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Ruthenium-catalyzed Regioselective Synthesis of Dienol Diesters

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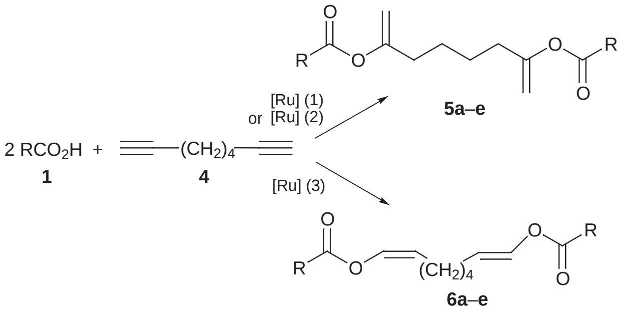
(Geminal, geminal) dienol diesters are obtained in one step by direct addition of carboxylic acids to terminal diynes in the presence of ruthenium catalysts such as $RuCl_2(PR_3)(arene)$ or $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ while the catalyst $[PPh_2(CH_2)_4PPh_2]Ru[\eta^3\text{-}CH_2{=}C(Me)CH_2]_2$ favours the formation of regioselective (*Z,Z*) dienol diesters.

Enol esters can be prepared by catalytic addition of carboxylic acids to terminal alkynes in the presence of a ruthenium phosphine catalyst of type $RuCl_2(PR_3)(arene)$.[1,2]

We report here, that binuclear ruthenium complexes containing bridging carboxylate ligands, of type $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$,[6,7] are efficient in activating octa-1,7-diyne towards regioselective addition of carboxylic acids to lead to (geminal, geminal) dienol diesters **5** (Scheme A).



Scheme A ([Ru](1):$RuCl_2(PPh_3)$(*p*-cymene), 100 °C, 15 h; [Ru](2):$[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$, 80 °C, 8 h; yields (%): R = H (81), Me (82), Ph (84), *Z*–$NHCH_2$ (82), Boc–NHCHMe (80), *Z*–NHCHMe (80); [Ru](3):$[Ph_2P(CH_2)_4PPh_2]Ru[\eta^3\text{-}CH_2{=}C(Me)CH_2]_2$, 60 °C, 4 h; yields (%): R = H (85), Me (92), Ph (88), *Z*–$NHCH_2$ (89), *Z*–NHCHMe (85).

The use of *N*-protected optically active amino acids, at 80 °C in toluene, afforded the corresponding dienol diesters in good yields (Table 1).

The catalytic addition of carboxylic acids with octa-1,7-diyne occurs at lower temperature (60 °C) in the presence of $[PPh_2(CH_2)_4PPh_2]Ru[\eta^3\text{-}CH_2{=}C(Me)CH_2)]_2$ containing diphosphine chelating ligands affording the corresponding (*Z,Z*) δ-dienol diesters **6** (Scheme A). Optically active dienol diesters were obtained, in good yields, from *N*-protected amino acids (Table 2).

Table 1 Ruthenium-catalyzed formation of (geminal, geminal) dienol diesters **5**[a]

Acid	Diester **5**	Mp or bp/°C	Yield (%)	$[\alpha]_D^{20}$ (*c* = 2, EtOH)
$PhCO_2H$	**5a**	Colourless liquid	84	—
HCO_2H	**5b**	Colourless liquid	81	—
$MeCO_2H$	**5c**	Colourless liquid	82	—
Z-Glycine	**5d**	White crystals mp 55–57	82	—
Z-(L)-Alanine	**5e**	Yellow oil	80	−38
BOC-(L)-Alanine	**5f**	Yellow crystals mp 61–63	80	−42

[a] *Reaction conditions*: carboxylic acid or *N*-protected amino acid (20 mmol); octa-1,7-diyne (10 mmol); toluene (20 ml); $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ (0.2 mmol).

Table 2 Ruthenium-catalyzed formation of (*Z,Z*)dienol diesters[a]

Acid	Diester **6**	Mp or bp/°C	Yield (%)	$[\alpha]_D^{20}$ (*c* = 2, EtOH)
$PhCO_2H$	**6a**	Colourless liquid bp 155 (2.5 mm Hg)	88	—
HCO_2H	**6b**	Colourless liquid bp 170 (2.5 mm Hg)	85	—
$MeCO_2H$	**6c**	White crystals; mp 84–86	92	—
Z-Glycine	**6d**	Yellow oil	89	—
Z-(L)-Alanine	**6e**	White crystals; mp 90–92	85	−45.3

[a] *Reaction conditions*: carboxylic acid or *N*-protected amino acid (20 mmol); octa-1,7-diyne (10 mmol); toluene (20 ml); $[Ph_2P(CH_2)_4PPh_2]Ru[\eta^3\text{-}CH_2{=}C(Me)CH_2]_2$ (0.2 mmol).

Techniques used: ^{1}NMR, IR, MS, microanalysis

Schemes: 5

References: 8

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