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NOVEL VINYL KETONE - ACETYLENE CROSS-COUPLING CATALYZED BY $RhCl(PMe_3)_3$

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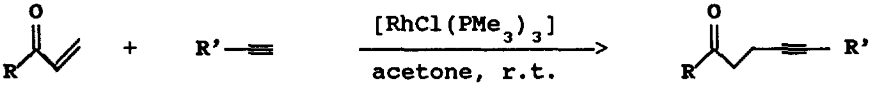
Abstract: $RhCl(PMe_3)_3$ is an effective catalyst of cross-coupling of vinyl ketones with terminal acetylenes to form γ,δ-acetylenic ketones.

We previously reported that $RhCl(PMe_3)_3$ is a selective catalyst of dimerization of vinyl ketones into 1,5-diketones [1,2] and 1-alkynes into conjugated enynes [3]. Cross-condensation of terminal acetylenes with methyl 2,3-pentadienoate in the presence of palladium (II) compounds has been recently reported [4]. In this paper we describe preliminary results of cross-coupling of vinyl ketones with terminal alkynes in the presence of the rhodium (I) trimethylphosphine complex.



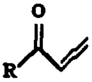
1 2 3a-e

a-(R=Me,R'=n-Pr), b-(R=Me,R'=n-He),
c-(R=Me,R'=Ph), d-(R=Me,R'=n-Bu),
e-(R=cyclopropyl,R'=n-Bu)

Exposure of an equimolar mixture of vinyl ketone 1 and alkyne 2 in the presence of 1% mol $RhCl(PMe_3)_3$ [5] in acetone at room temperature gave γ,δ-acetylenic ketone 3 with high selectivity.

Typical procedure. 0.75 g (10.7 mmol) of methyl vinyl ketone (MVK) and 1.18 g (10.7 mmol) of 1-octyne were added to 0.047 g (0.107 mmol) of $RhCl(PMe_3)_3$ in 3 ml acetone under argon atmosphere. This mixture was stirred at room temperature for 48 h. Unconverted MVK, 1-octyne and solvent were removed in vacuo and distillation at c.a. 10^{-3}mm Hg gave 0.902 g of 5-dodecyn-2-one 3b[6]. Other alkynones were prepared similarly. Results are given in the Table. All synthesized compounds have been fully characterized by IR, ^1H, ^{13}C NMR and mass-spectroscopy.

Table. Synthesis of γ,δ-acetylenic ketones [a]

	$R'-\equiv$	Conversion, %		Product	Yield 3		
					%, to converted		mol/ mol Rh
		1	2		1	2	
R = Me	R'= n-Pr	58	64	3a	95	86	55
Me	n-He	50	51	3b	92	90	47
Me [b]	Ph	31	34	3c	91	89	28
Me [c]	n-Bu	97	100	3d	94	91	91
cyclo- [b] propyl	n-Bu	22	26	3e	92	87	20

[a] 10.7 mmol vinyl ketone, 10.7 mmol 1-alkyne, 0.107 mmol $RhCl(PMe_3)_3$, 3 ml acetone, room temperature, 48 h; [b] 96 h; [c] 108 h.

At higher temperature the rate of formation of 3 increases but selectivity of the reaction decreases due to a by-process of dehydrodimerization of alkynes. At 20°C dialkynes **4** are not practically formed.

$$2\ \underset{\mathbf{2}}{R'-\equiv} \xrightarrow[\text{acetone, } 80^{\circ}C,\ 5h]{[RhCl(PMe_3)_3]} \underset{\mathbf{4}}{R'-\equiv-\equiv-R'} \quad (40\text{-}50\%)$$

References and Notes

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6. 3b: b.p. 70-72°C/20 mm Hg; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7 Hz), 1.25-1.40 (8H, m), 2.11 (2H, tt, J = 7; 2.25 Hz), 2.17 (3H, s), 2.40 (2H, m), 2.63 (2H, m); ^{13}C NMR ($CDCl_3$) δ 13.33 (C-7), 13.88 (C-12), 18.53 (C-4), 22.42 (C-11), 28.37 (C-9), 28.81 (C-8), 29.71 (C-1), 31.22 (C-10), 42.86 (C-3), 78.25 (C-6), 80.75 (C-5), 206.86 (C-2); IR (neat): 2360 (C≡C), 1722 (C=O); MS, m/z 180 (M^+), 151, 122, 109, 95, 81, 67, 55, 43 (base).

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