DEHYDRODIMERIZATION OF VINYL KETONES CATALYZED BY THE $[RhCl(C_2H_4)_2]_2$–$SnCl_2$ SYSTEM

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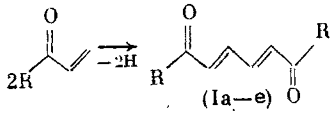
There have been reports of the catalytic dimerization [1] of vinyl ketones in the presence of transition metal complexes.

We have discovered a new catalytic reaction of vinyl ketones, namely, the dehydrodimerization of these compounds to form dienic 1,6-diketones (Ia)-(Ie).



R = Me (a), Ph (b), p-MeC_6H_4 (c), cyclopropyl (d), 5-methyl-2-furyl (e).

The reaction proceeds at 80°C in the presence of the 1:2 $[RhCl(C_2H_4)_2]_2$–$SnCl_2$ catalytic system and leads to the formation of (2E, 4E)-2,4-hexadiene-1,6-diones (Ia)-(Ie). The conversion of the vinyl ketones was 25-50%. The selectivity of the formation of dehydrodimers (Ib)-(Ie) δ was 55-85%, while the selectivity for the formation of (Ia) was only 30%.

A sample of 0.52 g (3.92 mmoles) 1-phenyl-2-propen-1-one was added to a mixture of 0.0038 g ($9.8\cdot10^{-3}$ mmole) $[RhCl(C_2H_4)_2]_2$ and 0.00444 g ($2\cdot10^{-2}$ mmole) $SnCl_2\cdot2H_2O$ in 3 ml acetone and the solution obtained was heated in a glass ampul for 10 h at 80°C. Workup of the reaction mixture gave 0.21 g (Ib). The yield of this product was 85% relative to the vinyl ketone consumed (42 moles/g-atom Rh) and the vinyl ketone conversion was 49%, mp 180-181°C [3].

Dehydrodimers (Ia)-(Ie) were isolated and characterized by PMR, ^{13}C NMR, and IR spectroscopy.

This reaction is the first example of the catalytic dehydrodimerization of α,β-unsaturated carbonyl compounds.

LITERATURE CITED

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