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Synthesis of Unsaturated Acids by 1,2-Addition of Formic Acid to Conjugated Dienes Catalyzed by Palladium on Carbon in the Presence of Mono and Bidentate Phosphines.

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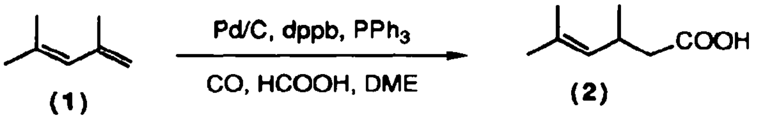
Abstract : Di-, and trisubstituted 1,3-dienes are converted to γ,δ-unsaturated acids by use of formic acid, carbon monoxide, and catalytic quantities of Pd-C / PPh_3 / $Ph_2P(CH_2)_4PPh_2$ in 1,2-dimethoxyethane. A β,γ-unsaturated acid was obtained when the monosubstituted diene, isoprene, was used as the reactant.

Numerous papers and patents have appeared on the subject of the transition metal complex catalyzed hydrocarboxylation and hydroesterification of conjugated dienes. Depending on the reaction conditions, unsaturated and/or saturated mono and/or diacids or diesters are formed, with dimerization and carbonylation reactions occuring in some cases. Examples include the formation of esters of 3,8-monodienoic acid by palladium acetate catalyzed carbonylation of 1,3-butadiene in alcohol,[1] the oxidative carbonylation of the same substrate in methanol catalyzed by $PdCl_2$ to give dimethyl-2-butene-1,4-dicarboxylate,[2] and the rhodium dicarbonyl iodide dimer catalyzed 1,4-addition, under acidic conditions, affording 3-pentenoic acid as the major product.[3] There are no examples, to our knowledge, of the hydrocarboxylation of conjugated dienes which proceeds with good selectivity for net 1,2-addition of formic acid to one of the double bonds of the diene.

We have recently shown that palladium on carbon, together with 1,4-bis(diphenylphosphino)butane [dppb], can catalyze the addition of formic acid (or oxalic acid) to alkenes.[4] It seem conceivable that the Pd/C-dppb system, either as such or appropriately modified, could catalyze the carbonylation of conjugated dienes, hopefully with some selectivity. Indeed, quite selective 1,2-addition of formic acid to a diene does take place, with a modified catalytic system, resulting in the formation of γ,δ-unsaturated acids in reasonable yields. We now communicate the interesting results of this investigation.

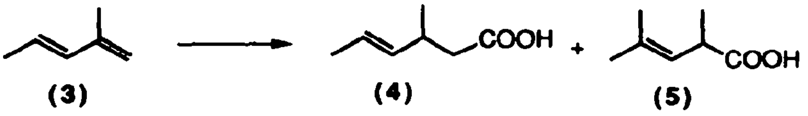
Only trace amounts of 3,5-dimethyl-4-hexenoic acid (**2**) were formed on treatment of 2,4-dimethyl-1,3-pentadiene (**1**), in 1,2-dimethoxyethane (DME), with two equivalents of formic acid, catalytic quantities of 10% Pd/C, dppb, and 6.2 atmospheres of carbon monoxide at 110 °C for 24h (eq. 1).



(eq. 1)

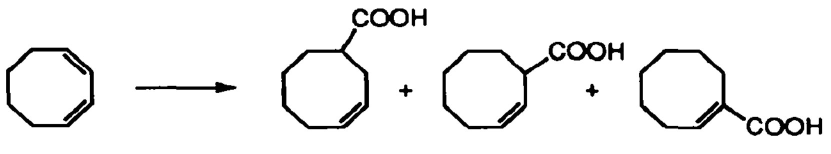
It was previously observed, that in the palladium catalyzed addition of formic acid to alkynes, that the presence of <u>both</u> a bidentate and a monodentate phosphine were beneficial for the reaction.[4,5] When the reaction of **1** with carbon monoxide and formic acid was repeated with triphenylphosphine, under otherwise identical reaction conditions, the γ,δ-unsaturated acid (**2**) was isolated as the only product in 60% yield of <u>pure</u> material (the crude was much higher). Only traces of **2** were detected in the absence of PPh_3 (i.e. both PPh_3 and dppb are required for the reaction), and no reaction occurs using nitrogen instead of a carbon monoxide atmosphere. The optimum ratio of **1** / dppb / PPh_3 / Pd-C was 179 / 5.0 / 2.5 / 1.0.[6]

The conversion of **1** to **2** indicates selective 1,2-addition of formic acid to the least substituted double bond of the diene (i.e. 1,1-disubstituted vs. trisubstituted). Reaction occured in 78% selectivity at the same type of 1,1-disubstituted double bond of 2-methyl-1,3-pentadiene (**3**) giving 3-methyl-4-hexenoic acid (**4**), with the remainder (22%) being the isomerized β,γ-unsaturated acid **5**, the total isolated yield being 48%.



(eq. 2)

The major product of the reaction of a cyclic diene (i.e. formally 1,4-disubstituted) 1,3-cyclooctadiene (**6**), under the usual conditions, was the γ,δ-unsaturated acid, **7**, with isomeric acids (**8**,**9**) formed as by-products [total yield, 52% (eq. 3)].

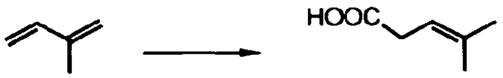


(6) (7) (8) (9)

48 : 15 : 37

(eq. 3)

Finally, it is noteworthy that, in the case of isoprene (**10**), a monosubstituted diene, the process is selective but affords only the β,γ-unsaturated acid (**11**) in 57% yield of pure product (eq. 4).



(10) (11)

(eq. 4)

In conclusion, trisubstituted and disubstituted 1,3-dienes undergo hydrocarboxylation with formic acid catalyzed by Pd/C, PPh_3, and dppb with 1,2-addition being the principal pathway. The monosubstituted diene, isoprene, also reacted in a selective manner but gave only the β,γ-unsaturated acid. These reactions occur under quite mild conditions (6.2 atm, 110 °C), afford products not readily accessible by other routes, and show superior selectivity to known catalytic diene hydrocarboxylation processes.

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6. The following general procedure was used : a mixture of 5.0 mmol of diene, 30 mg (0.028 mmol) of Pd/C, 10 mmol of formic acid, 18.5 mg (0.071 mmol) of PPh_3, and 60 mg (0.14 mmol) of dppb in 5 mL of DME was placed in a 45-mL autoclave. After purging with CO, the autoclave was pressurized to 6.2 atm. and heated at 110 °C for 24h. The reaction was worked up by rotary evaporation of the solvent, and the residue was dissolved in 30 mL of ether and extracted with 0.5 M NaOH. The aqueous solution was neutralized with 1 M HCl and extracted with ether. The ether extract was dried ($MgSO_4$) and distilled under reduced pressure affording the acid.The products were characterized by comparison of physical and spectral data [i.e. NMR (^1H, ^{13}C), MS] with literature results.[7-11]

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