Tetrahedron Letters,Vol.29,No.35,pp 4435-4436,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

AEROBIC OXIDATIVE-CARBONYLATION OF OLEFINS.
A CONVENIENT PREPARATION OF β-HYDROXYALKANOIC ACID DERIVATIVES FROM OLEFINS

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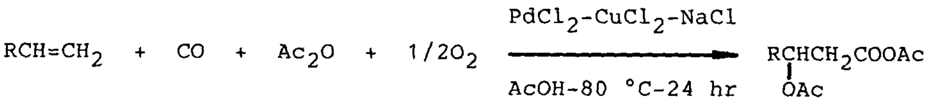
Abstract: A variety of β-hydroxyalkanoic acid derivatives were prepared by palladium catalyzed aerobic oxidative-carbonylations of terminal olefins at normal pressure of carbon monoxide and oxygen mixed gas.

From synthetic point of view, oxidative-carbonylations of olefins are one of the most attractive carbonylations, because two different functional groups can be introduced simultaneously into both carbon atoms of carbon-carbon double bonds. For example, James and Stille1) have demonstrated that β-methoxy esters have been obtained by palladium catalyzed carbonylation of olefins using excess amounts of $CuCl_2$ as oxidant under pressurized conditions. Numerous efforts to realize these functionalization using oxygen as oxidant have been made until now. However, main products have been reported to be succinates2) or acrylic acids3) under high pressure conditions, or non-oxidative products under normal pressure.4) Here we wish to report a practical preparation of β-hydroxyalkanoic acid derivatives by aerobic oxidative-carbonylation of olefins under atmospheric pressure.



$$RCH{=}CH_2 + CO + Ac_2O + 1/2O_2 \xrightarrow[AcOH\text{-}80\ °C\text{-}24\ hr]{PdCl_2\text{-}CuCl_2\text{-}NaCl} \underset{\displaystyle OAc}{RCH}CH_2COOAc \quad (1)$$

When 1-hexene (1 mmol) was heated in acetic acid (4 ml) and acetic anhydride (1 ml) in the presence of $PdCl_2$ (5 mol%), $CuCl_2$ (10 mol%), and NaCl (1 mmol) under atmospheric pressure of CO and O_2 (*ca.* 2/1 v/v) at 80 °C for 24 hr, acetic β-acetoxyheptanoic anhydride was isolated in 84% yield after the usual workup. Although most parts of sodium chloride used remained insoluble under these conditions, an adequate amount of NaCl are required for satisfactory yields of the products (Table 1). The yields also depended clearly on the quantity of acetic anhydride. No reaction took place in the absence of acetic anhydride, and 3-acetoxyheptanoic acid itself was obtained in lower yield on using an equimolar amount of acetic anhydride. In sharp contrast with the Fenton's result3) that the addition of anhydride to the reaction medium has a marked effect on the selective formation of acrylic acid under high pressure conditions, less than 2% yield of 2-heptenoic acid was formed under the present conditions. Functionalized olefins such as allyl

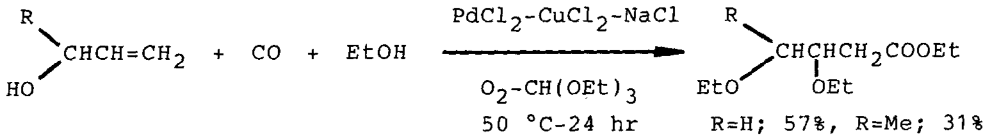
Table 1. Aerobic Oxidative-Carbonylation of Terminal Olefins a)

Run	R	NaCl(eq.)	AcOH(ml)	Ac_2O(ml)	Yield(%)
1	n-C_4H_9	1	4	1	84
2	n-C_4H_9	0.2	4	1	42
3	n-C_4H_9	1	4	0.1	35 b)
4	n-C_6H_{13}	1	4	1	87
5	n-C_9H_{19}	1	4	1	95
6	$PhCH_2$	1	4	1	86
7	$CH_2=CH(CH_2)_6$	1	4	1	78 c)
8	$AcOCH_2$	0.5	4	1	55
9	AcO	0.25	1.25	0.75	53
10 d)	AcO	0.25	1.25	0.75	89
11 e)	AcO	0.25	1.25	0.75	65

a) All reactions were carried out at 1 mmol scale of olefin fitted with a rubber balloon containig CO and O_2 (*ca.* 2/1 v/v) mixed gas in the presence of $PdCl_2$ (2.5-6 mol%) and $CuCl_2$ (7.5-15 mol%) at 80 °C. b) The product was 3-acetoxyheptanoic acid. c) The product was acetic 3-acetoxy-10-undecenoic anhydride. d) The reaction was done under pressurized conditions (CO; 20 atm, O_2; 20 atm). e) The reaction was run in propanoic acid-propanoic anhydride mixed solvent, and propanoic 3,3-dipropionyloxypropanoic anhydride was obtained.

acetate and vinyl acetate were also carbonylated under similar conditions to afford acetic 3,4-diacetoxybutanoic anhydride and acetic 3,3-diacetoxypropanoic anhydride in moderate yields, respectively. In the case of vinyl acetate, pressurized conditions gave us a satisfactory yield of the product.

We also found that the oxidative-carbonylation of functionalized olefins 5) in alcohol was achieved by using oxygen in the requisite presence of NaCl. Thus, β,γ-diethoxybutanoates were prepared from allylic alcohols with triethyl orthoformate (3 eq.) and catalytic amounts of $PdCl_2$ (5 mol%), $CuCl_2$ (15 mol%), and NaCl (50 mol%) at normal pressure of CO and O_2 (Eq. 2).



R=H; 57%, R=Me; 31%

(2)

Mechanistic studies and applications of the present functionalizations are now in progress.

References and Notes

1) D. E. James and J. K. Stille, J. Am. Chem. Soc., 98, 1810 (1976). 2) D. M. Fenton and P. J. Steinwand, J. Org. Chem., 37, 2034 (1972). 3) K. L. Olivier, D. M. Fenton, and J. Biale, Hydrocarbon Processing, 1972, Nov. 95; D. M. Fenton and K. Olivier, Chemtech, 1972, 220. 4) H. Alper, J. B. Woell, B. Despeyroux, and D. J. H. Smith, J. Chem. Soc., Chem. Commun., 1983, 1270; B. Despeyroux and H. Alper, Ann. N. Y. Acad. Sci., 415, 148 (1984); S. B. Fergusson and H. Alper, J. Chem. Soc., Chem. Commun., 1984, 1349. 5) Non-functionalized olefins, *e.g.* 1-alkenes, underwent hydroesterification 4) in low yield under the same reaction conditions.

(Received in Japan 23 June 1988)