The Regiospecific Palladium Catalysed Hydrocarboxylation of Alkenes under Mild Conditions

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Alkenes react with carbon monoxide, water, oxygen, hydrochloric acid, and palladium and copper chlorides, to give branched chain acids in good yields.

The hydrocarboxylation of alkenes to carboxylic acids with carbon monoxide and water, in the presence of palladium compounds or other catalysts, is a process of considerable industrial importance. Scrutiny of the numerous patents and publications which have appeared on this subject reveal that drastic conditions (high pressures, moderate to high temperatures) are required to effect this transformation, and that the reaction generally gives mixtures of straight chain and branched chain acids.[1-3] This communication describes an exceedingly mild method for achieving the hydrocarboxylation of a variety of alkenes, using homogeneous catalysis. Furthermore, with one exception, this reaction is completely regiospecific.

When carbon monoxide and oxygen are bubbled through a solution of tetrahydrofuran containing a terminal alkene (**1**), palladium and copper chlorides, and limited quantities of water and hydrochloric acid, the branched chain acids (**2**), are formed in good to excellent yields [equation (1)]. These reactions, which occur at room temperature and atmospheric pressure, are usually complete after 4 h, although usually they were left to stir overnight. Simplicity in execution and work-up is an added feature of the reaction. The yields of acids are given in Table 1.

$$\underset{(\mathbf{1})}{RCH{=}CH_2} + CO + H_2O \xrightarrow[O_2,\ \text{room temp., 1 atm}]{PdCl_2, CuCl_2, HCl} \underset{(\mathbf{2})}{RCH(CO_2H)Me} \quad (1)$$

The following general procedure was used: carbon monoxide was bubbled through a solution containing tetrahydrofuran (30 ml) and water (1 ml). Palladium(II) chloride (0.140 g, 0.78 mmol) was added, followed by concentrated hydrochloric acid (1.0 ml) and copper(II) chloride, and then oxygen was bubbled through the mixture. The alkene (7.8 mmol) was added and the reaction mixture was stirred at room temperature for 4 h or overnight. Distilled water (50 ml) was added, the product was extracted 3 times with hexane, dried, and concentrated. Pure acid was obtained by treatment with 1 M NaOH, extraction with diethyl ether, and acidification.

Table 1. Acids obtained by the hydrocarboxylation of alkenes.

Alkene	Reaction time/h	Product[a]	Yield, %
(**1**), R = n-C_8H_{17}	4	(**2**), R = n-C_8H_{17}	100
cis-Dec-2-ene	4	(**2**), R = n-C_8H_{17}	59
trans-Dec-2-ene	4	(**2**), R = n-C_8H_{17}	30
trans-Dec-2-ene	18	(**2**), R = n-C_8H_{17}	77
Cyclododecene	18	Cyclododecanecarboxylic acid	64
cis-4-Methylpent-2-ene	18	2,4-Dimethylpentanoic acid	84
(**1**), R = *p*-MeC_6H_4	18	(**2**), R = *p*-MeC_6H_4	58
(**1**), R = C_6H_{11}	18	(**2**), R = C_6H_{11}	82[b]
Octa-1,7-diene	18	$HO_2C(Me)CH[CH_2]_4CH(Me)CO_2H$	93
Deca-1,9-diene	19	$HO_2C(Me)CH[CH_2]_6CH(Me)CO_2H$	100
trans-Hept-3-ene	18	2-Ethylhexanoic and 2-n-propylpentanoic acids	75[c]

[a] Products were identified by comparison of physical data [m.p. and i.r., (^{1}H and ^{13}C) n.m.r., and mass spectra] with those of authentic materials. [b] An unidentified by-product was also formed. [c] The products were formed in a 1:1 ratio.

This remarkably mild process occurs for a variety of terminal alkenes containing aliphatic and aromatic R groups. Note that for di-alkenes such as octa-1,7-diene and deca-1,9-diene, the branched chain diacid is formed exclusively (*i.e.*, no linear products or unsaturated monoacids). Even more dramatic are the results obtained with alkenes having the double bond at the 2-position. For example, *cis*- or *trans*-dec-2-ene react under the described conditions to give only 2-methyldecanoic acid. Similarly, only 2,4-dimethylpentanoic acid was isolated using *cis*-4-methylpent-2-ene as the substrate. No isomeric acids were formed in these reactions. The regiospecificity did break down using an alkene with the double bond at the 3-position (hept-3-ene).

The proportion of water used has a significant influence on the reaction. The reaction fails when water is used as the only solvent, or admixed with tetrahydrofuran where the amount of water is greater than 5 mol. equiv. The reaction is also sensitive to the concentration of hydrochloric acid, with low concentrations being preferred. The consequences of effecting the reaction in the absence of oxygen include a slower rate of reaction (if any reaction occurs at all) and reduced product yields. Variation in the rate of bubbling of carbon monoxide and/or oxygen through the solution had no observable effect on the hydrocarboxylation reaction.

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