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The Reaction of Propargyl Compounds with Carbon Monoxide and Water in the Presence of Iron Carbonyl Catalyst

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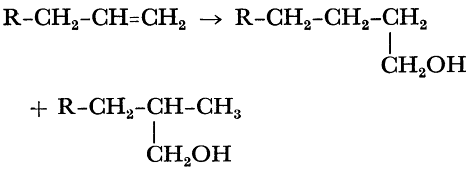
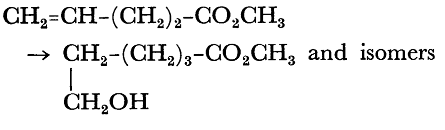
The reaction of propargyl alcohol as well as its acetate and methyl ether with carbon monoxide and water in the presence of ironpentacarbonyl-amine catalyst under oxymethylation conditions proved to proceed at a much faster rate than that of 1-butyn-4-ol, 1-pentyn-5-ol and alkylacetylenes accompanied by elimination of the functional groups at C-3 to give dimethyl methylsuccinate. 3-Methyl-1-butyn-3-ol and 1-ethynylcyclohexanol reacted in a similar manner, but gave mixtures of unsaturated monoesters and diesters, saturated and unsaturated. The faster rate of reaction and the product obtained were interpreted by a scheme involving a concerted attack of hydroirontetracarbonyl anion, $HFe(CO)_4^-$, at the terminal position to split off the group at C-3. The mononuclear hydrido anion was assumed to be an active catalytic species in the reaction on the basis of both the infrared spectra of the catalyst system under the reaction conditions and the efficiency of potassium hydroxide as a base component.

In a series of investigations[1] on the oxymethylation of unsaturated compounds by carbon monoxide and water (or hydrogen) in the presence of ironpentacarbonyl and a base, we found that this type of catalyst could bring about three kinds of reactions, oxymethylation, hydrogenation and carboxylation and that the principal course of the reaction depends on the structure of reactants as shown in the following reactions.

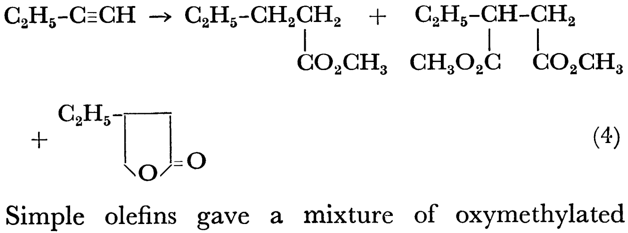


$$\mathrm{R\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle CH_2OH}{CH_2} + R\text{-}CH_2\text{-}\underset{\displaystyle CH_2OH}{CH}\text{-}CH_3}\qquad(1)$$

$$\left.\begin{array}{l}\mathrm{CH_2{=}CH\text{-}CO_2CH_3 \rightarrow CH_3\text{-}CH_2\text{-}CO_2CH_3}\\ \mathrm{CH_2{=}CH\text{-}CH_2OH \rightarrow CH_3\text{-}CH_2\text{-}CH_2OH}\end{array}\right\}\qquad(2)$$

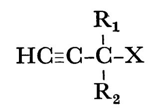


$$\mathrm{CH_2{=}CH\text{-}(CH_2)_2\text{-}CO_2CH_3 \rightarrow \underset{\displaystyle CH_2OH}{CH_2}\text{-}(CH_2)_3\text{-}CO_2CH_3 \text{ and isomers} + CH_3\text{-}(CH_2)_3\text{-}CO_2CH_3}\qquad(3)$$

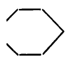


$$\mathrm{C_2H_5\text{-}C{\equiv}CH \rightarrow C_2H_5\text{-}CH_2\underset{\displaystyle CO_2CH_3}{CH_2} + C_2H_5\text{-}\underset{\displaystyle CH_3O_2C}{CH}\text{-}\underset{\displaystyle CO_2CH_3}{CH_2}} + \ldots\qquad(4)$$

Simple olefins gave a mixture of oxymethylated products at 175°C, while α,β-unsaturated esters, nitriles and allylic alcohols were hydrogenated exclusively to the corresponding saturated compounds at a somewhat lower temperature. However, oxymethylation of the substituted compounds was found to occur when the double bond was separated from ester or hydroxyl group by more than one methylene group (Eq. (3)).[1d] A similar effect of a neighboring double bond was observed by examining the time dependence of the products in the oxymethylation of isomeric hexadienes.[1b] This paper deals with an extention of the neighboring substituent effect to acetylenic compounds, and presents both unusual behaviours of propargyl alcohol and its derivatives (I) and a probable structure of an active catalytic species in the reaction.



$$\mathrm{HC{\equiv}C\text{-}\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{C}}\text{-}X}$$

	Ia	Ib	Ic	Id	Ie
$R_1 =$	H	H	H	CH_3	
$R_2 =$	H	H	H	CH_3	
$X =$	OH	OAc	OCH_3	OH	OH

Results and Discussion

Products and their yields under vairous reaction conditions are summarized in Table 1. The reaction of propargyl alcohol proceeded rapidly at 175°C under concurrent formation of an unidentified by-product even in a short reaction time such as 40 min. The main product (II) formed as the sole product at 125°C was confirmed to be dimethyl methylsuccinate. Propargyl acetate and 3-methoxy-1-propyne showed similar reactivities and both afforded II in comparable yields. Formation of II from these compounds regardless of their functional groups can be explained by the route in which addition of methoxycarbonyl groups proceeded under elimination of the groups at C-3 *i. e.*, OH, OAc or OCH_3. Elimination accompanied by carboxylation also occurred in the reaction of the substituted propargyl alcohols, 3-methyl-1-butyn-3-ol (Id) and 1-ethynylcyclohexanol (Ie). However, these compounds afforded complex mixtures consisting of an unsaturated monoester and both saturated and unsaturated diesters. The structural features of these products suggest a reaction scheme in which the first carboxylation occurred exclusively at the terminal position and the subsequent step involving either the second carboxylation or hydrogenation led to the final products. The latter step seems to be considerably slower than the former for compounds which are sterically hindered by substitution at C-3. On the other hand, the reaction of 1-butyn-4-ol was found to proceed at a much slower rate as shown in Fig. 1.

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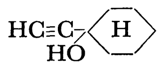
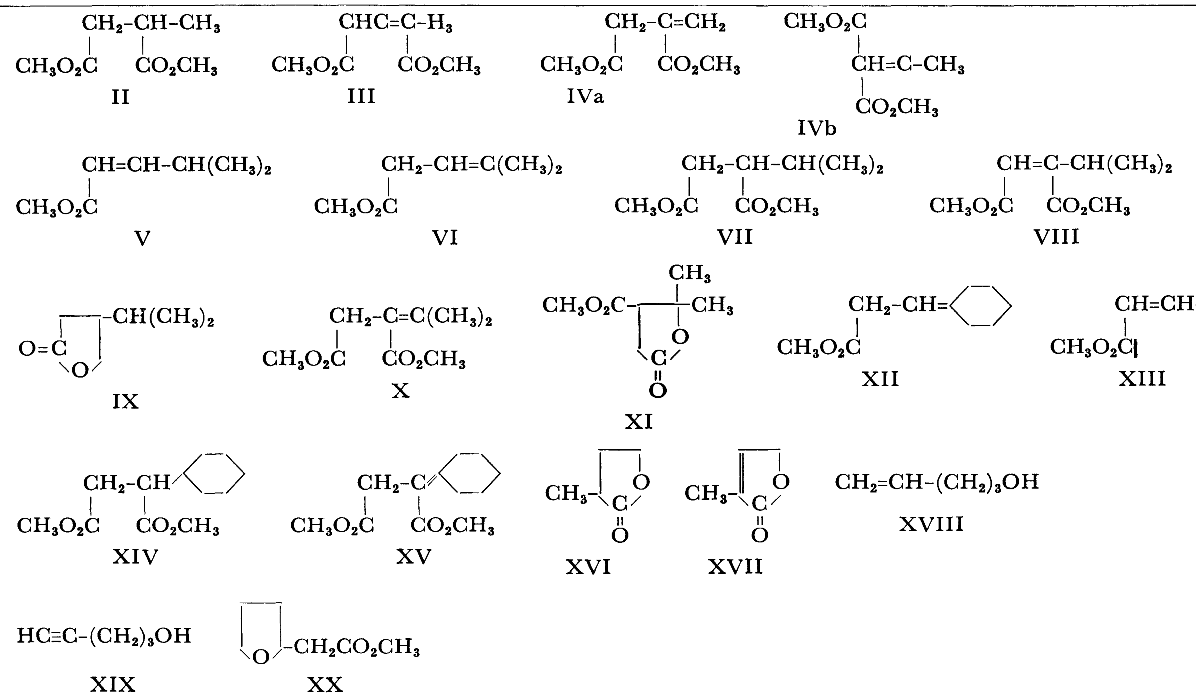
[1] a) T. Matsuda and T. Nakamura, *Kogyo Kagaku Zasshi*, **71**, 511 (1968), b) T. Matsuda and H. Honda, *ibid.*, **74**, 919 (1971), c) T. Matsuda, H. Kondo, and T. Nakamura, *ibid.*, **74**, 1135 (1971), d) T. Matsuda, H. Uchida, Y. Komori, and M. Nishikawa, *Nippon Kagaku Kaishi*, **1972**, 1103.

Table 1. Products obtained from propargyl and related compounds and their yields

Material	Reaction conditions No	Temp, °C	Time, hr	Products,[a] g
$HC\equiv C-CH_2OH$	1	175	6	II: 6.5, others: 2.0
	2	175	0.66	II: 6.7, others: 0.57
	3	125	8	II: 13.3
	4	150	5	II: 20.6, others: 1.79
	5[b]	150	5	II: 7.8, III: 1.7, IVa: 1.5, IVb: 1.4
	6[c]	125	6	II: 0.52, III: 0.7, IVa: 0.3, IVb: 0.12, others: 1.06
$HC\equiv C-CH_2OAc$	7	150	6	II: 10.8, others: 0.53
$HC\equiv C-CH_2OCH_3$	8	150	3	II: 7.16, others: 1.74
$HC\equiv C-C(CH_3)_2$	9	150	8	V: 0.96, VI: 3.22, VII: 3.14, VIII: 0.41, IX: 1.52, X: 4.95, XI: 0.48, others: 3.83
	10	70	144	V: 1.02, VI: 0.36, VII: 1.99, VIII: 3.07, IX: 2.87, X: 4.78, XI: 1.86, others: 1.2
	11	150	6	XII: 3.2, XIII: 1.4, XIV: 3.5, XV: 8.3
$HC\equiv C-(CH_2)_2OH$	12	150	25	XVI: 4.3, XVII: 1.7
$HC\equiv C-(CH_2)_3OH$	13	150	14	XVIII: 1.38, XIX: 1.49, XX: 2.46, others: 3.07

a)



b) Potassium hydroxide (0.10 mol) was used in place of triethylamine.

c) The reaction was carried out under the initial carbon monoxide pressure, 3 kg/cm².

Formation of the product identified as α-methyl-γ-butyrolactone and α-methylcrotonolactone can be explained by a different pathway in which the addition of a methoxycarbonyl occurrs at β-carbon and then the hydroxyl group at C–3 takes part in the cyclization to give lactones. This means that the mechanism of formation of these lactones differs from that of the γ-lactones obtained from the reaction of alkylacetylenes (Eq. (4)). Although several compounds are left unidentified, the products from 1-pentyn-5-ol seem to be those which retained the original hydroxyl moiety. Thus, it is concluded that the elimination process plays an important role in the reaction of propargyl compounds, and gives rise to both the increased reaction rate and the characteristic feature of the products. A similar carbonylation under elimination of a functional group has been reported by Nogi and Tsuji[2] in the palladium catalyzed reactions of propargyl compounds in alcoholic solvents.

When we proceed to formulate a reaction course which includes the elimination of the electronegative group from the propargyl position, the formation of an intermediate of allenic structure would have to be considered as a possible pathway. However, the

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[2] T. Nogi and J. Tsuji, *Tetrahedron*, **25**, 4099 (1969).

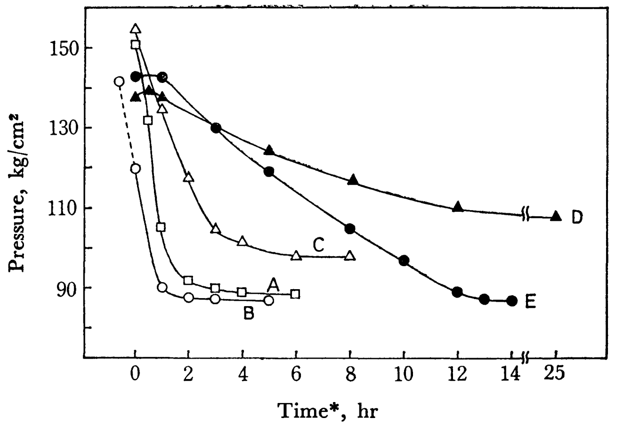


Fig. 1. Pressure changes in the reactions of typical acetylenic compounds at 150°C.
* Abscissa indicates the time elasped from the point reached at 150°C.
A: propargyl acetate.
B: propargyl alcohol with KOH, the pressure reached to a maximum at 125°C.
C: 3-methyl-butyn-3-ol.
D: 1-butyn-4-ol.
E: 1-pentyn-5-ol.

reaction of allene under the same conditions proved to be more sluggish than that of propargyl alcohol and led to a complex mixture in which neither methylsuccinate nor the corresponding unsaturated compounds was detected.

The reaction of propargyl alcohol utilizing potassium hydroxide in place of triethylamine was found to proceed in a similar way but at an increased rate, and provided an interesting difference from the oxymethylation of olefins, where potassium hydroxide proved to be a nearly ineffective base. Although the result suggests that the active species in the reaction of propargyl compounds is mononuclear hydroirontetracarbonyl anion, $HFe(CO)_4^-$, it is not clear why both triethylamine and potassium hydroxide act as an equally effective base, if we take into consideration the fact that the nature of the base is responsible for the formation of different kind of hydrido ironcarbonyls[3] according to the following reactions.

$$Fe(CO)_5 + 3KOH \rightarrow K^+HFe(CO)_4^- + K_2CO_3 + H_2O \qquad (5)$$

$$3Fe(CO)_5 + NR_3 + 2H_2O \rightarrow HFe_3(CO)^-_{11}H\overset{+}{N}R_3 + 2CO_2 + 2CO + H_2 \qquad (6)$$

A qualitative examination of these catalyst systems by infrared spectra revealed that the hydrido species formed under the present experimental conditions was not trinuclear but mononuclear anion, irrespective of the base utilized as shown in Fig. 2. This would imply that not only the nature of the base but also the presence of carbon monoxide under pressure is an important factor in determining the structure of hydrido ironcarbonyl species in solution. It is of interest that the absorption at 1880 cm^{-1} attributable to the mononuclear anion in methanol persisted unchanged for 6.5 hr at 150°C in the presence of triethylamine (Fig. 2a), but when potassium hydroxide was used, the anion initially formed in a larger quantity decreased rapidly and completely collapsed to ironpentacarbonyl after being heated for 3 hr at the same temperature (Fig. 2b), possibly by the consumption of potassium hydroxide due to repetition of reaction (5) and the following.

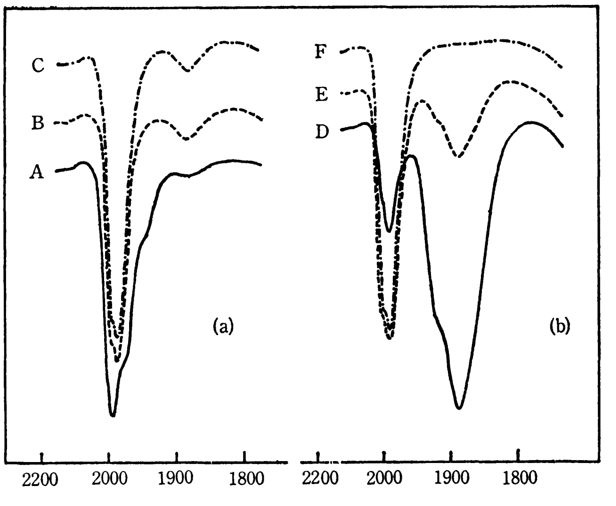
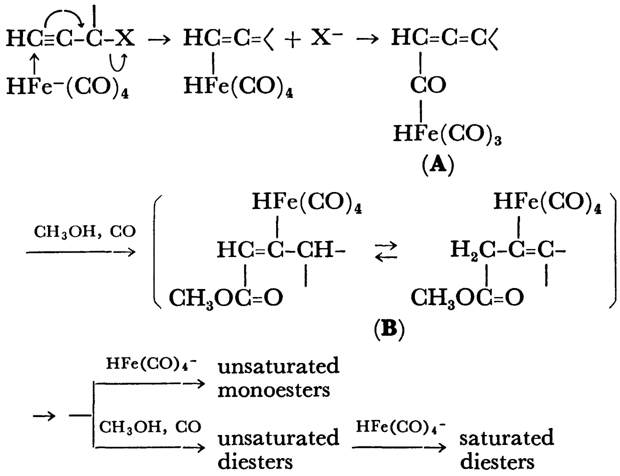


Fig. 2. Time dependence of catalyst mixtures at 150°C under carbon monoxide pressure in MeOH.
(a) $HFe_3(CO)^-_{11}H\overset{+}{N}Et_3$-$NEt_3$-$H_2O$; A: a starting mixture, B: after 1 hr, C: after 6.5 hr.
(b) $Fe(CO)_5$-KOH-H_2O; D: at the point reached at 125°C, E: after 0.5 hr, F: after 3 hr.

$$K^+HFe(CO)_4^- + H_2O \xrightarrow{CO} Fe(CO)_5 + H_2 + K_2CO_3 \qquad (7)$$

We thus propose the scheme for the reactions of propargyl compounds as follows.



The essential step would be the concerted attack of mononuclear hydrido ironcarbonyl anion at the terminal carbon to split off the anion X$^-$, the following insertion of carbon monixide giving an acyl iron intermediate (**A**). Although the subsequent step leaves considerable ambiguity in the present stage of experiment, the reaction of methanol to **A** probably

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[3] R. B. King and F. C. A. Stone, "Inorganic Syntheses", Vol. VII, p. 193 (1963), W. McFarlane and G. Wilkinson, *ibid.*, Vol. VIII, p. 181 (1966).

affords another iron containing intermediate (**B**), which reacts in two ways: 1) hydrogenation by the hydrido anion to give unsaturated monoesters and 2) second carboxylation to unsaturated diesters. The facile formation of the hydrido anion from ironpentacarbonyl in the presence of potassium hydroxide would be resposible for the observation that pressure drop in experiment 5 started at a lower temperature (125°C) than 150°C (Fig. 1, curve B). However, potassium hydroxide essential for the regeneration of the hydrido anion from ironpentacarbonyl is consumed irreversibly to form potassium carbonate under the reaction conditions according to reactions (5) and and (7). The process constitutes a side reaction which inactivates the catalysis system and is presumably a principal factor distinguishing the function of potassium hydroxide from that of tertiary amines, and accounts for the formation of unsaturated diesters in experiment 5 as compared to nearly none in experiment 4 and also for the previous result[1a] where the catalysis system containing potassium hydroxide was nearly ineffective in the oxymethylation of olefins which required longer reaction time(20—30 hr) and higher reaction temperature (170—175°C).

Experimental

Materials. Commercial propargyl alcohol was purified by distillation. Propargyl acetate was prepared by acetylation propargyl alcohol. 3-Methoxy-1-propyne was obtained by debromination of 2,3-dibromo-1-methoxypropane.[4] 3-Methyl-1-butyn-3-ol, 1-ethynylcyclohexanol and 1-butyn-4-ol were synthesized by the reaction of sodium acetylide with acetone, cyclohexanone and ethylene oxide in liquid ammonia, respectively.[5] 1-Pentyn-5-ol was obtained by treatment of tetrahydrofurfuryl chloride with sodium amide in liquid ammonia.[6]

General reaction procedure. Acetylenic compound (0.25 mol), triethylamine (0.25 mol), water (0.40 mol), ironpentacarbonyl (0.05 mol) and 70 ml of methanol were placed in a 300 ml autoclave. After air was displaced with carbon monoxide, carbon monoxide was introduced until pressure became 90—100 kg/cm^2. The mixture was heated under stirring to the desired temperature ranging from 70 to 175°C in about one hour and held at the reaction temperature until the pressure drop substantially ceased. To a dark green reaction mixture was added 100—150 ml of saturated sodium chloride solution and the organic component was taken up by ether. After neutralizing the remaining amine, the ethereal solution was dried and concentrated. The product collected by distillation of the residue was analyzed by gas chromatography and the yeilds of each component were calculated by assuming a proportionality between peak area and weight. The main components of the product were separated by gas chromatography and determined by infrared spectra, NMR and elementary analysis.

Product Identification. The principal product (II) obtained from Ia, Ib and Ic was confirmed as dimethyl methylsuccinate by its infrared spectrum, NMR and elementary analysis (Found: C, 57.72%; H, 7.74%) and further substantiated by comparison with an authentic sample. The other three components found in the reaction of propargyl alcohol using potassium hydroxide as a base were separated analytically by gas chromatography. They gave the following results.

III: dimethyl methylmaleate, NMR: 2.25 (d, 3H), 3.72 (s, 3H), 3.73 (s, 3H) and 6.67 (quar, 1H). Found: C, 53.40; H, 6.53%. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37%.

IVa: dimethyl itaconate, NMR: 3.24 (d, 2H), 3.64 (s, 3H), 3.73 (s, 3H), 5.65 (m, 1H) and 6.22 (m, 1H).

IVb: dimethyl methylfumarate, NMR: 2.2 (d, 3H), 3.67 (s, 3H), 3.73 (s, 3H) and 5.75 (quar, 1H). Found: C, 53.20; H, 6.53%. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37%.

Their structure were further confirmed by hydrogenation to form dimethyl methylsuccinate.

Distillation of the reaction product from 3-methyl-1-butyn-3-ol gave two fractions. Two components V and VI in the lower fraction (64.0/85 —91.0°C/65 mmHg) and five components VII–XI in the higher fraction (105—147°C/4 mmHg were separated by gas chromatography and analyzed. No alcoholic component could be detected.

V: methyl β-isopropylacrylate (*cis* and *trans* mixture), NMR: 1.05 (d, 6H), 1.85—2.64 (m, 1H), 3.60 (s, 3H), 5.55 (quar, 1H) and 6.71 (quar, 1H). Found: C, 64.76; H, 9.16%. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44%.

VI: methyl 4-methyl-3-pentenoate, NMR: 1.59 (s, 3H), 1.70 (d, 3H), 2.87 (d, 2H), 3.55 (s, 3H) and 5.17 (m, 1H). Found: C, 65.89; H, 9.64%.

VII: dimethyl isopropylsuccinate, NMR: 0.91 (s, 6H), 1.90—2.75 (m, 4H), 3.56 (s, 3H) and 3.58 (s, 3H). Found: C, 57.48; H, 8.59%. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57%.

VIII: dimethyl isopropylmaleate or fumarate, NMR: 1.10(d, 6H), 2.50 (m, 1H), 3.50(s, 3H), 3.57 (s, 3H) and 5.58 (d, 1H). Found: C, 58.37; H, 7.76%. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.85%.

IX: 3-isopropyl-γ-butyrolactone, $\nu_{C=O}$; 1780 cm^{-1}, NMR: 0.93 (d, 3H), 0.96 (d, 3H), 1.45 (m, 1H), 1.80—2.60 (m, 3H) and 3.50—4.40 (m, 2H). Found: C, 65.60; H, 9.24%. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44%

X: dimethyl isopropylidenesuccinate, NMR: 1.80 (s, 3H), 2.10 (s, 3H), 3.25 (s, 2H), 3.60 (s, 3H) and 3,65 (s, 3H). Found: C, 59.02; H, 7.77%.

XI: 4,4-dimethyl-3-methoxycarbonyl-γ-butyrolactone, $\nu_{C=O}$; 1780, 1740 cm^{-1}. NMR: 1.25 (s, 3H), 1.58 (s, 3H), 2.4—3.32 (m, 3H) and 3.73 (s, 3H). Found: C, 55.85; H, 7.26%. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03%.

Four compounds separated in a similar manner from the product of 1-ethynylcyclohexanol were identified as follows.

XII: methyl 3-cyclohexylidenepropionate, NMR: 1.53 (m, 6H), 2.10 (m, 4H), 2.94 (d, 2H), 3.62 (s, 3H) and 5.21 (t, 1H).

XIII: methyl trans-β-cyclohexylacrylate, NMR: 1.50 (m, 11H), 3.68 (s, 3H), 5.69 (quar, 1H) and 6.85 (quar, 1H).

XIV: dimethyl cyclohexylsuccinate, NMR: 1.61 (m, 6H), 1.95 (m, 4H), 2.48 (m, 4H), 3.62 (s, 3H) and 3.64 (s, 3H).

XV: dimethyl cyclohexylidenesuccinate, NMR: 1.63 (m, 6H), 2.22 (m, 2H), 2.65 (m, 2H), 3.28 (s, 2H), 3.62 (s, 3H) and 3.68 (s, 3H).

The gas chromatogram of the product from 1-butyn-4-ol indicated the presence of two principal components XVI and XVII, but no alcoholic component such as *n*-butanol and 3- or 2-butenol-1. Assignment of their lactone structures

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4) I. M. Heilbron, E. R. H. Jones, and R. N. Lacey, *J. Chem. Soc.* **1946** 28.

5) A. L. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.*, **67** 484 (1945).

6) E. R. H. Jones, G. Eglinton, and M. C. Whiting, "Organic Syntheses", Coll. Vol. IV, p. 755 (1963).

based on the higher carbonyl absorptions and the absence of methoxycarbonyl group were characterized by the NMR peak in 3.50 to 3.75 ppm region. The saturated lactone could be differentiated from an authentic β-methyl isomer by their γ-proton signals in the 3.5—4.5 ppm region.

XVI: α-methyl-γ-butyrolactone, $\nu_{C=O}$; 1770 cm^{-1}. NMR 1.22 (d, 3H), 1.67—2.17 (m, 1H), 2.17—2.82 (m, 2H) and 4.0—4.33 (m, 2H). Found: C, 59.94; H, 8.27%. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05%.

XVII: α-methyl-γ-crotonolactone, $\nu_{C=O}$; 1760 cm^{-1}, $\nu_{C=C}$; 1660 cm^{-1}. NMR: 1.9 (quar, 3H), 4.72 (m, 2H) and 7.18 (quar, 1H). Found: C, 60.50; H, 6.29%. Calcd for $C_5H_6O_2$: C, 61.21; H, 6.17%.

Distillation of the product from 1-pentyn-5-ol gave two fractions. Owing to the complex nature and less volatility, attempted separation of the components in the higher fraction by gas chromatography afforded no pure samples. The three principal components in the lower fraction were separated by gas chromatography, two of them being confirmed as 1-pentene-5-ol and the strating material by comparison of their infrared spectra and in accordance with the retention times. The other component was proved to be methyl tetrahydrofuryl acetate by comparison with an authentic compound.

XX: methyl tetrahydrofuryl acetate, $\nu_{C=O}$; 1742 cm^{-1}. Found: C, 57.89; H, 8.71%. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39%.

Infrared Examination of the Catalysis System. A catalyst mixture in methanol containing ironpentacarbonyl (or $HFe_3(CO)_{11}^{-}HN^{+}Et_3$), a base and water in the same ratio as that used in the above reactions under the initial carbon monoxide pressure of 100 kg/cm^2 was heated to 150°C under stirring. A small aliquot was withdrawn from the vessel to a glass pressure sampler at a suitable interval starting from the instant 150°C was reached (or from 125°C in the presence of potassium hydroxide). The change of the ironcarbonyl species was followed by infrared spectra immediately taken after sampling, using the absorptions at 1995 cm^{-1} for ironpentacarbonyl and 1880 cm^{-1} for mononuclear hydroirontetracarbonyl anion. Light brownish yellow color of each aliquot at the time of sampling was indicative of the absence (or disappearance) of trinuclear hydrido species, which is readily discernible by its strong deep red color with a quantity less than 0.1%. The color of the samples, however, gradually turned pink due to slow conversion of the mononuclear anion to trinuclear species under atmospheric pressure.