

General Synthesis of 2-Acyloxy-1,3-dienes in One Step from Carboxylic Acids and Butenyne Derivatives

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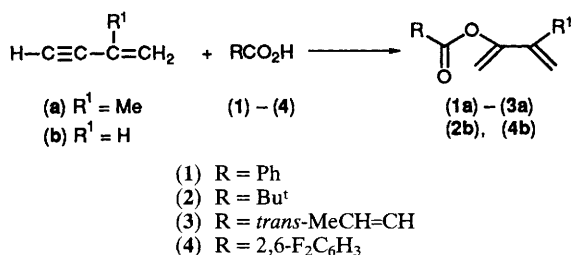
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2-Acyloxy-1,3-dienes are obtained by regioselective addition of carboxylic acids and *N*-protected amino acids to vinylacetylene derivatives, with (arene)(phosphine)ruthenium(II) complexes as catalysts.

Functional buta-1,3-diene derivatives have been shown to be valuable reagents in synthesis *via* Diels–Alder reactions: examples include 2-silyloxy-,¹ 2-morpholino-,² or 1-acyloxy-³ compounds. Whereas 1,3-dien-1-yl acetates can be prepared easily by reaction of isopropenyl acetate with α,β -unsaturated aldehydes or ketones and lead to Diels–Alder products,^{3,4} the access to 1,3-dien-2-yl carboxylates is not straightforward: they have been obtained from vinylacetylene and carboxylic acids in the presence of mercury salts but in very low yields due to polymerization.⁵

We report here a general method for the regioselective synthesis of 2-acyloxy-1,3-dienyl carboxylates from ruthenium–phosphine complex-catalysed addition of carboxylic acids and *N*-protected amino acids to the easily accessible 2-methylbutenyne (**a**) and vinylacetylene (**b**).⁶ It is based on our previous observation that carboxylic acids regioselectively add to prop-2-ynyl alcohol derivatives, in the presence of a ruthenium catalyst, to produce β -oxopropyl esters.⁷

The reaction of benzoic acid (1 equiv.) with a slight excess of the enyne (**a**) and $[\text{RuCl}_2(\text{PMe}_3)(p\text{-cymene})]^8$ (0.01 equiv.) in toluene at 80 °C for 24 h led to (**1a**). Gas chromatography of the crude product showed the presence of a small amount of its isomer $\text{PhCO}_2\text{CH}=\text{CHC}(\text{Me})=\text{CH}_2$, but distillation under reduced pressure (b.p. 24–26 °C, 13 mmHg), afforded pure (**1a**) in 84% yield† (Scheme 1). Similarly, the dienes (**2a**) (77%) and (**3a**) (76%) or (**2b**) (60%) and (**4b**) (70%)† were



Scheme 1. General conditions: the carboxylic acid (10 mmol), the enyne (**a**) or (**b**) (12 mmol), and the catalyst $[\text{RuCl}_2(\text{PMe}_3)(p\text{-cymene})]$, acid/catalyst = 100; toluene (10 ml) in an autoclave at 80 °C for 24 h. Yields are given in the text after reduced pressure distillation (10 mmHg).

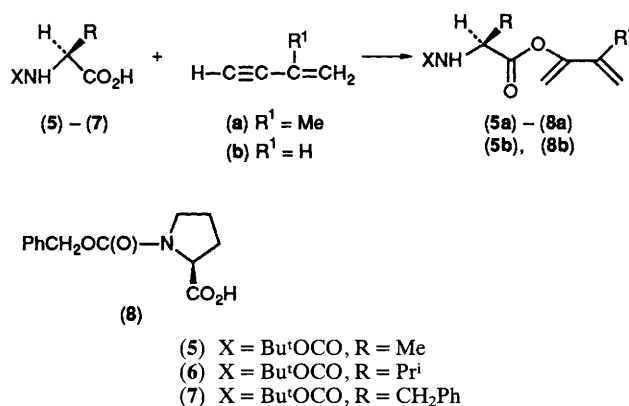
† Satisfactory elemental analyses and high resolution mass spectrum analyses were obtained for dienes (**1a**)–(**8b**). Selected spectroscopic data: (**1a**): ^1H NMR (CDCl_3 ; 80 MHz): δ 5.21 [s, $\text{OC}(\text{=CH}_2)$], 5.02 [s, $\text{Me-C}(\text{=CH}_2)$], and 2.00 (s, $\text{MeC}=\text{}$); IR (film): ν_{max} 1750 (C=O) and 1615 (C=C) cm^{-1} .

(**7a**): ^1H NMR (CDCl_3 ; 80 MHz): δ 4.96 (m, 5H, $2\text{CH}_2=\text{CHNH}$), 3.14 (d, PhCH_2CH , $^3J_{\text{HH}}$ 5.12 Hz), 1.90 [s, $\text{MeC}(\text{=CH}_2)$], and 1.41 (s, Me_3C); IR (film): ν_{max} 1750 (CO amide), 1715 (CO ester), and 1610 (C=C) cm^{-1} .

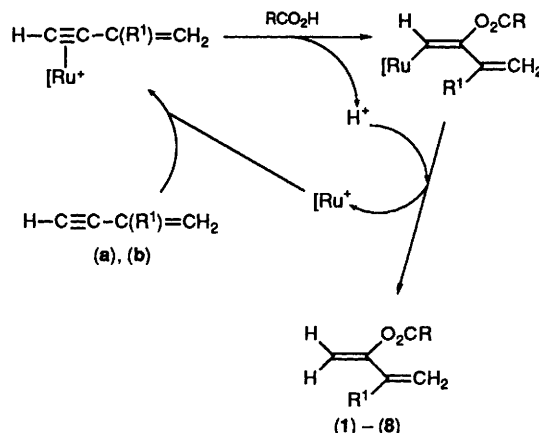
(**9**): ^1H NMR (CDCl_3 ; 80 MHz): δ 8.08 (m, 2H, Ph), 7.55 (m, 3H, Ph), 3.49 (m, 2H, CHCH), 2.71 (m, 4H, CH_2CH), and 1.70 (s, $\text{MeC}=\text{}$); IR (KBr): ν_{max} 1800 (CO anhydride) and 1750 (CO ester) cm^{-1} .

isolated, respectively from the butenyne (**a**) and (**b**), in their pure form after distillation.

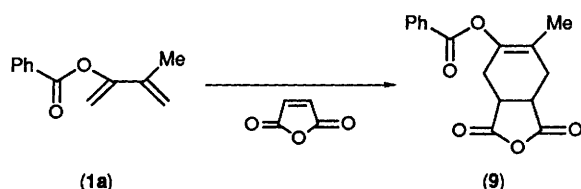
The reaction cannot be extended directly to amino acids. However, *N*-protected amino acids (**5**)–(**8**) regioselectively add in the presence of $[\text{RuCl}_2(\text{PMe}_3)(p\text{-cymene})]$ (0.01 equiv.) to butenyne derivatives (**a**) for 24 h and (**b**) for 15 h at 80 °C. Thus the optically active esters (**5a**) (65%), (**6a**) (68%), (**7a**) (64%), (**8a**) (87%), (**5b**) (62%), and (**8b**) (58%)† were isolated. It is noteworthy that the catalytic reaction proceeds without significant racemization of the amino acid derivatives, for hydrolysis in aqueous HCl (1 M) at 25 °C of (**7a**) $\{[\alpha]_{\text{D}}^{20} -40^\circ$ (c 1, EtOH) $\}$, obtained from the pure, optically active amino acid (**7**) $\{[\alpha]_{\text{D}}^{20} +20 \pm 2^\circ$ (c 1, EtOH) $\}$ affords compound (**7**) with $[\alpha]_{\text{D}}^{20} +18 \pm 2^\circ$ (c, 1, EtOH).



Scheme 2. General conditions: the *N*-protected amino acid (10 mmol), the enyne (**a**) or (**b**) (12 mmol), and the catalyst $[\text{RuCl}_2(\text{PMe}_3)(p\text{-cymene})]$ acid/catalyst = 100; in toluene (10 ml) in an autoclave at 80 °C for 24 h for (**a**) and for 15 h for (**b**). The dienes were purified on a silica gel column [(**8a**) and (**8b**)] or by crystallization from ether–hexane (1:5) [(**5a**), (**6a**), and (**7a**)].



Scheme 3



Scheme 4. Conditions: tetrahydrofuran, 60 °C.

The derivatives (1b)—(8b) of vinylacetylene polymerize in a few hours at room temperature whereas the esters (1a)—(8a) are more stable and polymerize at 25 °C only after a few days. However, all the diene derivatives of types (a) and (b) can be stored in dichloromethane solution at −20 °C at least for one month without polymerization.

Complexes of type $[\text{RuCl}_2(\text{PR}_3)(\text{arene})]$, especially those containing the basic PMe_3 ligand, appear to give the best yield and the highest selectivity for formation of 2-dienyl esters. The mechanism of the reaction may involve the activation, towards the carboxylate, of the ruthenium η^2 -co-ordinated alkyne bond, the addition of the carboxylate group at the C(2), rather than the C(1) alkyne, carbon atom being favoured by electron-releasing phosphine ligands (Scheme 3).

The functional diene (1a) in tetrahydrofuran reacts with maleic anhydride at 60 °C and gives after 24 h a 60% yield of the cycloaddition product (9). The transformation (1) \rightarrow (1a)

\rightarrow (9) can be achieved in one flask. When 1.5 equiv. of maleic anhydride was added to the catalytic mixture of PhCO_2H , isopropenylacetylene, and 0.01 equiv. of the ruthenium catalyst in toluene, after 24 h at 80 °C compound (9) was isolated in 40% yield (Scheme 4).

This preliminary study shows that the one-step regioselective synthesis of 2-acyloxy-1,3-dienes is general and has potential for the access to Diels-Alder reaction products.

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