Ruthenium Complex-catalysed Highly Selective Codimerisation of Acetylenes and Alkenes

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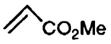
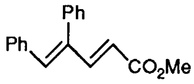
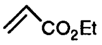
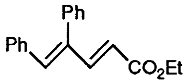
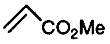
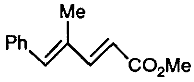
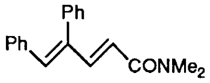
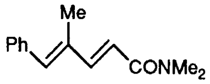
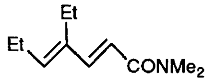
2,4-Dienes are prepared in high yields with high regioselectivity by the codimerisation of acetylenes and alkenes in the presence of a catalytic amount of Ru(cod)(cot) at 80 °C; cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5,-triene.

Recently, ruthenium complex-catalysed carbon–carbon bond forming reactions have been developed.[1] We have reported the efficient [2 + 2] cross-cycloaddition of acetylenes and norbornene catalysed by $RuH_2(PBu_3)_4$ or Ru(cod)(cot)–PBu_3[2] and the linear codimerisation of terminal acetylenes and 1,3-dienes catalysed by trialkylphosphine ruthenium complexes.[3] We now report the selective linear codimerisation in the presence of a catalyst of acetylenes and alkenes with an electron-attracting group to give 2,4-dienes in high yields (Scheme 1). A representative procedure is as follows; to a mixture of Ru(cod)(cot) (0.2 mmol) and diphenylacetylene (5 mmol) under argon was added pyridine (20 mmol) and methyl acrylate (10 mmol). The mixture was stirred at 80 °C for 10 h. Kugelrohr distillation afforded 1.7 g (86%) of methyl (2*E*,4*Z*)-4,5-diphenylpenta-2,4-dienoate. This stereochemistry of the alkene was determined by means of nuclear Overhauser effect experiments for H^b on irradiating H^c (for the position of the proton, see Scheme 1).

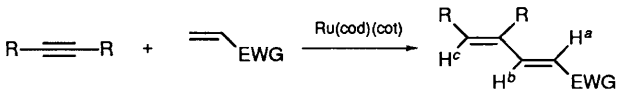
Representative results are shown in Table 1. The reaction of diphenylacetylene with ethyl acrylate gave ethyl (2*E*,4*Z*)-4,5-diphenylpenta-2,4-dienoate in 93% yield. Ru(cod)(cot) is the best catalyst in this reaction. $Ru_3(CO)_{12}$ and $RuCl_3{\cdot}3H_2O$ in pyridine showed no catalytic activity. The best yield was obtained in pyridine, while in triethylamine, toluene and tri-n-butylamine as solvent, the yields were low.

In the reaction of diphenylacetylene with *N*,*N*-dimethyl-

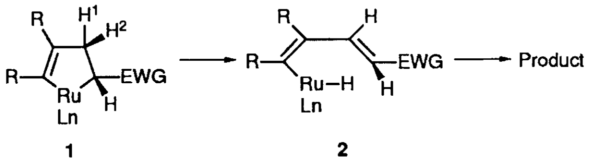
Table 1 Ru(cod)(cot)-catalysed codimerisation of acetylenes and alkenes[a]

Run	Acetylene	Alkene	Conditions[b]	Reaction time / h	Product	Yield / %
1	PhC≡CPh		A	20		87
2	PhC≡CPh		A	20		93
3	PhC≡CMe		A	20		15[c]
4	PhC≡CPh		B	0.25		81
5	PhC≡CMe		B	1		87
6	EtC≡CEt		B	9		54
7	$Bu^tC≡CH$		B	9		25

[a] Alkene (10 mmol), acetylene (5 mmol); Ru(cod)(cot) (cod = cycloocta-1,5-diene; cot = cycloocta-1,3,5-triene; 0.2 mmol), 80 °C under Ar. [b] A: pyridine (20 mmol); B: Alkene (10–20 mmol), without solvent. [c] Determined by GLC.



Scheme 1 EWG = electron-withdrawing group



Scheme 2

acrylamide, however, pyridine was not necessary. This reaction proceeded without solvent; in pyridine the yield was very low (7%). Methylphenylacetylene reacted with methyl acrylate to give the corresponding product in poor yield (7%), but it reacted with *N,N*-dimethylacrylamide to afford (2*E*,4*Z*)-*N,N*-dimethyl-4-methyl-5-phenylpenta-2,4-dienamide in 87% yield with complete regioselectivity. Diethylacetylene did not react with methyl acrylate, while it reacted with *N,N*-dimethylacrylamide to give *N,N*-dimethyl-(2*E*,4*E*)-4-ethylhepta-2,4-dienamide in 54% yield.

These results indicate that the Ru(cod)(cot)-catalysed codimerisation of acetylenes and alkenes is strongly affected by the solvent, ligand and the substituents on the acetylenes or alkenes.

Taking into account the mechanism of the [2 + 2] cycloaddition of norbornenes and dimethyl acetylenedicarboxylate, which is rationalised to proceed *via* a ruthenacyclopentene complex,[2] one of the plausible mechanisms is as follows.

Coordination of an acetylene and an alkene to a zero-valent ruthenium complex may give a ruthenacyclopentene complex **1** followed by the β-elimination of the β-hydrogen H^1 or H^2 **2** and successive reductive elimination would give the product (Scheme 2).†

Although several linear cooligomerisations of alkenes and acetylenes are known,[4] to our knowledge, this is the first example of an efficient catalytic linear codimerisation of acetylenes and alkenes to produce conjugated dienes.

This work was supported in part by a Grant-in-Aid for Scientific Research No. 02650625 from the Japanese Ministry of Education, Science and Culture.

Received, 2nd January 1991; Com. 1/00016K

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† The following two mechanisms cannot be ruled out completely. (i) Successive insertion of acetylene and alkene into a ruthenium–hydride bond followed by β-elimination. (ii) Oxidative addition of the sp^2 C–H bond of the alkene to ruthenium(0) complex followed by the insertion of acetylene and reductive elimination.