents of products from the reaction of alkynes with 1 mol % Hg(OAc)₂ in methanol at 53 °C (0.1% TsOH).

Entry	Substrate	t/h	Unchanged alkyne	Vinyl ether	Ketone	Dialkoxyalkane
1	Hex-1-yne	18.5	— ^a	—	99.2	0.8
2	Oct-1-yne	0.3	23.0	11.0	8.0	58.0
		24	0.3	—	13.8	85.9
3	Oct-4-yne	45	73.7	0.7	19.8	5.8
4	Oct-1-yn-3-ol	24	—	—	—	24 ^b
6	Oct-2-ynoic acid ^c	1	9.4	10.5 ^d	23.5 ^e	56.7 ^f
		21.3	2.2	5.2 ^d	20.9 ^e	71.7 ^f
8	Phenylethyne	0.7	97.6	0.1	1.3	1.0
		10	77.1	3.3	3.3	16.3
		24	66.0	1.5	0.9	31.6
		48	38.5	0.3	0.2	61.1
9	3-Phenylpropynoic acid ^b	2	90.3 ^g	0.8 ^h	7.2 ⁱ	1.6 ^j
		23	64.3	0.4	29.3	6.0
		72	58.6	—	38.6	2.8
11	Diphenylethyne	2	48.8	—	9.6	41.5
		8	21.7	—	33.5	45.2
		48	2.3	—	68.9	28.8
13	1-Ethynylcyclohexanol	0.3	99.8	0.1	0.1	—
		1.3	99.8	—	0.1	0.1
		24	99.7	—	0.1	0.2
		72	99.7	—	0.1	0.2
14	1-Ethynylcyclohexylamine	3	100	—	—	—
		72	100	—	—	—

^a Same R_f as the solvent. ^b Unidentified species (76%) with high molecular mass (M⁺ 284). ^c Decarboxylates. ^d 2-Methoxyhept-2-ene. ^e Heptan-2-one. ^f 2,2-Dimethoxyheptane. ^g Phenylethyne. ^h PhC(OMe)=CHCO₂H. ⁱ Acetophenone. ^j 1,1-Dimethoxy-1-phenylethane.

**Figure 3.** Gas chromatographic percentages for the reaction between oct-4-yne and mercury(II) acetate (200:1) in methanol at 50 °C**Figure 4.** Gas chromatographic percentages for the reaction between oct-1-yne and mercury(II) acetate (1:1) in methanol at 50 °C

mercurials obtained from phenyl ethyne,²² oct-1-yne, and oct-4-yne, both in AcOH and in methanol, no evidence of the intermediacy of RC(OAc)(OMe)CH(HgOAc)R' was found. Moreover, we have no evidence either in favour or against the claim

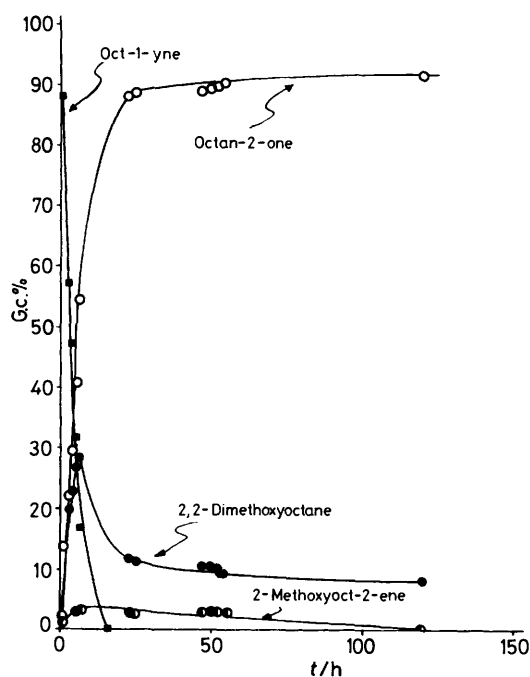
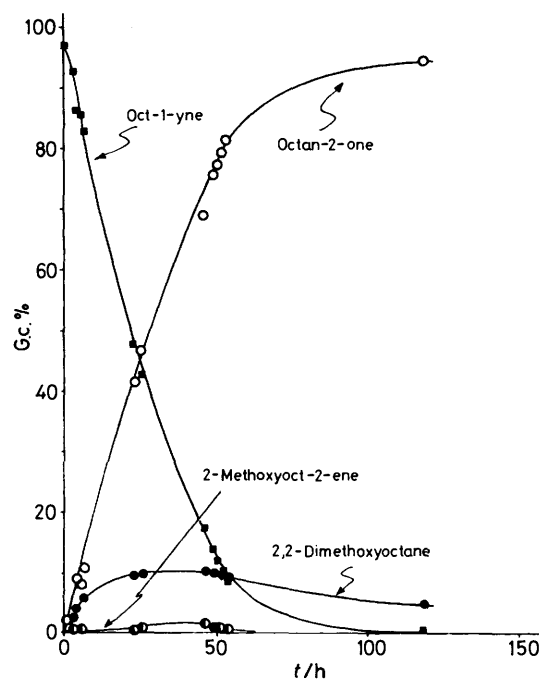
that vinylmercurials evolve by two parallel routes, as reported for AcOHgCH=CHOAc.²⁴

With respect to the orientation observed with unsymmetrically substituted alkynes, terminal alkynes are functionalized

Table 4. Gas chromatographic percents of products from the reaction of alkynes with 1 mol % Hg(OAc)₂ in methanol at 53 °C

Entry	Substrate	t/h	Unchanged alkyne	Vinyl ether	Ketone	Dialkoxyalkane
1	Hex-1-yne	20	— ^a	—	33.6	66.4
2	Oct-1-yne	0.6	99.2	—	—	0.8
		19	97.8	—	0.6	1.6
		44	97.7	—	—	2.3
3	Oct-4-yne	45	81	1.1	12.5	5.6
4	Oct-1-yn-3-ol	26	96.4	—	—	3.6
6	Oct-2-ynoic acid ^c	3	1.0	—	99.0 ^c	—
		18.5	0.8	—	98.1 ^c	1.1 ^d
		5	99.9	—	0.05	0.05
8	Phenylethyne	24	99.2	—	0.3	0.5
		72	98.0	—	1.3	0.7
		96	97.8	—	1.8	0.4
		5	77.7 ^e	4.0 ^f	6.8 ^g	11.5 ^h
9	3-Phenylpropynoic acid ^b	22.5	74.5 ^e	10.9 ^f	6.9 ^g	11.5 ^h
		72	63.3 ^e	—	7.7 ^g	29.0
		6	99.6	—	0.4	—
11	Diphenylethyne	72	97.9	—	2.1	—
		72	99.9	—	0.1	—
13	1-Ethynylcyclohexanol	3.5	99.9	—	0.1	—
		25	97.8 ⁱ	—	0.1	—
		72	91.7 ⁱ	—	—	—
14	1-Ethynylcyclohexylamine	23	100	—	—	—
		72	100	—	—	—

^a Same R_f as the solvent. ^b Decarboxylates. ^c Heptan-2-one. ^d 2,2-Dimethylheptane. ^e Phenylethyne. ^f PhC(OMe)=CHCO₂H. ^g Acetophenone. ^h 1,1-Dimethoxy-1-phenylethyne. ⁱ Small amount of an unidentified species with a high R_f .

**Figure 5.** Gas chromatographic percentages for the reaction between oct-1-yne and mercury(II) acetate (20:1) in methanol at 50 °C**Figure 6.** Gas chromatographic percentages for the reaction between oct-1-yne and mercury(II) acetate (200:1) in methanol at 50 °C

at the 2-carbon, as is generally observed for the conversion alkyne \rightarrow ketone.²⁵ Methyl 3-phenylpropynoate and methyl 2-octynoate yielded a single regioisomer, the electron-withdrawing effect of the methoxycarbonyl group being the determining factor in directing the nucleophilic attack on the cationic intermediate in the first reaction. Apparently, the transition state of the product-determining step is more stable with a partial positive charge on the β -carbon atom with respect to the

methoxycarbonyl group. The observed orientation confirms the literature data discussed in terms of triple bond polarization, rather than transition state stability.¹⁹

3-Phenylpropynoic acid and oct-2-ynoic acid undergo decarboxylation when treated with small amounts of mercury(II) acetate in methanol even at 0 °C. Decarboxylation may occur either on the substrate, phenylethyne being detected, or on the products (oct-2-ynoic acid was still present when decarboxyl-

ated species were detected). 1-Ethynylcyclohexanol showed no dehydration product, as reported for the reaction with Hg^{II} species in aqueous solution.¹⁹

In conclusion, the results obtained with the present re-investigation of the reaction between alkynes and mercuric species in methanol allow a reliable reaction pattern to be drawn. It is possible to select the opportune reaction conditions (e.g. reactants ratio and reaction time), in order to obtain the desired product, which may be the ketone, the dialkoxyalkane, or, in favourable cases, the enol ether (Table 1).

In contrast, the reaction of alkenes with mercury(II) acetate under similar conditions was not catalytic (see Experimental section). With 5 mol % $\text{Hg}(\text{OAc})_2$, only 5% of the alkene was transformed into product, while Hg^{II} was reduced to metallic mercury. Apparently, the mercuriated product from addition undergoes nucleophilic attack by the solvent instead of protodemercuration. Therefore, the usual solvomercuration-demercuration reaction is the only practical way to ethers from alkenes.²⁶

Experimental

¹H N.m.r. spectra were recorded on a Bruker WP-80 and a Varian EM-360 spectrometers with CDCl_3 or CCl_4 as solvents and Me_4Si as the internal standard. Gas chromatographic analyses were performed using a Hewlett-Packard 5830A instrument, equipped with a 1 m 2% OV 17 Chromosorb GAW-DMCS column, or with a Varian VISTA 6000 instrument, equipped with a 0.5 m 5% OV 101 Chromosorb GHP 100—120 column. Mercuriated species are not detected under the conditions used. Gas chromatographic-mass spectrometry (g.c.-m.s.) analyses were performed with a Kratos MS 80 spectrometer.

Materials.—Methyl 3-phenylpropynoate, methyl oct-2-ynoate, and 1,4-diacetoxybut-2-yne were prepared according to literature methods, as previously described.¹⁰ All the other alkynes, the alkenes, and mercury(II) acetate were commercially available products and were used without further purification after checking their purity. Mercury(II) acetate solutions in methanol contained 0.1% AcOH in order to avoid decomposition.²⁷

Product Analysis.—*General procedure.* A mixture of alkyne (0.5 M), $\text{Hg}(\text{OAc})_2$ (2.5×10^{-2} M), and toluene-*p*-sulphonic acid (5×10^{-4} M), in methanol were kept in a sealed vessel with a Teflon septum, and heated at 53 °C in a thermostatted bath. Samples (1 μl) were extracted at timed intervals and were subject to gas chromatography. The results are reported in Table 2. After 3 days, the reaction mixture was concentrated, poured into water, and extracted with diethyl ether. The organic phase was washed, dried (anhydrous Na_2SO_4), and evaporated. A small portion of the crude reaction product was examined by g.c.-m.s., the remaining amount was either distilled or fractionated by column chromatography, and examined by ¹H n.m.r. spectrometry.

In blank experiments, the alkynes remained unchanged in a methanol solution of 0.1% TsOH for a time comparable with that used in the reaction with mercury(II) acetate.

Product analysis was performed in a similar way with 5 mol % $\text{Hg}(\text{OAc})_2$ without TsOH (Table 2) and with 1 mol % $\text{Hg}(\text{OAc})_2$ with and without TsOH (Tables 3 and 4). The results obtained with 1 mol % $\text{Hg}(\text{OAc})_2$ are comparable to those with 5 mol % $\text{Hg}(\text{OAc})_2$, but the conversion in the former case is slower (Tables 3 and 4).

The composition of products isolated from the reaction of alkynes with 5 and 1 mol % mercury(II) acetate are reported in Table 1.

Characterization of the Products.—Since the products are common organic compounds, only significant ¹H n.m.r. chemical shifts and mass spectrometry data are given.

From hex-1-yne: hexan-2-one [δ 2.02 (s, COMe); M^+ 100, M_r 100.16] and 2,2-dimethoxyhexane [δ 3.03 (s, OMe); 145 ($M^+ - 1$), 115 ($M^+ - \text{OMe}$), M_r 146.23].

From oct-1-yne: octan-2-one [δ 1.98 (s, COMe); M^+ 128, M_r 128.21], 2,2-dimethoxyoctane [b.p. 72 °C at atmospheric pressure; δ 3.02 (s, OMe); 173 ($M^+ - 1$), M_r 174.28], and 2-methoxyoct-2-ene (M^+ 142, M_r 142.24).

From oct-4-yne: 4-methoxyoct-4-ene [δ 3.25 (s, OMe); M^+ 142, M_r 142.24], octan-4-one [δ 2.45 (t, COCH_2); M^+ 128, M_r 128.21], and 4,4-dimethoxyoctane [δ 3.08 (s, OMe); 173 ($M^+ - 1$), 143 ($M^+ - \text{OMe}$), M_r 174.28].

From oct-1-yn-3-ol: 2-methoxy-1-en-3-ol [δ 3.18 (s, OMe); M^+ 158, M_r 158.24], 3-hydroxyoctan-2-one [δ 2.12 (s, COMe); M^+ 144, 101 ($M^+ - \text{COMe}$), 83 ($M^+ - \text{H}_2\text{O} - \text{COMe}$); M_r 144.21], and 2,2-dimethoxyoctan-3-ol [δ 3.30 (s, OMe); 159 ($M^+ - \text{OMe}$), M_r 190.28].

From 1,4-diacetoxybut-2-yne: 1,4-diacetoxy-2,2-dimethoxybutane [δ 3.47 (s, OMe) and 2.07 (s, OCOMe); M^+ 234, M_r 234.25].

From oct-2-ynoic acid: heptan-2-one [δ 2.00 (s, COMe)] and 2,2-dimethoxyheptane [δ 3.02 (s, OMe)].

From methyl 2-octynoate: methyl 3-methoxyoct-2-enoate [δ 3.53 (s, OMe), 4.38 (s, =CH-), and 3.53 (s, CO_2Me); M^+ 186, M_r 186.25], methyl 3-oxo-octanoate [δ 3.35 (s, $\text{COCH}_2\text{CO}_2\text{Me}$) and 3.62 (s, CO_2Me); M^+ 172, M_r 172.22], and methyl 3,3-dimethoxyoctanoate [δ 3.07 (s, OMe), 2.50 (s, CH_2COMe), and 3.55 (s, CO_2Me); 187 ($M^+ - \text{OMe}$), M_r 218.29].

From phenylethyne: α -methoxystyrene [δ 3.65 (s, OMe); M^+ 134, M_r 134.18], acetophenone [δ 2.45 (s, COMe); M^+ 120, M_r 120.14], and 2,2-dimethoxy-1-phenylethane [δ (CCl_4) 7.0—7.3 (complex, 5 H, ArH), 1.43 (s, 3 H, Me), and 3.07 (s, 6 H, OMe)].

From phenylpropynoic acid: acetophenone and 2,2-dimethoxy-1-phenylethane as above, and 3-methoxy-3-phenylpropionic acid [δ 9.0 (br s, 1 H, CO_2H)].

From methyl phenylpropynoate: methyl 3-methoxy-3-phenylpropenoate [δ (CCl_4) 7.41 (complex, 5 H, ArH), 5.28 (s, 1 H, =CH-), 3.59 (s, 3 H, OMe), and 3.79 (s, 3 H, CO_2Me); M^+ 192, M_r 192.21] and methyl 3,3-dimethoxy-3-phenylpropanoate [δ (CCl_4) 7.41 (complex, 5 H, ArH), 3.25 (s, 6 H, OMe), 3.00 (s, 2 H, $\text{CH}_2\text{CO}_2\text{Me}$), and 3.42 (s, 3 H, CO_2Me); 193 ($M^+ - \text{OMe}$), M_r 224.25]. On standing, the dialkoxyalkane partly converts into methyl 3-phenyl-3-oxopropanoate [δ (CCl_4) 7.5 and 7.8—8.0 (complex, 5 H, ArH), 4.01 (s, 2 H, $\text{COCH}_2\text{CO}_2\text{Me}$), and 3.75 (s, 3 H, CO_2Me)].

From diphenylethyne: 1-methoxy-1,2-diphenylethene [δ *trans* and *cis* 3.25 and 3.67 (s, 3 H, OMe) and 5.90 and 5.62 (s, 1 H, =CH-); M^+ 210, M_r 210.27], 1,2-diphenylethanone [δ 4.08 (s, COMe); M^+ 196, M_r 196.24], and 1,1-dimethoxy-1,2-diphenylethane [δ 3.17 (s, 6 H, OMe), and 3.08 (s, 2 H, CH_2); M^+ 242, M_r 242.31].

From ethynylferrocene: acetylferrocene [m.p. 85—86 °C (lit., 85—86 °C²⁸), δ 2.22 (s, COMe); ν_{max} 1 676 (CO) cm^{-1}].

From 1-ethynylcyclohexanol: 1-acetylcyclohexanol [δ (CCl_4) 1.2—1.8 (complex, 10 H, C_5H_{10}), 3.53 (br s, 1 H, OH), and 2.22 (s, 3 H, COMe); M^+ 142, 124 ($M^+ - \text{H}_2\text{O}$), 99 ($M^+ - \text{COMe}$), and 81 ($M^+ - \text{COMe} - \text{H}_2\text{O}$); M_r 142.20], and 1-(1,1-dimethoxyethyl)cyclohexanol [δ (CCl_4) 1.2—1.8 (complex, 10 H, C_5H_{10}), 3.50 (br s, 1 H, OH), 1.27 (s, 3 H, Me), and 3.31 (s, 6 H, OMe); 170 ($M^+ - \text{H}_2\text{O}$), 157 ($M^+ - \text{OMe}$), M_r 188.26].

From 1-ethynylcyclohexylamine: the starting material was recovered quantitatively: M^+ 123, M_r 123.19.

Reaction Between Oct-4-yne and $\text{Hg}(\text{OAc})_2$.—Solutions in methanol of oct-4-yne (0.1 M) and $\text{Hg}(\text{OAc})_2$ (0.1 M; 1:1 ratio), (5×10^{-2} M; 20:1 ratio), and (5×10^{-4} M; 200:1 ratio) respec-

tively, were thermostatted at 50 °C. Samples (0.1 µl) were withdrawn at timed intervals and subject to gas chromatography. The results are shown in Figures 1—3.

Reaction Between Oct-1-yne and Hg(OAc)₂.—The procedure described above between oct-4-yne and Hg(OAc)₂ was adopted. The results are shown in Figures 4—6.

Reactions of Alkenes with 5 mol % Hg(OAc)₂.—*General procedure.* To alkene (styrene, *trans*-β-methylstyrene, and *trans*-oct-4-ene) (10 mmol) was added Hg(OAc)₂ (0.5 mmol) and TsOH (1 × 10⁻² mmol) in methanol and the resultant mixture heated at 50 °C. After some days, drops of metallic mercury separated in the bottom of the reaction vessel. Gas chromatographic analysis showed 95% alkene and 5% of a product with a higher R_f. The work-up was carried out as described for the alkynes.

5% 1,2-Dimethoxy-1-phenylethane [PhCH(OMe)CH₂OMe] was isolated from the reaction of styrene [δ (CCl₄) 7.13 (br s, 5 H, Ph), 4.15 (t, *J* 6 Hz, 1 H, PhCH(OMe)), 3.35 (d, *J* 6 Hz, CH₂OMe, 3.22 (s, CHOMe), and 3.17 (s, CH₂OMe)]. On prolonged heating polystyrene formed in large amount.

5% 1,2-Dimethoxy-1-phenylpropane [PhCH(OMe)CH(OMe)Me] was obtained from *trans*-β-methylstyrene [δ (CCl₄) 7.1 (br s, 5 H, Ph), 3.85 (d, *J* 4 Hz, 1 H, PhCH), 3.27 (m, 1 H, CHMe), 3.15 (s, 3 H, PhCH(OMe)), 3.05 (s, 3 H, CH(Me)OMe), and 1.1 (d, *J* 6 Hz, 3 H, Me); *M*⁺ 180, *M*_r 180.24].

5% 4,5-Dimethoxyoctane was formed from *trans*-oct-4-ene. [δ (CCl₄) 0.7—1.8 (complex, 16 H, alkyl protons), and 3.12 (s, 6 H, OMe)].

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