Hydration of Alkynes in Anhydrous Medium with Formic Acid as Water Donor

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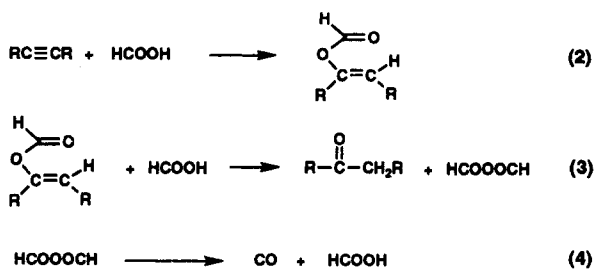
Formic acid has been found to hydrate alkynes in the absence of water to give oxo products and carbon monoxide. The scope of the reaction of alkynes and formic acid has been delineated. Hydrocarbon alkynes were found to be reactive in the absence of catalyst. Functionalized alkynes, in particular oxygenated alkynes, are inert toward formic acid but can be activated catalytically with $Ru_3(CO)_{12}$. Consequently, all the tested types of alkynes were found to give oxo products and CO with formic acid. The mechanism of the reaction was examined. With some alkynes, the primary oxo products underwent secondary reactions that gave rise to unexpected products.

In a recent paper[1] we have described an unexpected, noncatalytic, and simple reaction between two elementary kinds of organic compounds, namely alkynes and formic acid (eq 1).

$$RC{\equiv}CR + HCOOH \rightarrow RCOCH_2R + CO \quad (1)$$

The stoichiometry of the above reaction has been established experimentally.[1] Essentially, the process amounts to hydration of a triple bond but in the absence of water. Formally, in the present reaction, dry formic acid functions as a donor of a water molecule, hydrating the alkyne and thereby generating CO, surprisingly without the assistance of a catalyst. Formic acid serves also as the solvent, usually at the reflux temperature of the mixture. Yields, selectivity, and rates were found to be excellent.[1] Thus, simply mixing phenylacetylene with formic at *room temperature* generates acetophenone and carbon monoxide. Experimental evidence indicates that the overall process may be expressed in eqs 2–4, inasmuch as vinyl formates have been shown to act as intermediates and CO formed in a stoichiometric quantity relative to the oxo product.[1] The protonation of an sp carbon atom of an alkyne by formic acid in a highly polar solvent, formic acid, is most likely rate determining (eq 2).

It is the kinetic rather than the thermodynamic aspect of the reaction of alkynes with formic acid (eq 1) that is surprising. This general reaction has been previously overlooked by chemists, although acetophenone was observed as a byproduct in the treatment of phenylacetylene with formic acid in the preparation of α-(formyloxy)-styrene.[2] In our preliminary work only hydrocarbon alkynes (monoynes) had been studied.[1] In the present work, the scope of the reaction has been explored with an eneyne, diynes, and in particular, oxygen- and nitrogen-functionalized alkynes. Four examples are listed in Table I.



The reaction of 1 is extremely fast and was found to be complete within 10 min at the reflux temperature of the mixture, or 4 h at room temperature, with the evolution of CO. The rate enhancement in this case, as well as with phenylacetylene,[1] relative to dialkylacetylenes,[1] is attributed to stabilization by a conjugated π system of the positive charge developed on the substituted sp carbon atom upon protonation of the triple bond by formic acid (eq 2). 1-Ethynylcyclohexanol was found to be as reactive as the ethynylcyclohexene (1), presumably due to a prior fast dehydration reaction. Rupe et al.[3] observed the same reaction product using 1-ethynylcyclohexanol in 86% formic acid–water solution. Since no mention was made by these authors regarding the possibility of CO formation, we have repeated their reaction and found no CO evolution. Therefore, the reaction of 1-ethynylcyclohexanol with wet and dry formic acid must proceed via two different mechanisms.

The reaction of 1,7-octadiyne (2) proceeds beyond the hydration step to give 1-acetyl-2-methylcyclopentene and may take place via one of two mechanisms (Scheme I): (a) double hydration by formic acid of the 1,7-octadiyne (2) to 2,7-octadione (2b) which then undergoes an acid catalyzed intramolecular aldol condensation followed by acid-catalyzed dehydration or (b) single hydration by formic acid of the 1,7-octadiyne (2) to oct-7-yne-2-one (2a) which then undergoes an acid-catalyzed keto–yne cyclization. The thermal cyclization of the latter has been shown to occur at 260 °C (3 h).[4]

The choice between the above two mechanisms may be made by simply measuring the quantity of CO evolved, since 2 and 1 mol of CO are anticipated by mechanisms a and b, respectively (Scheme I). Experimentally, upon the refluxing of 1,7-octadiyne in formic acid, 1 mol of CO was evolved after 2.5 h while a second mole was generated during ca. 11 h (GC monitoring of the reaction has revealed transient signals that eventually converged into that of the product). Thus, mechanism a is operative, and the

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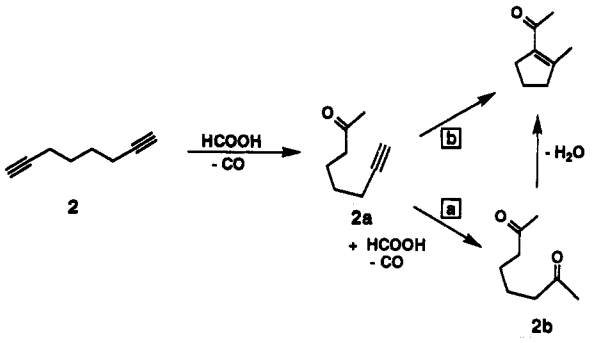
Table I.[a] Reactions of Alkynes with Formic Acid

no.	reactant	temp (°C)	time (h)	yield (%)	product
1	1-ethynylcyclohexene	100	0.17	96	1-acetylcyclohexene
1	1-ethynylcyclohexene	25	4.0	85	1-acetylcyclohexene
2	1,7-octadiyne	100	13.5	84	1-acetyl-2-methyl-cyclopentene
3	5,7-dodecadiyne	100	40.0	50	5,7-dodecadione
4	phenylpropiolic acid	100	0.5	92	acetophenone

[a] Evolution of CO was observed in all cases.

Scheme I



two triple bonds are being hydrated by formic acid but at different rates. The fact that the second hydration step is substantially slower than the first one corroborates our finding (vide infra) that the hydration rates by formic acid of oxygenated alkynes are strongly retarded.

The conjugated diyne, 5,7-dodecadiyne (3) (Table I), was transformed by formic acid to 5,7-dodecadione with a slow CO release. Only a moderate yield was obtained after 40 h of refluxing. Again, the first oxygen atom retards the hydration of the second triple bond.

Of the oxygenated alkynes studied (Table II), none, to our surprise, behaved as the above (Table I) or like the previously reported[1] hydrocarbon alkynes; i.e., the triple bond remained absolutely inert toward formic acid even after prolonged reaction periods. Thus, the following alkynols, 1-hexyn-3-ol (5), 2-butyn-1,4-diol or its diformate ester (6), 3-butyn-1-ol (7), and 1,4-bis(1-hydroxyethoxy)-2-butyne (14) gave, upon heating with formic acid, the corresponding formate esters with no evolution of gas and with no trace of the anticipated hydration oxo products or vinyl esters (eq 2). Thus, the triple bonds in propargylic and homopropargylic alcohols as well as propargylic ethers are unreactive toward formic acid. Even the water produced in the above esterification reactions did not add to the triple bond of these oxygenated alkynes in the presence of formic acid. Conversely, the possibility that the water produced in the above esterification reactions could have impeded the hydration reaction was ruled out. Thus, isolated (dried) formate esters of the alkynols 5, 6, 7 and 14 (Table II) were also found to be chemically inert toward formic acid.

In rationalizing the above behavior, we note that with *hydrocarbon* alkyne, *formic but not acetic acid* is reactive in eq 1. This behavior implies that formic acid possesses a threshold acid strength towards the protonation of the π system of triple bonds. With the oxygenated alkynes (Table II), the various oxygen atoms must effectively compete as Lewis bases with the π system for the rather weak formic acid. This in our opinion may account for the fact that neither the alkynols (Table II) nor their formate esters are reactive (eq 1). It also accounts for the behavior of the 5,7-dodecadiyne (3) mentioned above where the introduction of the first carbonyl group strongly retards the hydration of the second triple bond by formic acid.

The cyano group in (2-cyanophenyl)phenylacetylene (12) also inhibits the reaction in eq 1 inasmuch as 12 was completely inert toward formic acid, while the unsubstituted diphenylacetylene, under the same reaction conditions, readily gave deoxybenzoin.[1] Again, the nitrogen atom of the nitrile group must successfully compete with the alkyne π system for protonation by formic acid.

Phenylpropiolic acid (4) was converted to acetophenone (95%) by refluxing it in formic acid for 0.5 h (Table I). Decarboxylation of (4) precedes the very fast hydration by formic acid of the resulting phenyl acetylene (eq 5).

$$\underset{4}{\mathrm{PhC{\equiv}CCOOH}} \rightarrow [\mathrm{PhC{\equiv}CH}] \xrightarrow[-\mathrm{CO}]{\mathrm{HCOOH}} \mathrm{PhCOCH_3} \quad (5)$$

Alkynoic acids esters were also found to be indifferent to formic acid. Methyl 2-octynoate (8) and dimethyl acetylenedicarboxylate (13) are chemically stable in boiling formic acid. Of course, being conjugated to the carboxyl group, the π system in this class of alkynes suffers from diminished electron density that impedes protonation of the triple bond.

From the above results we conclude that the reaction depicted in eq 1 constitutes an extremely efficient, selective and simple new method for hydration of alkynes that requires the presence of neither water nor mineral or Lewis acids. However, it is limited to *hydrocarbon* alkynes.

It stands to reason that this limitation could be overcome if a vinyl ester could be generated via a *nonionic* addition reaction of formic acid to an alkyne, thus circumventing the protonation step (eq 2) of the alkyne π system. The vinyl ester so produced could subsequently, in situ, undergo reactions given in eqs 3 and 4 all in one pot. In fact, such a nonionic addition reaction of carboxylic acids to alkynes has been previously reported by us[5] to proceed in toluene solutions under catalysis of $Ru_3(CO)_{12}$. The vinyl esters produced thereby were found to be stable under the reaction conditions, as the reactions were carried out in dilute solutions (toluene usually) and with a very small excess of the carboxylic acid.[6] This catalytic reaction was found to be completely general, as all types of alkynes and carboxylic acids tested were found to generate vinyl esters in good yields.[5,9]

Thus, $Ru_3(CO)_{12}$ catalysis by refluxing alkynols 5–7 (Table II), or their pre-formed formate esters, *in formic acid* in the presence of $Ru_3(CO)_{12}$ (0.2–1% mol) for 1-5 h gave the expected keto formates with the evolution of CO.[7]

Methyl 2-octynoate (8) gave the expected methyl 3-oxooctanoate in 72% isolated yield after 2.5 h at reflux temperature under $Ru_3(CO)_{12}$ catalysis (eq 6). Prolonging the reaction time gave 2-heptanone, quantitatively.

$$\underset{8}{\mathrm{C_5H_{11}C{\equiv}CCOOCH_3}} + \mathrm{HCOOH} \xrightarrow[-\mathrm{CO}]{\mathrm{Ru_3(CO)_{12}}} \mathrm{C_5H_{11}COCH_2COOCH_3} \quad (6)$$

$$\mathrm{C_5H_{11}COCH_2COOCH_3} \rightarrow \text{2-heptanone}$$

(5) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689. Rotem, M.; Goldberg, I.; Shvo, Y. *Organometallics* **1984**, *3*, 1758. Rotem, M.; Goldberg, I.; Shmueli, U.; Shvo, Y. *J. Organomet. Chem.* **1986**, *314*, 183.

(6) Alkyne hydration products were not formed under the above reaction conditions.

(7) In a blank reaction omitting the alkyne, $Ru_3(CO)_{12}$ was found to decompose formic acid, however, at a substantial slower rate.

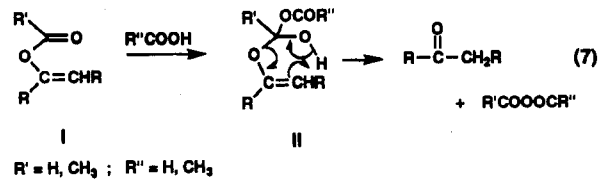
Table II.[a] Reactions of Alkynes with Formic and Acetic Acids Catalyzed by $Ru_3(CO)_{12}$

no.	reactant	acid	time (h)	yield (%)	product
5	1-hexyn-3-ol	formic	1.0	85	3-(formyloxy)-2-hexanone
5	1-hexyn-3-ol	acetic	3.0	100	3-acetoxy-2-hexanone
6	2-butyn-1,4-diol diformate	formic	5.0	75	1,4-bis(formyloxy)-2-butanone
7	3-butyn-1-ol	formic	3.0	4.5	4-(formyloxy)-2-butanone
8	methyl 2-octynoate	formic	2.5	72	methyl 3-oxooctanoate
9	diphenylacetylene	acetic/formic	3.0	100	deoxybenzoin
10	4-octyne	acetic	52.0	21	4-octanone
				75	4-acetoxyoct-4-ene
11	1-octyne	acetic	14.0	77	2-octanone
12	(2-cyanophenyl)phenylacetylene	formic	15.0	66	3-phenylisocoumarin
13	dimethyl acetylenedicarboxylate	formic	7.0	50	2,3,4-tricarbomethoxy-2-pyrone
14	1,4-bis(1-hydroxyethoxy)-2-butyne diformate	formic	2.0	92	ethylene glycol diformate

[a] All reactions were carried out at their reflux temperatures.

Since in the above reactions the addition of formic acid to alkynes has now been induced by $Ru_3(CO)_{12}$ rather than by an acid, the overall transformation may become independent of the strength of the carboxylic acid that is being used. Thus, refluxing 1-hexyn-3-ol (5), 4-octyne (10), and 1-octyne (11) in *acetic acid* in the presence of a catalytic amount of $Ru_3(CO)_{12}$ gave 3-acetoxy-2-hexanone, 4-octanone, and 2-octanone, respectively (Table II), albeit at substantially slower rates relative to formic acid. With diphenylacetylene (9) under the above conditions (AcOH/$Ru_3(CO)_{12}$) the reaction stopped at the stage of α-acetoxystilbene, which resisted further treatment with acetic acid but after isolation and treatment with formic acid (*no* Ru catalyst) was quantitatively transformed into deoxybenzoin (Table II). The implication is that with the system AcOH/$Ru_3(CO)_{12}$ the acidolysis step (eq 3) is now rate determining.

This behavior does not detract from the synthetic utility of the hydration reaction, since *formic acid* was found to generate ketones from alkynes in all the tested cases. However, the above results bear on the mode of acidolysis of the vinyl esters (eq 7). Aside from the acid strength,



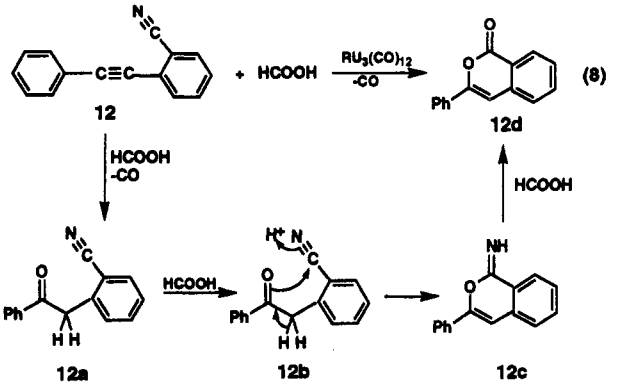
(7)

the acidolysis rate also depends on the basicity of the carbonyl oxygen atom of the vinyl ester of I (eq 7) that is destined to be protonated. The carbonyl group of acetoxystilbene is less basic than that of acetoxyoctyne. This is anticipated on structural–electronic grounds and is also supported by infrared data; the C=O stretching bands in the infrared spectra (CCl_4) of 4-acetoxyoct-4-ene and α-acetoxystilbene are, respectively, at 1750 and 1765 cm^{-1}. Thus, the stronger formic, but not acetic, acid can protonate the less basic carbonyl oxygen atom of α-acetoxy stilbene.

Thus, inert oxygenated alkynes have now been successfully activated by $Ru_3(CO)_{12}$, making the hydration reaction by formic acid feasible with various oxygenated alkynes as well. In some cases, however, functionalized alkynes gave rise to interesting secondary reaction products. Three such cases are reported below.

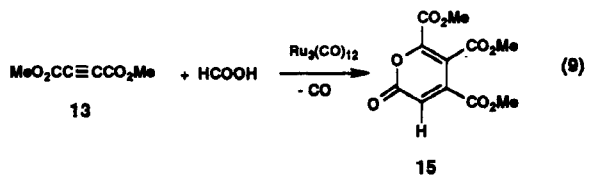
3-Phenylisocoumarin (12d) was obtained (66%) upon reacting (2-cyanophenyl)phenylacetylene (12) for 15 h in formic acid at 100 °C in the presence of $Ru_3(CO)_{12}$ (Scheme II, eq 8).

Scheme II



A reaction pathway is postulated above (Scheme II) whereby the initial regiospecific hydration product 12a, in the presence of formic acid, undergoes secondary transformations probably via 12b and 12c to the isocoumarin 12d. GC monitoring of the reaction has revealed several transient intermediates which have finally converged into the signal of 12d.

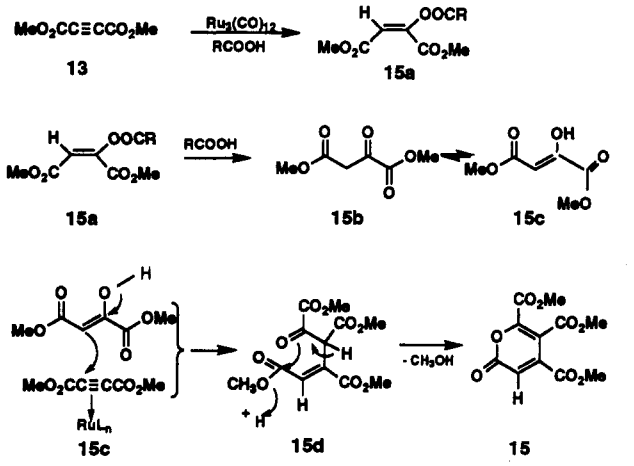
A totally unexpected crystalline product (15), an α-pyrone, resulted in 50% isolated yield from dimethyl acetylenedicarboxylate and formic or acetic acid (eq 9).



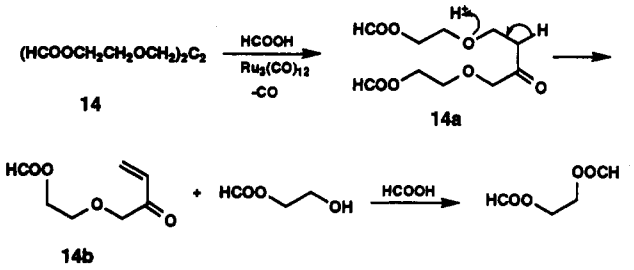
Elemental analysis, MS, and NMR data support structure 15 after ruling out several isomeric structures. Upon catalytic hydrogenation, 15 absorbed 2 equiv of hydrogen, resulting in a diastereomeric mixture of 2,3,4-tricarbomethoxy-4-hydroxypentanoic acid lactone (^1H NMR). The mixture was not separated, but its sharp infrared carbonyl stretching band at 1742 cm^{-1} is indicative of a six- rather than five-membered ring saturated lactone, thus supporting the ring size of 15. ^1H and ^{13}C NMR spectra of 15 and its tetrahydro derivative were in agreement with the above structure (see Experimental Section). In particular, the ^{13}C NMR spectrum of tetrahydro-15 showed four signals in the range of 164.1–176.2 ppm assigned to the four carbomethoxy carbonyl C atoms. Since no signals could be detected at lower field, tetrahydro-15 must be devoid of a keto carbonyl group, and consequently 15 must possess a 2-pyrone nucleus.

A tentative mechanism that may account for the formation of 15 from dimethyl acetylenedicarboxylate in formic or acetic acid (eq 9) is presented in Scheme III.

Scheme III



Scheme IV



Support for this proposed mechanism is based on the following experimental facts: (a) Dimethyl acetoxymaleate (**15a**) (mixed with isomeric dimethyl acetoxyfumarate) was isolated upon chromatography of a reaction mixture starting from dimethyl acetylenedicarboxylate/AcOH/$Ru_3(CO)_{12}$. (b) Dimethyl oxosuccinate (**15b**) was formed by heating **15a**, obtained above, in acetic or formic acid. In both acids **15b** disappeared with time but without giving rise to **15** (no $Ru_3(CO)_{12}$). (c) The heating of a fresh solution of dimethyl oxosuccinate (**15b**) with dimethyl acetylenedicarboxylate (**15b**) in acetic and formic acid (no $Ru_3(CO)_{12}$) also did not generate the pyrone (**15**). It is therefore concluded that a ruthenium complex most probably intervenes in the addition step of dimethyl oxosuccinate to dimethyl acetylenedicarboxylate, (**15c**), generating the adduct **15d** which is finally cyclized to **15**, as depicted in Scheme III.

In the third case, the only product that could be isolated and identified from the $Ru_3(CO)_{12}$-catalyzed reaction mixture of 1,4-bis(1-hydroxyethoxy)-2-butyne or its diformate ester (**14**) and formic acid is ethylene glycol diformate. Its formation is rationalized in Scheme IV.

Compound **14a** is the primary catalyzed hydration product of the alkyne **14**. Ethylene glycol monoformate is cleaved from **14a** by a facile acid-catayzed β-elimination process (**14b**), which is further formylated under the reaction conditions (92%). Quantitative determination of ethylene glycol diformate produced in the above reaction indicates that only one ethylene glycol unit is cleaved off. No other definable product related to the vinyl ketone fragment **14b** could be isolated from the reaction mixture.

It is noteworthy that in none of the cases studied has the usual facile aromatic trimerization of alkynes[8] been observed. This is attributed to the presence of carboxylic acids which with the ruthenium cluster generate complexes of the general structure $[(RCOO)_2(CO)_2Ru_2]_n$ reported by us[5] and others. It has been demonstrated that these are active catalytic species in the addition reactions of carboxylic acids to alkynes.[9]

Conclusion. Hydration of alkynes is a well known and documented reaction, usually requiring strong mineral and Lewis acids.[10] The potential utility of transition metal complexes in the hydration of alkynes has been recently demonstrated.[11] In all cases water is required. The present paper presents rather unique experimental conditions that require neither water nor a strong acid to achieve the above transformation. The preparative utility of this reaction has been illustrated in this work.

Experimental Section

General. Formic acid (98%) was dried and purified according to a published procedure.[12] The commercial alkynes were purified by distillation. GC analyses were carried out using 10% Carbowax 20M TPA on Chrom W 80/100 and SE-30 on acid-washed Chromosorb-W, using glass columns, l = 150 cm, i.d. = 0.6 cm. NMR spectra were measured in $CDCl_3$ solutions with TMS as internal standard using Bruker FT-200 and 360 MHz instruments. Mass spectra were measured with Finnigan-Mat Model ITD 800 spectrometer. IR spectra were recorded on a Nicolet 205 FT-IR spectrometer and GC on Varian Models 3700 and 3300 instruments.

1-Acetoxycyclohexene. A solution of 1-ethynylcyclohexene (1) (4.5 g) in formic acid (40 mL) was kept at room temperature for 4 h after which all of the ethynylcyclohexene disappeared (GC monitoring); at reflux the reaction is over after 10 min. Evolution of CO was observed. Methylene chloride (100 mL) was added, and the resulting solution was washed with several portions of water and then with sodium bicarbonate solution (5%) to neutrality and once more with water. The organic layer was dried over $MgSO_4$ and filtered, the solvent removed in vacuum, and the residue distilled, bp 135 °C/25 mmHg to give 1-acetylcyclohexene (4.18 g, 85.5%): MS m/z 124 (M^+, 100), identical with an authentic sample.

An identical product was obtained (0.99 g, 96%) in 97% purity (^{1}H-NMR) by refluxing 1-ethynylcyclohexanol (1.0 g) in formic acid (10 mL) for 10 min.

1-Acetyl-2-methylcyclopentene. 1,7-Octadiyne (**2**) (0.64 g, 6.04 mmol) and formic acid (7 mL) were refluxed while the evolved gas was collected and measured in an inverted graduate cylinder over water at 25 °C. A volume of 134 mL (5.98 mmol) was measured after 2.5 h; further heating for 11 h generated an additional 132 mL of gas. After the mixture was cooled to room temperature, water was added and the reaction mixture was extracted with several portions of dichloromethane. The combined extracts were washed with water, sodium carbonate solution, and then water and finally dried over $MgSO_4$. The residue obtained after removal of the solvent in vacuum was distilled in a Kugelrohr apparatus at 90–95 °C/25 mmHg to give a colorless oil, 1-acetyl-2-methylcyclopentene[13] (0.625 g, 84%): ^{1}H NMR δ 2.65 (m, 2H), 2.50 (t, J = 8 Hz, 2H), 2.24 (s, 3H), 2.08 (s, 3H), 1.82 (quint, J = 8 Hz, 2H); IR (CH_2Cl_2) ν 1710, 1670 cm^{-1}; MS m/z 124 (M^+, 100), 109 (49, M^+ – Me).

5,7-Dodecanedione. A solution of 5,7-dodecadiyne (**3**) (1.5 g, 9.24 mmol) and formic acid (20 mL) was refluxed for 40 h after which ca. 50% conversion was measured (GC). The reaction mixture was worked up as described above, and the residue after evaporation of the organic solvent was chromatographed on silica. The column was eluted with 1:9 methylene chloride/petroleum

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ether and then with 9:1 methylene chloride/petroleum ether, and an oil, dodeca-5,7-dione (0.854 g, 47%), was obtained, giving red coloration with ferric chloride solution: ^{1}H NMR (mixture of enol form, 84% and diketo form 16%) δ 0.92 (t, J = 7.2 Hz, 6H), 1.27–1.66 (m, 10H), 2.30 (t, J = 8 Hz, 3.36 H), 2.50 (t, J = 6 Hz, 0.64 H), 3.55 (s, 0.32 H), 5.49 (s, 0.84 H); IR (CH_2Cl_2) ν 1725, 1702, 1611 cm^{-1}; MS m/z 198 (M^+, 4.2), 155 (M – C_3H_7, 6), 141 (M – C_4H_9, 55.4), 113 (M – C_4H_9CO, 18), 85 ($C_5H_9CO^+$, 100).

Acetophenone. Refluxing (0.5 h) phenylpropiolic acid (4) (1.0 g, 6.84 mmol) in formic acid (10 mL) resulted in strong evolution of gas. Acetophenone was identified by GC as the sole product (95%) of the reaction mixture determined by quantitative GC analysis (3-heptanone as internal standard).

3-(Formyloxy)-2-hexanone. 1-Hexyn-3-ol (5) (2.5 g, 25.5 mmol) and formic acid (15 mL) were refluxed for 15 min, after which all starting material had disappeared (GC) without gas evolution (formation of 3-(1-hexynyl) formate). $Ru_3(CO)_{12}$ (30.0 mg, 0.047 mmol) was added. Heating was resumed for 45 min (strong evolution of CO), at which time the reaction was over. Formic acid was evaporated in vacuum at 50 °C and the residue distilled in a Kugelrohr apparatus at 120 °C/20–25 mmHg to yield a colorless oil, 3-(formyloxy)-2-hexanone (3.13 g, 85.2%): ^{1}H NMR δ 0.95 (t, J = 7.2 Hz, 3H), 1.45 (m, 2H), 1.78 (m, 2H), 2.19 (s, 3H), 5.14 (t, J = 6 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR δ 160.98 (ester CO), 32.90, 26.77, 19.05, 14.27; IR ν 1721–1740 (v brd), 1174 cm^{-1}; MS m/z 115 (10, M^+ – CHO), 101 (10, M^+ – C_3H_7), 73 (100).

3-Acetoxy-2-hexanone. 1-Hexyn-3-ol (5) (1.0 g, 10.2 mmol), acetic acid (10 mL), and $Ru_3(CO)_{12}$ (30.0 mg, 0.047 mmol) were refluxed for 5 h to give complete conversion (GC) to 3-acetoxy-2-hexanone.[14]

1,4-Bis(formyloxy)-2-butanone. Refluxing 2-butyne-1,4-diol and formic acid for 3 h (no evolution of gas was noted) followed by workup as described for 1-acetoxycyclohexene gave 1,4-butynediol diformate (6) which was filtered through silica and finally crystallized from ethanol, mp 36 °C (lit.[15] mp 35.5 °C).

2-Butyne-1,4-diol diformate (6) (3.424 g, 24 mmol), formic acid (35 mL), and $Ru_3(CO)_{12}$ (87.6 mg, 0.136 mmol) were refluxed for 5 h. After the removal of formic acid in vacuum, the residue was chromatographed on silica with methylene chloride–petroleum ether mixture to give the oil, 1,4-bis(formyloxy)-2-butanone (2.88 g, 75%): ^{1}H NMR δ 2.85 (t, J = 6 Hz, 2H), 4.46 (t, J = 6 Hz, 2H), 4.80 (s, 2H), 8.02 (s, 1H), 8.16 (s, 1H); MS m/z 101 (33, M^+ – $HCOOCH_2$), 73 (11, M^+ – $HCOOCH_2CO$).

4-(Formyloxy)-2-butanone. 3-Butyn-1-ol (7) (1.0 g, 14.3 mmol) and formic acid (5 mL) were refluxed for 15 min, after which all starting material disappeared (GC), but without gas evolution (formation of 3-(1-butynyl) formate). $Ru_3(CO)_{12}$ (48.3 mg, 0.075 mmol) was added, and the reflux was resumed for an additional 3 h (evolution of CO). The formic acid was removed by vacuum evaporation at room temperature and the residue distilled in a Kugelrohr apparatus to give a clear oil, 4-(formyloxy)-2-butanone (0.75 g, 45%), bp 85 °C/20 mmHg (lit.[16] 76–8 °C/10 mmHg); ^{1}H NMR δ 2.21 (s, 3H), 2.8 (t, J = 6 Hz, 2H), 4.43 (t, J = 6 Hz, 2H), 8.03 (s, 1H); IR ν (CCl_4) 1732 (vs), 1181, 1158 cm^{-1}; MS m/z 116 (5, M^+), 101 (2, M^+ – Me), 71 (2, M^+ – OCHO), 70 (22.1), 43 (100).

Methyl 3-Oxooctanoate. Methyl 2-octynoate (8), (1.0 g, 6.48 mmol), formic acid (10 mL), and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) were refluxed for 2.5 h. Formic acid was removed by vacuum evaporation, and the residue was taken in dichloromethane and chromatographed on silica. With mixtures of dichloromethane–ethyl acetate there was obtained first an oil, 2-heptanone (0.1 g, 14%), identical with an authentic sample, followed by a second fraction, oil, methyl 3-oxooctanoate (0.716 g, 72%): ^{1}H NMR δ 0.87 (t, J = 6.6 Hz, 3H), 1.25–1.6 (m, 6H), 2.51 (t, J = 8.0 Hz, 2H), 3.43 (s, 2H), 3.72 (s, 3H); IR (neat) ν 1750 cm^{-1}; MS m/z 172 (M^+, 1.4), 130 (3, M^+ – OMe), 113 (10.2, M^+ – MeCOO), identical with reported spectral data.[17] Carrying out the reaction for a longer time (15 h) led to 2-heptanone as a sole product. Heating methyl 2-oxooctanoate in formic acid with no catalyst added brought about decomposition of the methyl 2-oxooctanoate to 2-heptanone.

Deoxybenzoin. Diphenylacetylene (9) (1.0 g, 5.61 mmol), acetic acid[18] (10 mL), and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) were refluxed for 3 h, at which time all the diphenylacetylene was converted to a mixture of (*E*)- and (*Z*)-α-acetoxystilbenes. Further refluxing of the above mixture in acetic acid for 10 h did not effect its composition. The mixed vinyl esters were isolated by addition of water and extraction with methylene chloride. The extracts were washed with sodium carbonate solution (10%) followed by water and evaporation of the solvent. There was obtained an isomeric mixture of (*E*)- and (*Z*)-α-acetoxystilbenes, oil (1.15 g): ^{1}H NMR δ 2.2 (s, 3H), 6.47 and 6.57 (s, 1H), 7.11–7.56 (m, 10H). A solution of the above mixture (0.5 g) in formic acid (5 mL) was refluxed for 3 h after which it was quantitatively converted (GC) to deoxybenzoin (gas chromatographic identification by coinjection of an authentic deoxybenzoin sample).

4-Octanone. 4-Octyne (10) (1 g, 9.07 mmol), AcOH[14] (10mL), and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) were refluxed for 4 h after which all starting material disappeared (GC). The reaction was refluxed for additional 48 h, and the reaction mixture was worked up as described above for deoxybenzoin. There was obtained an oil (1.2 g) that was found to contain 4-octanone (0.25 g, 21.5%) by GC analysis with phenol as an internal standard. The rest of the material was identified as 4-acetoxyoct-4-ene (75%).

2-Octanone. 1-Octyne (11) (1 g, 9.07 mmol), AcOH[14] (10mL), and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) were refluxed for 2 h after which all starting material disappeared (GC). After an additional 12 h of reflux, the reaction mixture was worked up as described for deoxybenzoin.. There was obtained 2-octanone, oil (0.9 g, 77%), identified by comparison with an authentic sample (^{1}H NMR).

3-Phenylisocoumarin. (2-Cyanophenyl)phenylacetylene[19] (12) (0.18 g, 0.89 mmole), formic acid (3 mL), and $Ru_3(CO)_{12}$ (20 mg, 0.031 mmol) were refluxed for 15 h. The acid was removed in vacuum and the residue chromatographed on silica. With a mixture of dichloromethane (3)–petroleum ether (1), there was obtained a solid, 3-phenylisocoumarin (0.13 g, 66%), mp 88 °C, after crystallization from methylene chloride–petroleum ether (lit.[20] mp 89–90 °C). The spectral properties of the product were found to be identical with the reported ones.[17] There was no reaction at all in the absence of the catalyst.

2,3,4-Tricarbomethoxy-2-pyrone. Dimethyl acetylenedicarboxylate (13) (3.55 g, 25 mmol), acetic acid (9.0 g, 150 mmol), and $Ru_3(CO)_{12}$ (105.6 mg, 0.165 mmol) were refluxed for 7 h. Water was added and the mixture extracted with several portions of methylene chloride. The combined extracts were washed with water and sodium carbonate solution and then again with water, dried over $MgSO_4$, and evaporated in vacuum. The residue was chromatographed on silica with dichloromethane–ethyl acetate solutions of increasing polarity. The compounds emerged in the following order: (a) liquid, mixture of dimethyl acetoxymaleate and dimethyl acetoxyfumarate, 1.3 g; (b) solid, dimethyl oxosuccinate, 25 mg [mp 72–5 °C (lit.[21] mp 73–5 °C); m/z 160 (M^+, 3.5), identical with an authentic sample by GC comparison]; and (c) solid, 2,3,4-tricarbomethoxy-2-pyrone (1.68 g, 49.7%) [mp 128 °C after crystallization from methylene chloride–petroleum ether: ^{1}H NMR δ 3.937 (s, 3H), 3.948 (s, 3H), 3.953 (s, 3H), 7.13 (s, 1H); ^{13}C NMR δ 53.48, 53.75, 116.7, 122.7 (CH), 141.87, 147.6, 157.7, 158.8, 161.9, 163.9; IR ν 1742 cm^{-1}; MS m/z 270 (M^+, 69.4), 211 (M^+ – COOMe, 100). Anal. Calcd for $C_{11}H_{10}O_8$: C, 48.8; H, 3.7. Found: C, 48.7; H, 3.7].

2,3,4-Tricarbomethoxy-2-pyrone obtained above (0.270 g, 1 mmol) in ethanol (10 mL) was hydrogenated in the presence of Pd/C (10%, 10 mg) at atmospheric pressure and ambient temperature. Hydrogen (60 mL, ca. 2 mmol) was absorbed. The catalyst was filtered off and the solvent removed in vacuum to

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give a colorless semisolid (271 mg) diastereomeric mixture of 2,3,4-tricarbomethoxy-4-hydroxypentanoic acid lactone: ^{1}H NMR δ 2.5–3.3 (m, 4H), 3.6–3.9 (7 singlets, 9H, OMe), 4.99 (d, J = 3 Hz); IR ν 1742 cm^{-1}; MS m/z 259 (M^+ – Me, 11), 243 (M^+ – OMe, 7.4), 215 (M^+ – COOMe, 73).

Dimethyl maleate and fumarate (mixture, 0.120 g) and AcOH (1.5 mL) were refluxed for 5.5 h. GC analysis indicated the presence of the starting material (80% by area) and dimethyl oxosuccinate (20% by area) only. Similar results were obtained after 0.5 h using formic acid.

Ethylene Glycol Diformate. 1,4-Bis(1-hydroxyethoxy)-2-butyne, technical grade (20 g, 4.34 mmol), and formic acid (50 mL) were refluxed for 4 h. Evaporation of the acid in vacuum gave a residue which was filtered through a silica column to give 1,4-bis(1-hydroxyethoxy)-2-butyne diformate (14) (7.0 g). 1,4-Bis(1-hydroxyethoxy)-2-butyne diformate obtained above (1.0 g, 4.34 mmol), formic acid (10 mL), and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) were refluxed for 2 h. The acid was removed in vacuum, and the residue was taken in dichloromethane and chromatographed on a silica column to give an oil, ethylene glycol diformate (0.47 g, 92%): ^{1}H NMR δ 4.42 (s, 4H), 8.1 (s, 2H); IR (neat) ν 1725 cm^{-1}, identical with an authentic sample.

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