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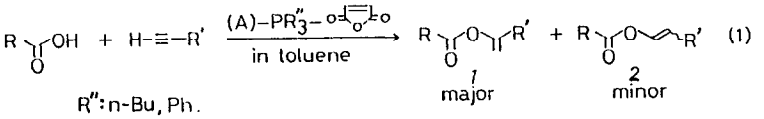
RUTHENIUM COMPLEX CATALYZED SELECTIVE ADDITION OF CARBOXYLIC ACIDS TO ACETYLENES GIVING ENOL ESTERS

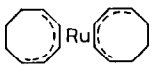
Take-aki Mitsudo,* Yoji Hori, Yasushi Yamakawa, and Yoshihisa Watanabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Summary : Carboxylic acids react with acetylenes in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium-PR_3-maleic anhydride in toluene to give enol esters in good to excellent yields with high regioselectivity.

Enol esters have proven to be valuable intermediates.[1] Addition of carboxylic acids to alkynes is a useful method for preparing enol carboxylates.[2,3] Recently, we have reported a novel selective addition of α,β-unsaturated carboxylic acids and benzoic acid to terminal acetylenes catalyzed by bis(η^5-cyclooctadienyl)ruthenium (A)/P(n-Bu)$_3$.[3] However, saturated acids such as acetic acid and propanoic acid did not react with acetylenes at all by the catalytic system.

We succeeded in the addition of saturated carboxylic acids to acetylenes by modifying the catalytic system by adding a catalytic amount of maleic anhydride (eq. 1), the results of which we now report.





(A)

In a typical procedure, a mixture of n-octadecanoic acid (stearic acid) (2.85 g, 10 mmol), 3,3-dimethyl-1-butyne (0.82 g, 10 mmol), the complex (A) (0.032 g, 0.1 mmol), tri-n-butylphosphine (0.040 g, 0.2 mmol), maleic anhydride (0.020 g, 0.2 mmol), and toluene (5.0 ml) was heated in a heavy-walled sealed tube at 80 °C for 4 h. Careful vacuum distillation of the reaction mixture afforded 3.24 g (yield 88 %) of 3,3-dimethyl-1-buten-2-yl octadecanoate (run 8). All products were characterized spectroscopically and satisfactory analytical data were obtained.

In the presence of a catalytic amount of the complex (A) / PR_3 / maleic anhydride, the addition of saturated carboxylic acids to acetylenes gave the corresponding enol esters in 76-99 % yields with high regioselectivity for the major product (eq. 1); Table, (runs 1-8). Alkyl substituents on the α-carbon of the carboxylic acids had no effect on the yields and the selectivities (runs 2-8). To elucidate the effect of the functional groups, such as carbonyl, hydroxy, and N-acetyl groups on the reactivity of the carboxylic acid, the runs 10-

Table Addition of Carboxylic Acids to Acetylenes[a)]

$$RCOOH + HC{\equiv}C\text{-}R' \longrightarrow \underset{1}{RCOO\text{-}\overset{\overset{CH_2}{\|}}{C}\text{-}R'} + \underset{2}{RCOOCH{=}CH\text{-}R'}$$

run	R	R'	y_1[b)]	y_2[b)]	run	R	R'	y_1	y_2
1	Me	n-Bu	(99)	[1]	9[c)]	Me	Ph	52	[16]
2	Et	n-Bu	72	[2]	10[d)]	PhCO	n-Bu	(88)	[11]
3	i-Pr	n-Bu	77	[3]				59	
4	t-Bu	n-Bu	69	[7]	11[e)]	PhCH(OH)	n-Bu	(77)	[10]
5	1-adamantyl	n-Bu	(91) 80	[2]	12[f)]	$CH_3COCH_2CH_2$	n-Bu	(60)	[4]
6	cyclohexyl	n-Bu	84	[4]	13[g)]	$CH_3CONHCHCH_3$	n-Bu	31	[4]
7	benzyl	n-Bu	80	[2]					
8	n-$C_{17}H_{35}$	t-Bu	88	[1]					

a) Acid, 10 mmol; Acetylene, 10 mmol; [Ru](A), 0.1 mmol; PBu_3, 0.2 mmol; Maleic anhydride, 0.2 mmol; Solvent, Toluene, 5.0 ml; 80°C, 4h. b) Isolated yield. G.L.C. yield for the major and the minor product were given in ( ) and [ ] respectively. c) AcOH, 5.0 ml without a solvent; 12h. d) PPh_3, 0.2 mmol; 8h. e) Solvent, DME, 5.0 ml; [Ru](A), 0.2 mmol; PPh_3, 0.4 mmol; 4h. f) 8h. g) Solvent, DME, 5.0 ml; [Ru](A), 0.2 mmol; 24h.

13 were performed. These acids also gave satisfactory results when an appropriate phosphine ligand and solvent such as dimethoxyethane (DME) were selected. In contrast, in the absence of maleic anhydride, the reactions of saturated acids did not occur and the starting materials were recovered. In the addition reaction of α,β-unsaturated acids and benzoic acid to terminal acetylenes,[3)] maleic anhydride is not required ; α,β-unsaturated carboxylic acids and benzoic acid play a role of π-acid ligand by themselves. These results reveal that the ruthenium complex catalyzes the addition reaction of various carboxylic acids to acetylenes in the presence of a catalytic amount of a tertiary phosphine and an electron deficient olefin. Thus the ruthenium complex catalyzed novel selective synthesis of enol esters has been established.

Studies on the scope and mechanism of the present reaction are now in progress.

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