The Alkoxy–Alkoxycarbonylation of Allenes

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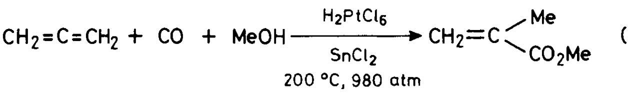
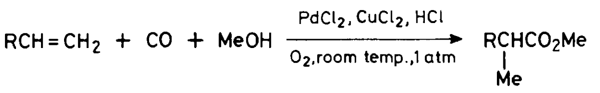
Allene undergoes alkoxy–alkoxycarbonylation under exceedingly mild conditions ($CO–O_2–MeOH–PdCl_2–CuCl_2$, 0 °C, 1 atm) affording methyl 2-methoxymethylacrylate in good yield; in the case of 1,1-disubstituted allenes the reaction is regiospecific although the product yields are lower.

The metal complex catalysed hydroesterification of unsaturated substrates by carbon monoxide and alcohol is an industrially important reaction.[1] When applied to allene,[2] this reaction gives different results depending on the metal catalyst used. In 1959, a patent by Jenner and Lindsey[3] claimed that the use of chloroplatinic acid and tin chloride catalyses the conversion of allene into methyl methacrylate in 40% yield [equation (1)]. The same product was obtained in 50% yield using a ruthenium carbonyl complex at 140 °C and 700—900 atm,[4] and in up to 62% yield with a nickel carbonyl complex and methacrylic acid as the co-catalyst (23—24 atm, 140 °C).[5] A poor yield of diethyl itaconate was obtained when palladium chloride was employed as the catalyst and ethanol as the alcohol (150 °C, 100 atm).[6] All of these reactions occur under drastic conditions. The hydroesterification (and hydrocarboxylation) of olefins can be achieved in high yield, in a regiospecific manner, and under exceptionally mild conditions (room temp., 1 atm), by oxidative carbonylation with palladium and copper(II) chloride under acidic conditions [equation (2)].[7,8] It was of interest to learn whether allene, and several substituted allenes, would also react under such gentle conditions, and in a selective fashion. We now describe the results of this investigation.



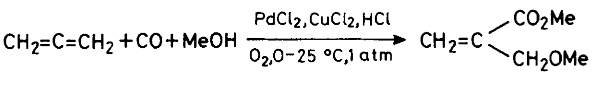
$$CH_2{=}C{=}CH_2 + CO + MeOH \xrightarrow[\text{SnCl}_2,\ 200\ ^\circ\text{C},\ 980\ \text{atm}]{\text{H}_2\text{PtCl}_6} CH_2{=}C(Me)CO_2Me \qquad (1)$$



$$RCH{=}CH_2 + CO + MeOH \xrightarrow[\text{O}_2,\text{room temp.},1\ \text{atm}]{\text{PdCl}_2,\ \text{CuCl}_2,\ \text{HCl}} RCH(Me)CO_2Me \qquad (2)$$

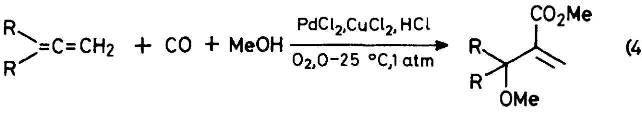
Treatment of allene with carbon monoxide, oxygen, palladium and copper(II) chloride, and hydrochloric acid in methanol afforded methyl 2-methoxymethylacrylate (**1**) in 85% yield [equation (3)]. This reaction occurs in an ice bath and is complete after 8—10 h. Compound (**1**) was identified by comparison of spectral results [i.r.(neat) ν_{CO} 1725, $\nu_{C=C}$ 1640 cm^{-1}; ^1H n.m.r. $\delta(CDCl_3)$ 3.35 (OCH_3), 3.70 (CO_2CH_3), 4.03 (CH_2O), 5.77, 6.18 ($CH_2{=}$); ^{13}C n.m.r. $\delta(CDCl_3)$ 51.85 (OCH_3), 58.54 (CO_2CH_3), 70.84 (CH_2O), 125.97 ($CH_2{=}$), 137.10 ($>C{=}$), 166.35 (CO_2CH_3); *m/z* 130 (M^+)] with literature data reported for (**1**).[9,10] Compound (**1**) has previously been synthesized in low yield by carbonylation of propargyl alcohol in methanol with $PdCl_2$ or palladium on carbon as catalysts (100 °C, 97 atm),[9] or by treatment of methyl 2-bromoethylacrylate with triphenylphosphine followed by reaction with sodium methoxide and propionaldehyde.[10] Methyl methacrylate is not an intermediate in the conversion of allene into (**1**) since, under identical reaction conditions to those described for allene, it is inert.

The disubstituted allenes, 3-methylbuta-1,2-diene (**2**,R=Me) and vinylidenecyclohexane (**2**,R,R=$[CH_2]_5$), underwent



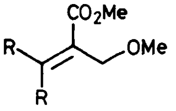
$$CH_2{=}C{=}CH_2 + CO + MeOH \xrightarrow[\text{O}_2,0\text{–}25\ ^\circ\text{C},1\ \text{atm}]{\text{PdCl}_2,\text{CuCl}_2,\text{HCl}} CH_2{=}C(CO_2Me)CH_2OMe \qquad (3)$$

(1)

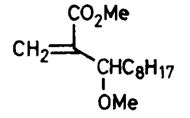


(4)

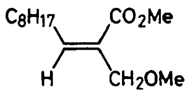
(2) **(3)**



(4)



(5)



(6)

hydroesterification in a similar manner to allene giving the methoxy unsaturated esters (**3**,R=Me, R,R=[CH_2]$_5$)† with the methoxy group becoming attached to the most substituted terminal carbon of the allene unit [equation (4)]. While the yields of pure products were not high (**3**,R=Me, 19%; R,R= [CH_2]$_5$,46%) the reaction is a regiospecific one. None of the isomeric compound (**4**) was detected in these reactions.‡ In the case of the monosubstituted allene, undeca-1,2-diene, the isomeric alkoxyesters (**5**) and (**6**) were found in a 4 : 3 ratio as determined by n.m.r. spectroscopy.

The following general procedure was used: carbon monixde and oxygen were slowly bubbled through an ice-cold solution of methanol (60 ml). Palladium chloride (0.178 g, 1.00 mmol) was added, followed by conc. HCl (1 ml), copper(II) chloride (1.07 g, 8.00 mmol), and then the allene (10—30 mmol). The reaction was stirred at ice-bath temperature for 4—6 h (except for vinylidenecyclohexane which was an overnight reaction). Work-up consisted of hexane extraction, drying, and distillation (or rotary evaporation, followed by treatment with carbon tetrachloride).

In conclusion, allene and several substituted allenes undergo hydroesterification, under remarkably mild conditions, to give alkoxy esters. The latter, particularly (**1**) are of considerable industrial potential.

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† Compound (**3**, R=Me); i.r.(neat) ν_{CO} 1724, $\nu_{C=C}$ 1640 cm^{-1}; ^{1}H n.m.r.($CDCl_3$) δ 1.38, 1.43 (R groups), 3.15 (OCH_3), 3.72 (CO_2CH_3), 5.70, 6.02 (CH_2=); *m/z* 158(M^+); (**3**, R,R=[CH_2]$_5$); ^{1}H n.m.r. ($CDCl_3$) δ 1.30—2.00 ([CH_2]$_5$), 3.09 (OCH_3), 3.70 (CO_2CH_3), 5.57, 5.93 (CH_2=); ^{13}C n.m.r. ($CDCl_3$) δ 21.62, 25.47, 33.21 ([CH_2]$_5$), 49.57 (OCH_3), 51.72 (CO_2CH_3), 77.10 (saturated quaternary carbon), 123.60 (CH_2=), 145.66 ($>$C=), 168.09 (CO_2CH_3); *m/z* 198(M^+).

‡ A by-product of these reactions is $R_2CHC(CO_2Me)=CH_2$.