

Selective Palladium Catalysed Monohydroesterification of Diols

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Olefins react with diols (*e.g.* ethylene glycol) under oxidative carbonylation and acidic conditions, using palladium and copper(II) chloride as catalysts, to give hydroxy esters in good yields; this mild reaction (room temperature, 1 atm) is a regioselective one.

The hydroesterification of olefins and other unsaturated substrates is an industrially important reaction.¹ Palladium chloride can catalyse the hydroesterification² and hydrocarboxylation³ of olefins under mild conditions. This regiospecific reaction, which occurs in acidic alcohol, enables one to prepare branched chain esters from olefins. A question which

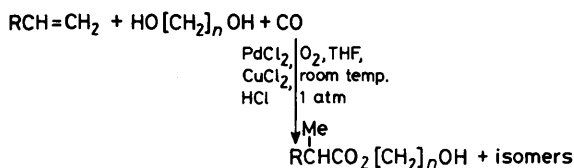
arises is whether the use of diols will result in chemoselective monohydroesterification and also if such a reaction is regio-specific. We now report that monohydroxy esters can be easily prepared in this manner, and that the process is a regioselective but not a regiospecific one.

When dec-1-ene is treated with carbon monoxide and

oxygen, using palladium and copper(II) chlorides as catalysts (room temperature, 1 atm), in ethylene glycol, no reaction takes place, in marked contrast to the behaviour of mono alcohols. This is probably because the reaction mixture is heterogeneous. However, if a 10 : 1 ratio of diol : olefin is used in tetrahydrofuran (THF), then reaction occurs, affording hydroxy esters in 98% yield (Scheme 1). This reaction also proceeds well in acetone. Much reduced product yields resulted using lower (*e.g.* 1 : 1) or higher (26 : 1) proportions of diol to olefin. The ratio of olefin to palladium chloride was 10 : 1, and that of CuCl_2 : PdCl_2 was 8 : 1 in these reactions.† The selectivity for the anticipated hydroxy ester is 70%, the remainder being isomeric hydroxy esters. Other diols, including propane-1,3-diol, butane-1,4-diol, and hexane-1,6-diol, react with dec-1-ene to give the corresponding esters of 2-methyldecanoate as the major product (see Table 1 for distribution of products). The internal olefins, *cis*- and *trans*-dec-2-ene, behave similarly and even *trans*-hept-3-ene displays considerable selectivity for hydroxyethyl 2-ethylhexanoate. Good selectivity was also observed for several other olefins, including propylene. In no case were diesters formed.

There are several significant differences when one compares the above reactions with the hydroesterification of olefins using mono alcohols, or the hydrocarboxylation reaction. While, as noted previously, the latter processes are regiospecific, the diol reactions are regioselective. Furthermore, not only are the two esters obtained which arise from hydroesterification at the double bond, but isomeric esters are also formed as by-products. These isomeric esters apparently are not obtained by olefin isomerization followed by hydroesterification. When the reaction of dec-1-ene and butane-1,4-diol is monitored by *g.c.*, there is no accumulation of 2- or other internal decenes at any time, despite the formation of esters at the 3- and 4-carbons of the ten carbon chain. The diol-olefin reactions in THF are considerably slower than the mono alcohol-olefin reactions in neat alcohol, *e.g.* the time required for complete reaction of decenes with ethylene glycol is dec-1-ene (16 h) > *cis*-dec-2-ene (2 days) > *trans*-dec-2-ene (3 days). The reduced rate of reaction, as well as the use of dilute solutions of diol, may be responsible for the reactions being regioselective instead of regiospecific.

The selective monohydroesterification of olefins with diols provides a direct entry into functionalized esters. The hydroxy function can be easily manipulated thus allowing the synthesis of a variety of useful compounds. For example, oxidation of the hydroxy ester (1) by chromium trioxide-pyridine (*py*)⁴



Scheme 1

† General procedure: palladium chloride (0.8 mmol) was added to THF (30 ml) and conc. HCl (1 ml). Carbon monoxide was bubbled through the mixture until PdCl_2 had dissolved (yellow solution). Copper(II) chloride, olefin, and diol (diol : olefin : CuCl_2 : PdCl_2 = 100 : 10 : 8 : 1) were added, and oxygen was then bubbled through the solution along with carbon monoxide. The mixture was stirred and when reaction was complete (as followed by *g.c.*), water was added and the esters were isolated by extraction with hexane, followed by fractional distillation.

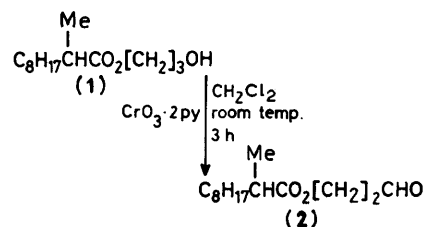
affords the aldehydic ester (2) in 84% yield. Unsaturated esters can be obtained either by Wittig reaction of the resultant aldehyde or by dehydration of the hydroxy ester.

In conclusion, diol monoesters are of significant industrial value as precursors to sex pheromones, as fungicides, and as cross-linking agents in polymer chemistry. The described monohydroesterification of diols is an exceedingly simple method for preparing diol monoesters. This reaction has merit when compared to other synthetic routes to such compounds,

Table 1. Hydroesterification of olefins with diols.

| Olefin | Diol ^a | Yield of esters/% | Product distribution ^b |
|------------------|-------------------|--|--|
| Dec-1-ene | A | 98 | $\text{C}_8\text{H}_{17}\text{CHMeCO}_2[\text{CH}_2]_2\text{OH}$, 70 |
| | | | $\text{C}_9\text{H}_{19}\text{CH}_2\text{CO}_2[\text{CH}_2]_2\text{OH}$, 20 |
| | B | 95 | $\text{C}_7\text{H}_{15}\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 4 |
| | | | $\text{C}_6\text{H}_{13}\text{CH}(\text{Pr}^n)\text{CO}_2[\text{CH}_2]_2\text{OH}$, 6 |
| C | 95 | $\text{C}_8\text{H}_{17}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_3\text{OH}$, 64 | |
| | | $\text{C}_9\text{H}_{19}\text{CH}_2\text{CO}_2[\text{CH}_2]_3\text{OH}$, 28 | |
| | | $\text{C}_7\text{H}_{15}\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_3\text{OH}$, 4 | |
| | | $\text{C}_6\text{H}_{13}\text{CH}(\text{Pr}^n)\text{CO}_2[\text{CH}_2]_3\text{OH}$, 4 | |
| D | 95 | $\text{C}_8\text{H}_{17}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_4\text{OH}$, 72 | |
| | | $\text{C}_9\text{H}_{19}\text{CH}_2\text{CO}_2[\text{CH}_2]_4\text{OH}$, 16 | |
| | | $\text{C}_7\text{H}_{15}\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_4\text{OH}$, 5 | |
| | | $\text{C}_6\text{H}_{13}\text{CH}(\text{Pr}^n)\text{CO}_2[\text{CH}_2]_4\text{OH}$, 7 | |
| cis-Dec-2-ene | A | 77 | $\text{C}_8\text{H}_{17}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 74 |
| | | | $\text{C}_9\text{H}_{19}\text{CH}_2\text{CO}_2[\text{CH}_2]_2\text{OH}$, 7 |
| | | | $\text{C}_7\text{H}_{15}\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 10 |
| | | | $\text{C}_6\text{H}_{13}\text{CH}(\text{Pr}^n)\text{CO}_2[\text{CH}_2]_2\text{OH}$, 4 |
| trans-Dec-2-ene | A | 67 | $\text{C}_8\text{H}_{17}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 68 |
| | | | $\text{C}_9\text{H}_{19}\text{CH}_2\text{CO}_2[\text{CH}_2]_2\text{OH}$, 12 |
| | | | $\text{C}_7\text{H}_{15}\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 8 |
| | | | $\text{C}_6\text{H}_{13}\text{CH}(\text{Pr}^n)\text{CO}_2[\text{CH}_2]_2\text{OH}$, 12 |
| trans-Hept-3-ene | A | 56 | $\text{C}_4\text{H}_9\text{CH}(\text{Et})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 60 |
| | | | $(\text{C}_3\text{H}_7)_2\text{CHCO}_2[\text{CH}_2]_2\text{OH}$, 23 |
| | | | $\text{C}_5\text{H}_{11}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 17 |
| Propene | A | | $(\text{Me})_2\text{CHCO}_2[\text{CH}_2]_2\text{OH}$, 80 |
| | | | $\text{C}_3\text{H}_7\text{CO}_2[\text{CH}_2]_2\text{OH}$, 20 |
| Vinylcyclohexane | A | 70 | $\text{C}_6\text{H}_{11}\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 27 |
| | | | $\text{C}_6\text{H}_{11}\text{CH}_2\text{CO}_2[\text{CH}_2]_2\text{OH}$, 65 |
| Deca-1,9-diene | A | 95 | $\text{HO}[\text{CH}_2]_2\text{OCOCH}(\text{Me})[\text{CH}_2]_6\text{CH}(\text{Me})\text{CO}_2[\text{CH}_2]_2\text{OH}$, 76 |
| | | | isomeric diesters, 24 |

^a A = Ethylene glycol; B = propane-1,3-diol; C = butane-1,4-diol; D = hexane-1,6-diol. ^b Determined by *g.c.* Products identified by spectral analysis [*i.r.*, *n.m.r.* (¹H, ¹³C), mass] and by comparison with authentic samples in some cases.



including the recently reported palladium(II) catalysed cleavage of cyclic acetals by t-butyl hydroperoxide,⁵ a two-step procedure involving acetalisation of diols with aldehydes (not ketones) followed by oxidative ring opening.

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