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# ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS—XXXIX[1]

## PALLADIUM-CATALYSED CARBONYLATION OF PROPARGYL COMPOUNDS

T. NOGI and J. TSUJI

Basic Research Laboratories. Toyo Rayon Co., Kamakura. Japan

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**Abstract**—Pd catalyzed carbonylations of propargyl chloride and acetylenic alcohols have been carried out. Propargyl chloride gave 3-chloro-3-butenoate and itaconate in alcohol. Propargyl alcohol yielded in methanol methyl 2-methoxymethylacrylate, itaconate and aconitate. Carbonylation of 2-methyl-3-butyn-2-ol in alcohol produced teraconate and other products, but in benzene teraconic anhydride was obtained selectively. Similarly carbonylation of 2,5-dimethyl-3-hexyn-2,5-diol gave diisopropylidenesuccinic anhydride as a main product in benzene, and diisopropylidenesuccinate in alcohol. The mechanism of these carbonylation reactions is discussed. The reactions described in this paper afford very useful synthetic methods for itaconic acid and their derivatives.

### INTRODUCTION

PROPARGYL COMPOUNDS have been carbonylated using nickel carbonyl. Chiusoli obtained itaconic acid and 2,3-butadienoic acid by the reaction of propargyl chloride with nickel carbonyl in water.[2] Ethyl 3-bromo-3-butenoate was obtained by the reaction of propargyl bromide in ethanol.[3] Also the formation of a cyclopentanone derivative from 1-bromo- and 1-iodo-2-heptyne has been reported.[4] On the other hand, the nickel catalyzed carbonylation of propargyl alcohol gave 2-hydroxymethylacrylate and 4-hydroxycrotonate.[5] In addition, the formation of a derivative of 2,3-butadienoic acid from 2-methyl-3-butyn-2-ol is known.[6]

We have found that Pd is a versatile catalyst for carbonylation of various types of olefinic compounds.[7] In addition, acetylenic compounds can also be carbonylated using Pd catalysts. The carbonylations of acetylene,[8] acetylenemono- and dicarboxylates[9] and diphenylacetylene[10] giving mainly dicarbonylation products have been reported. We have found that Pd catalyzed carbonylation of propargyl compounds proceeds smoothly and gives products somewhat different from those of the nickel carbonyl catalysed reactions.[11] In this paper, results of the Pd catalyzed carbonylation of propargyl compounds are described.

### RESULTS AND DISCUSSION

Various allylic compounds such as allylic halides, esters, ethers, alcohols can be carbonylated using Pd as a catalyst and carbon monoxide is smoothly introduced at the allylic positions of these compounds.[12]

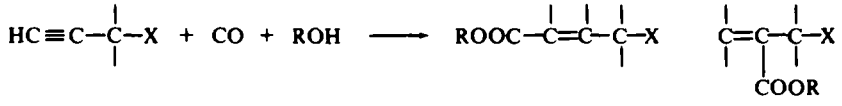
$$CH_2{=}CH{-}CH_2{-}X + CO \rightarrow CH_2{=}CHCH_2COX$$

X: halogen. OH. OR. $O{-}\overset{\overset{O}{\|}}{C}{-}R$

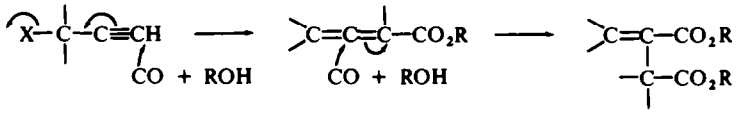
The allylic carbonylation proceeds through the formation of π-allyl complexes. Propargyl compounds are structurally related with allylic compounds; the former has a triple bond instead of a double bond, and similar carbonylation of propargyl compounds is expected. Any definite report, however, on a complex formed from propargyl compounds with Pd has never been given, except one report on the complex of a derivative of propargyl alcohol with palladium chloride. The structure of which was not definitely given.[13]

From our studies on the Pd catalyzed carbonylation of various acetylenic compounds, the Pd catalyzed carbonylation of propargyl compounds can be summarized in the following 4 types.

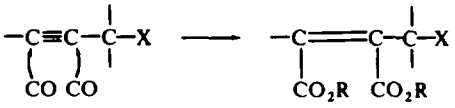
*Reaction A*. Simple addition of carbon monoxide to the triple bond to give unsaturated, allylic substituted acid derivatives.



*Reaction B*. Displacement of the group X by carbon monoxide with rearrangement (or carbonylation with propargyl rearrangement) to give allenecarboxylic acid derivatives. The allenecarboxylate is further carbonylated to give a diester.



*Reaction C*. *Cis*-Dicarbonylation of the triple bond to give allylic substituted maleic acid derivatives.



*Reaction D*. Allylic carbonylation of the products formed by the reactions A and C to give β, γ-unsaturated acid derivatives.

The carbonylation of propargyl compounds described in this paper can be explained by the above schemes. Certainly these reactions proceed through the formation of Pd complexes. However, no experimental evidence was obtained in connection with the formation of the intermediate complexes.

*Carbonylation of propargyl chloride in alcohol*. The carbonylation of propargyl chloride proceeds smoothly in methanol to give methyl 3-chloro-3-butenoate (I) and methyl itaconate (II). The ratio of these products depends on the reaction conditions, and the results of the carbonylation under different conditions are shown in Table 1. When the reaction is carried out in dilute solution, itaconate is the main product.

$$HC{\equiv}C{-}CH_2Cl + CO + CH_3OH \longrightarrow \underset{\underset{Cl}{|}}{H_2C{=}C{-}CH_2CO_2CH_3} + \underset{\underset{CH_2CO_2CH_3}{|}}{CH_2{=}C{-}CO_2CH_3}$$

I II

Resinous substances are formed during carbonylation in concentrated solution. The reaction proceeds in the presence of Pd and HCl. The reaction proceeds even at room temperature with palladium chloride, while with metallic Pd with HCl, heating is required.

TABLE I. CARBONYLATION OF PROPARGYL CHLORIDE

| Propargyl chloride g | Catalyst g | | Solvent ml | | Reaction Temp. °C | Reaction Time hr | Yield % I | Yield % II |
|---|---|---|---|---|---|---|---|---|
| 10 | $PdCl_2$ | 1 | MeOH | 50 | 20 | 1·5 | 17 | 30 |
| 5 | $PdCl_2$ | 1·5 | MeOH | 50 | 20 | 1·5 | trace | 66 |
| 10 | Pd—C | 2 | HCl(10%)/MeOH | 50 | 100 | 1·5 | 36 | 19 |
| 5 | Pd—C | 1 | HCl(10%)/MeOH | 50 | 100 | 1·5 | trace | 60 |
| 10 | Pd—C | 2 | MeOH | 50 | 100 | 1·5 | 0 | 0 |
| 10 | Pd—C | 2 | HCl(10%)/MeOH | 50 | 20 | 24 | 0 | 0 |
| 10 | $PdCl_2$ | 1 | EtOH | 50 | 20 | 1·5 | 18 | 30 |

*a* CO pressure 100 kg/cm²
*b* Pd—C: 10%
*c* Yield based on propargyl chloride.

The first step of the reaction seems to be the carbonylation with propargyl rearrangement (Reaction B) to form 2,3-butadienoate (III). Intramolecular migration of the chlorine to the β-position gives I. Further carbonylation of III produces itaconate easily. The fact that the carbonylation of ethyl 2,3-butadienoate (III) in

$$\underset{\underset{CO + CH_3OH}{|}}{HC{\equiv}C{-}CH_2{-}Cl} \longrightarrow \underset{III}{(H_2C{=}C{=}CH{-}CO_2CH_3)} \xrightarrow{Cl^-} \underset{I}{H_2C{=}\underset{\underset{Cl}{|}}{C}{-}CH_2{-}CO_2CH_3}$$

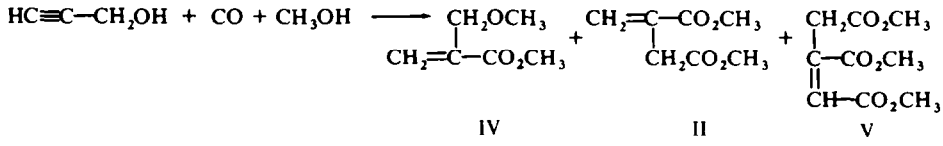
$$\xrightarrow{CO} \underset{II}{H_2C{=}\underset{\underset{CH_2CO_2CH_3}{|}}{C}{-}CO_2CH_3}$$

ethanol in the presence of palladium chloride proceeds smoothly at room temperature to give ethyl itaconate provides the evidence for the above mechanism.

$$\underset{III}{H_2C{=}C{=}CH{-}CO_2Et} + CO + EtOH \longrightarrow \underset{\underset{CH_2CO_2Et}{|}}{H_2C{=}C{-}CO_2Et}$$

II

*Carbonylation of propargyl alcohol.* One, two and three moles of carbon monoxide can be introduced into propargyl alcohol by carbonylation in methanol, giving methyl 2-methoxymethylacrylate (IV), itaconate (II) and aconitate (V). The ratio of these



three products depends on the amount of solvent, catalyst and concentration of HCl. The results under different conditions are shown in Table 2.

When propargyl alcohol is mixed with palladium chloride, a resinous substance is formed with heat evolution, but in the presence of solvent and carbon monoxide, the

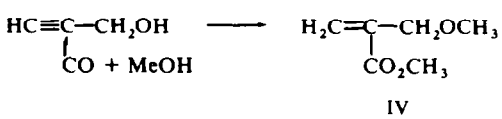
TABLE 2. CARBONYLATION OF PROPARGYL ALCOHOL

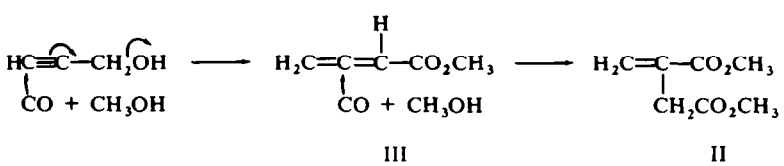
| Propargyl Alcohol g | Catalyst g | Solvent ml | | Reaction Temp. °C | Reaction Time hr | Yield % IV | Yield % II | Yield % V |
|---|---|---|---|---|---|---|---|---|
| 5 | $PdCl_2$ 1 | MeOH | 50 | 100 | 18 | 24 | 26 | 5 |
| 5 | $PdCl_2$ 2 | MeOH | 50 | 100 | 18 | 13 | 24 | 11 |
| 5 | $PdCl_2$ 1 | MeOH | 50 | 20 | 24 | 0 | 0 | 0 |
| 3 | Pd—C 1 | HCl(1%)/MeOH | 50 | 100 | 5 | 13 | 29 | 9 |
| 3 | Pd—C 1 | HCl(0·5%)/MeOH | 50 | 100 | 5 | 36 | 12 | 3 |
| 1 | Pd—C 0·5 | HCl(2%)/MeOH | 50 | 100 | 15 | trace | 63 | 10 |
| 5 | $PdCl_2$ 1 | EtOH | 50 | 100 | 24 | 19 | 31 | 7 |

*a* CO pressure 100 kg/cm$^2$
*b* Pd—C; 10%

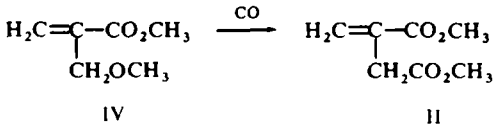
carbonylation proceeds smoothly. Under certain conditions, itaconate can be obtained as a main product. Thus this reaction should be a very useful and simple one step synthetic method of itaconate and aconitate.

The mechanism of the carbonylation of propargyl alcohol can be illustrated as follows: The ester IV is formed by the simple addition of carbon monoxide to the triple bond (reaction A), followed by the displacement of allylic OH with OMe. For the



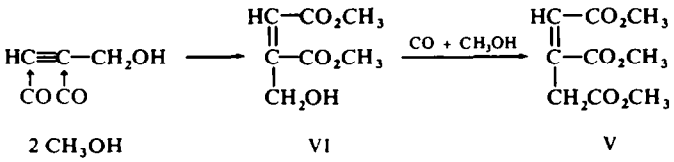


formation of itaconate (II), the following two paths may be considered. The reaction B gives 2,3-butadienoate (III), which is further carbonylated to give itaconate. The other path is the allylic carbonylation of IV, which is allylic ether (reaction D). The fact that IV is obtained only as a minor product of the carbonylation is explained by this path.



IV II

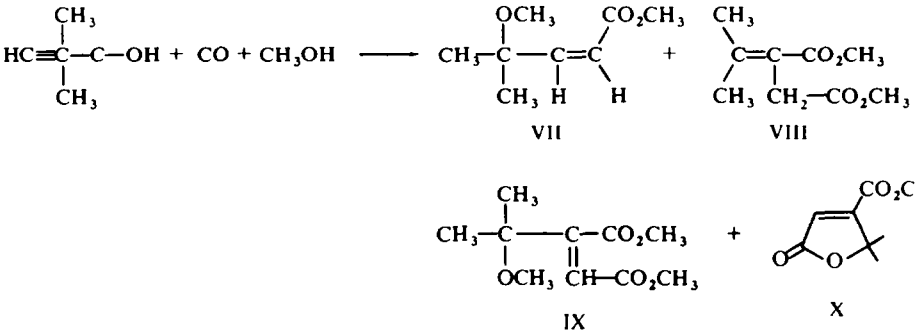
The most probable path for the aconitate formation is the *cis*-dicarbonylation of the triple bond (reaction C), giving a maleate derivative with allylic alcohol structure (VI). The allylic carbonylation (reaction D) of VI gives aconitate. The itaconate is not an



2 $CH_3OH$ VI V

intermediate of the aconitate formation, because itaconate (II) was recovered in an attempt to carbonylate itaconate (II).

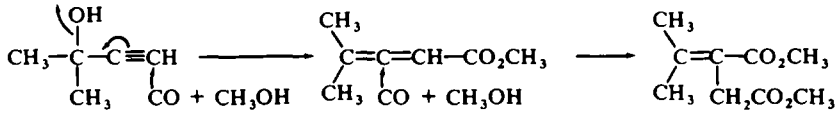
*Carbonylation of substituted propargyl alcohols in alcohol.* Carbonylation of substituted propargyl alcohol such as 2-methyl-3-butyn-2-ol gives a mixture of VII-X.



The products, methyl teraconate (VIII) and methyl 2,4-dihydro-2,2-dimethyl-5-oxo-3-furoate (X) could not be separated by distillation, but only after hydrogenation to methyl isopropylsuccinate and methyl terebate. The ratio of these products depends on the amount of catalyst and the concentration of HCl. With a small amount of the catalyst, the monocarbonylation predominates to give 4-methyl-4-methoxy-2-pentenoate (VII) as a main product. If a larger amount of the catalyst is used, VII and IX are not formed, but X and VIII are obtained in 1:1 ratio. In addition to these products, a small amount of unidentified unsaturated lactone was obtained.

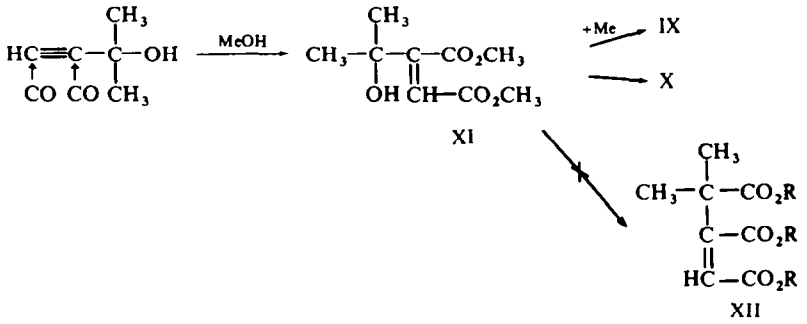
The following mechanism is considered. The ester VII is formed by a simple carbon monoxide attack at the terminal carbon of the triple bond (reaction A) followed by

replacement of the allylic alcohol with OMe. In this reaction, certainly the attack at the inner carbon is inhibited by steric effect. The diester VIII is formed undoubtedly by the reaction B; that is, the carbonylation with rearrangement, followed by the

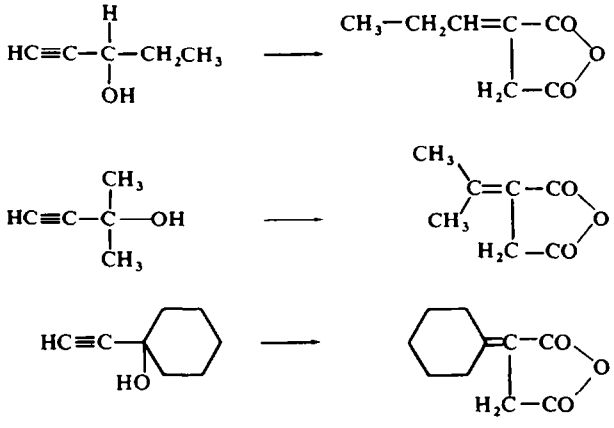


VIII

carbonylation of the allenecarboxylate. Dimethyl 3-methyl-3-methoxy-1-buten-1,2-dicarboxylate (IX) is formed by the *cis*-dicarbonylation (reaction C) of the triple bond. It should be noticed that the product of the *cis*-dicarbonylation is an allylic alcohol (XI). Different from the formation of aconitate via the allylic carbonylation, further carbonylation of XI giving tricarboxylate XII does not occur due to steric hindrance. The diester IX is formed by exchange of the allylic OH with OMe, and the lactone X is formed by the cyclization of XI.

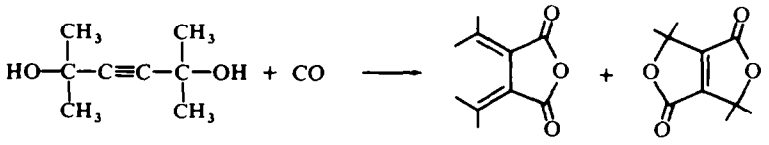


*Carbonylation of substituted propargyl alcohols in benzene.* The carbonylation of propargyl alcohol in benzene gives only resinous substances, but, substituted propargyl alcohols such as 1-pentyn-3-ol, 2-methyl-3-butyn-2-ol, and 1-ethynylcyclohexanol give substituted itaconic acid anhydrides selectively. The products are anhydrides of propylidenesuccinic acid (19%), teraconic acid (42%) and cyclohexylidenesuccinic



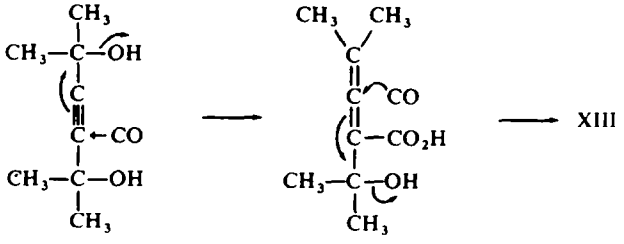
acid (45%). These anhydrides can be hydrolyzed to give dicarboxylic acids which are then reconverted into the anhydrides by heating at 200°. These anhydrides of itaconic acid derivatives are formed by the reacrion B. This reaction is very useful for the selective synthesis of substituted derivatives of itaconic acid.

*Carbonylation of substituted butyndiols.* The carbonylation of butyndiol, having propargyl alcohol functions on both sides of the triple bond, results in resinous material accompanied by a small amount of carbonylation products (IR spectrum). On the other hand the carbonylation of 2,5-dimethyl-3-hexyn-2,5-diol in benzene proceeds smoothly to give the anhydride of diisopropylidenesuccinic acid (49%, XIII), as a main product accompanied by a dilactone (14%). The structure of the dilactone was determined as bis (1-hydroxy-1-methylethyl) fumaric acid dilactone (XIV) from spectral data such as IR (1750 $cm^{-1}$) and NMR (singlet at 8·33), mol. wt. and

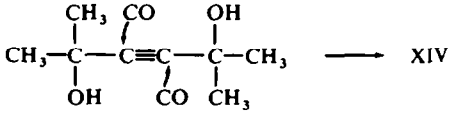


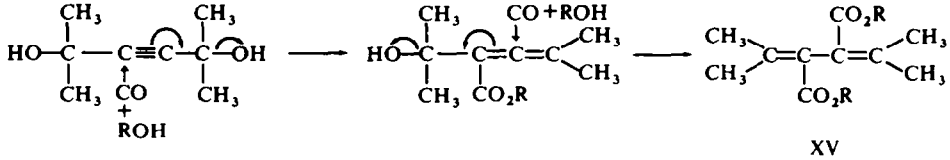
XIII XIV

elemental analysis. The anhydride (XIII) is certainly formed by the displacement of OH by carbon monoxide with rearrangement to give allenecarboxylate. The allylic carbonylation of the allenecarboxylate successively occurs to give XIII. The forma-



tion of the dilactone (XIV) is interesting. Considering the *trans* configuration of the lactone with regard to the carbonyl functions, XIV must be formed by the *trans* addition of two moles of carbon monoxide, followed by the lactonization.





XV

The carbonylation of 2,5-dimethyl-3-hexyn-2,5-diol was then tried in ethanol, containing HCl, which gives diisopropylidenesuccinate (XV) as a main product (53%), accompanied by a small amount of unidentified products. The result shows that the displacement of the both OH groups by carbon monoxide with rearrangement, was the predominate reaction path.

## EXPERIMENTAL

*Materials and apparatus.* Commerically available propargyl chloride and alcohol were used after distillation. Substituted propargyl alcohols were synthesized by the reaction of sodium acetylide with aldehydes or ketones in liquid ammonia.[14] Ethyl 2,3-butadienoate was synthesized by the isomerization of ethyl 3-butynoate[15], which was synthesized by chromium trioxide oxidation of 3-butyn-1-ol.[16] 3-Butyn-1-ol was synthesized by the reaction of acetylene with ethylene oxide.[17] Gas chromatography was carried out with Yanagimoto GC III (silicone DC-550 or apiezon grease 2 m length using He as a carrier gas). The NMR spectra were determined on Varian high resolution spectrometer model DP 60 using TMS as an internal standard, and expressed by $\tau$ value. The carbonylation was carried out in a glass vessel having a gas inlet capillary, which was placed in a 300 ml stainless steel autoclave. Carbon monoxide was charged up to 100 atm before the reaction. The autoclave was shaken during the reaction.

*Carbonylation of propargyl chloride.* Propargyl chloride (10 g), MeOH (50 ml) and $PdCl_2$ (1 g) in a glass vessel was placed in an autoclave. CO was charged up to 100 atm, and the reaction was carried out at room temp for 90 min with shaking. The reaction mixture was poured into water and extracted several times with ether. After evaporation of the ether, residue was distilled to give I at 50–60°/20 mm and II at 95–100°/15 mm. Methyl chlorobutenoate was confirmed by IR (1750 and 1638 $cm^{-1}$) and NMR spectra (4·44 ($=CH_2$), 6·11 ($CH_3$), 6·55 ($-CH_2-$) all singlet). Found: C, 44·40; H, 5·26. Calc. for $C_5H_7O_2Cl$: C, 44·63; H, 5·24. Catalytic hydrogenation of the ester using Pd-C in MeOH gave methyl n-butyrate.

Methyl itaconate was identified by IR (1730 and 1640 $cm^{-1}$) and NMR spectra (3·79, 4·31 ($=CH_2$), 6·31, 6·38 ($-CH_3$), 6·72 ($-CH_2-$) all singlet) and gas chromatography with an authentic sample. Catalytic hydrogenation gave methyl 2-methylsuccinate, which was identified with an authentic sample by IR spectrum and gas chromatography.

*Carbonylation of ethyl 2,3-butadienoate* (III). Ethyl 2,3-butadienoate (3 g), EtOH (30 ml) and $PdCl_2$ (0·5 g) reacted with CO (100 atm) at room temp for 90 min, and ethyl itaconate (3·1 g) was obtained and purified by distillation at 98–102°/15 mm, and identified by IR and NMR spectra and gas chromatography with an authentic sample.

*Carbonylation of propargyl alcohol.* Propargyl alcohol (5 g), MeOH (50 ml) and $PdCl_2$ (1 g) reacted with CO at 100° for 18 hr. Distillation of the products gave IV at 100–125°/760 mm, II at 95–100°/15 mm, and V at 140°/5 mm. The reaction was carried out similarly to the one in EtOH. The products were confirmed in the following way.

Methyl 2-methoxymethylacrylate (IV). Found: C, 55·19; H, 7·70. Calc. for $C_6H_{10}O_3$: C, 55·37; H, 7·75%; IR spectrum (1720 and 1640 $cm^{-1}$), NMR spectrum; two doublets at 3·81, 4·21 ($=CH_2$), 5·94 ($-CH_2-$) quartet, 6·26 ($-CO_2Me$), 6·65 ($-OMe$). Catalytic hydrogenation using PdC in MeOH absorbed 2-moles $H_2$ to give methyl isobutyrate, which was identical with an authentic sample by IR and NMR spectra and gas chromatography.

The methyl aconitate was identical with an authentic sample by IR (1730, 1660 $cm^{-1}$) and NMR spectra (3·17 ($=CH-$), 6·15 ($-CH_2-$), 6·22, 6·29, 6·37 ($-CH_3$)). Ethyl aconitate: Found: C, 55·83; H, 7·00; Mol. Wt., 255·4. Calc. for $C_{12}H_{18}O_6$: C, 55·80; H, 7·03%; Mol Wt., 258·3; identical by IR spectrum (1730 and 1660 $cm^{-1}$) NMR spectrum (3·18 ($=CH-$), 5·82 ($-OCH_2-$), 6·13 ($-CH_2-$), 8·71 ($-CH_3$)) and gas chromatography with an authentic sample, b.p. 120°/2 mm.

*Carbonylation of 2-methyl-3-butyn-2-ol in alcohol.* 2-Methyl-3-butyn-2-ol (10 g), MeOH (50 ml) and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. After the usual work-up, VII (5 g) was obtained at 78–102°/70 mm. A higher boiling fraction (2·5 g) was obtained at 105–120°/8 mm, which was separated by preparative gas chromatography into X, VIII and IX (ratio; 1:3:1). When the reaction was carried out with 3 g $PdCl_2$ a 1:1 mixture of VIII and X (6·2 g) was obtained at 108–115°/10 mm. The mixture was hydrogenated with Pd-C and methyl terebate and methyl isopropylsuccinate were separated by preparative gas chromatograpy. The products were identified as shown below.

*trans*-Methyl 4-methyl-4-methoxy-2-pentenoate (VII): Found: C, 60·55; H, 8·85; Mol. Wt., 163.

Calc. for $C_8H_{14}O_3$: C, 60·74; H, 8·92%; Mol. Wt., 159; IR (1730, 1660 and 1075 $cm^{-1}$) NMR (two doublets at 3·24, 4·16 (—CH=CH—, $J$; 17·4 c/s), three singlets at 6·35 (—$CO_2$Me), 6·87 (—OMe), 8·74 (—Me)).

Dimethyl teraconate (VIII): Mol. Wt. Found 180. Calc. for $C_9H_{14}O_4$: 186; IR (1740 and 1640 $cm^{-1}$) NMR (6·31, 6·35 (—$CO_2CH_3$), 6·70 (—$CH_2$—), 7·88, 8·15 (—$CH_3$ all singlet). Teraconic acid was obtained by hydrolysis with 10% NaOH aq and identified by IR spectrum and mixture m.p. with an authentic sample. (162°)

*cis*-Dimethyl 3-methyl-3-methoxy-1-buten-1,2-dicarboxylate (IX): Found: C, 55·30; H, 7·32; Mol. Wt., 214·5. Calc. for $C_{10}H_{16}O_5$: C, 55·54; H, 7·46%; Mol. Wt., 216; IR spectrum (1735, 1650 and 1070 $cm^{-1}$) NMR spectrum (4·11 (=CH—), 6·25, 6·31 (—$CO_2CH_3$), 6·87 (—$CH_3$), 8·71 (—$CH_3$) all singlet). Methyl 2,5-dihydro-2,2-dimethyl-5-oxo-3-furoate (X); IR spectrum (1765 and 1740 $cm^{-1}$), NMR (3·55 (=CH—), 6·16 (—$OCH_3$), 8·48 (—$CH_3$) all singlet).

Methyl terebate was obtained by catalytic hydrogenation over Pd-C in MeOH and identified with an authentic sample. Found: C, 55·65; H, 6·85. Calc. for $C_8H_{12}O_2$: C, 55·80; H, 7·03%; IR (1775 and 1740 $cm^{-1}$); NMR (6·29 (—OMe), 6·60–7·60 ($CH_2$—CH—), 8·43, 8·75 (Me)).

Methyl isopropylsuccinate: Found: C, 57·19; H, 8·57. Calc. for $C_9H_{16}O_4$: C, 57·43, H, 8·57%; IR (1740 $cm^{-1}$); NMR (6·36, 6·50 (—OMe), 7·20–7·80 (—CH—CH—$CH_2$), 9·08 (—Me)).

*Carbonylation of 2-methyl-3-butyn-2-ol in benzene.* 2-Methyl-3-butyn-2-ol (10 g), benzene (50 ml) and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. After the usual work-up, the residue was distilled to give teraconic anhydride 7·0 g (42%) at 95–100°/3 mm, which was identified by IR (1840 and 1770 $cm^{-1}$) and NMR (6·54 (—$CH_2$—), 7·69, 8·02 ($CH_3$—)) spectra. Teraconic acid was obtained by hydrolysis and identified in the following way: m.p. 162–163°, Found: C, 53·27; H, 6·39; Mol. Wt., 160. for $C_7H_{10}O_4$: C, 53·16; H, 6·37%, Mol. Wt., 158; IR (1655 and 1620 $cm^{-1}$); ozonization of teraconic acid produced acetone, which was identified as 2 1695, 4-dinitrophenylhydrazone, m.p. 126° (reported 126°).

*Carbonylation of 1-pentyn-3-ol.* 1-Pentyn-3-ol (10 g), dry benzene (50 ml) and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. The IR spectrum of the reaction mixture (1810 and 1775 $cm^{-1}$) showed the formation of anhydride. After hydrolysis with a warm NaOH aq, propylidenesuccinic acid (3·2 g, 19%) was obtained and recrystallized from acetone, m.p. 169–170° (reported 167°); IR spectrum (1710, 1675 and 1645 $cm^{-1}$). Found: C, 52·94; H, 6·30; Calc, for $C_6H_{10}O_4$: C, 53·16; H, 6·37%.

*Carbonylation of 1-ethynylcyclohexanol.* 1-Ethynylcyclohexanol (10 g), dry benzene (50 ml) and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. After the reaction, cyclohexylidenesuccinic anhydride (6·5 g; 45%) was obtained by distillation at 150–155°/9 mm. IR bands at 1840 and 1760 $cm^{-1}$ showed the formation of acid anhydride. Cyclohexylidenesuccinic acid was obtained by hydrolysis, recrystallized from acetone, and confirmed in the following way, m.p. 177-179° (reported 175°); Found: C, 60·32; H, 7·04; Mol. Wt., 195: Calc. for $C_{10}H_{14}O_4$: C, 60·59; H, 7·12%; Mol. Wt., 198; IR spectrum (1700, 1660 and 1610 $cm^{-1}$), ozonization gave cyclohexanone which was identified as 2,4-dinitrophenylhydrazone, m.p. 160–161° (reported, 161°).

*Carbonylation of 2,5-dimethyl-3-hexyn-2,5-diol in benzene.* 2,5-Dimethyl-3-hexyn-2,5-diol (4 g), benzene saturated with HCl (40 ml), and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. The IR spectrum of the crude reaction mixture showed the formation of acid anhydride (1820 and 1760 $cm^{-1}$). After evaporation of benzene, the residue was separated into a chloroform soluble part and an insoluble part. The latter was recrystallized from EtOH to give 2·5 g diisopropylidenesuccinic acid, which was converted into anhydride by warming with acetyl chloride. Diisopropylidenesuccinic anhydride (XIII), m.p. 56–58° (reported 59·5°); IR (1820 and 1760 $cm^{-1}$). Diisopropylidenesuccinic acid, m.p. 228–230° (reported 231); IR spectrum (1680, 1640 and 1620 $cm^{-1}$), Found: C, 60·51; H, 7·11. Calc. for $C_{10}H_{14}O_4$: C, 60·59; H, 7·12%.

The chloroform soluble part was evaporated and the residue was recrystallized from EtOH to give *hydroxy-1-methylethyl fumaric acid dilactone* XIV, m.p. 214–215°. Found: C, 61·22; H, 6·17; Mol. Wt., 195. Calc. for $C_{10}H_{12}O_4$: C, 61·21; H, 6·17%, Mol. Wt., 196; IR spectrum 1750 $cm^{-1}$, NMR spectrum 8·33 (—Me).

*Carbonylation of 2,5-dimethyl-3-hexyn-2,5-diol in alcohol.* 2,5-Dimethyl-3-hexyn-2,4-diol (3 g), EtOH containing HCl (5%; 35 ml) and $PdCl_2$ (1 g) were treated with CO at 100° for 15 hr. The reaction mixture was poured into water and extracted with ether. Ether was removed and the residue was distilled to give ethyl diisopropylidenesuccinate (3·0 g, 52·8%) at 110–125°/7 mm. Found: C, 65·80; H, 8·66;

Mol. Wt., 252. Calc. for $C_{14}H_{22}O_4$: C, 66·11; H, 8·72%; Mol. Wt., 254·3; IR spectrum 1730 $cm^{-1}$; NMR spectrum (5·92 (—$CH_2$—), 7·86, 8·30 (—$CH_3$), 8·80 (—$CH_3$)).

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