DIMERIZATION OF METHYL VINYL KETONE CATALYZED BY Rh(I) COMPLEXES

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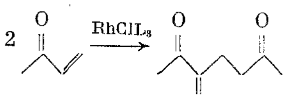
The catalytic dimerization of α,β-unsaturated carbonyl compounds is a promising method for the synthesis of various 1,5- and 1,6-difunctional products used for the preparation of polymers and heterocycles [1]. On the other hand, there is very little known on the dimerization of methyl vinyl ketone (MVK) despite its availability and common use in synthesis. The dimerization of MVK to 3-methylene-2,6-heptanedione (I) catalyzed by PPh_3 [2] or PPh_3 in conjunction with a salt of a transition metal such as Co, Ni, Fe and Mn [3] proceeds with 15-72% selectivity. The dimerization of MVK to diketone (I) is also observed as a side-reaction in the reaction of MVK with propionaldehyde catalyzed by $HRh(PPh_3)_4$ [4].

We have carried out the catalytic dimerization of MVK with high selectivity under mild conditions



(I)

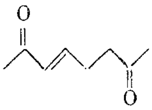
L = PMe_3.

$RhCl(PMe_3)_3$ is the active catalyst for the dimerization of MVK. The yield of diketone (I) relative to converted MVK in the dimerization catalyzed by this complex in acetone, 2-pentanone or propylene oxide, is 90-96%. We should note that the reaction proceeds in the absence of a reducing agent (H_2 or ROH), which is almost always necessary for the catalytic dimerization of acrylic monomers, leading to the partial or complete hydrogenation of the ethylenic bond of the dimer [5-7].

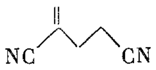
The data in Table 1 show that the nature of the ligands bound to Rh(I) has a significant effect on this reaction.

The high "head-to-tail" regioselectivity is retained upon replacing PMe_3 by PPh_3 but the activity of the catalyst drops considerably. In contrast to rhodium phosphine complexes, free PPh_3 has low efficiency as a catalyst for this reaction, while PMe_3 causes the predominant polymerization of MVK.

The use of $[RhCl(cyclooctene)_2]_2$ as the catalyst for the dimerization of MVK completely alters the regioselectivity to "tail-to-tail" with the formation of linear unsaturated dimer (II) (no other isomer was detected). However, this reaction is significantly complicated by the polymerization of MVK.



(II)



(III)

As in the case of MVK, a "head-to-tail" dimer (III) is formed regioselectively in the dimerization of acrylonitrile catalyzed by $RhCl(PMe_3)_3$ but the rate of this reaction is several times less. The formation of dimers from acrylonitrile in the presence of the Rh(I) cyclooctene complex as well as from methyl acrylate in the presence of both catalysts does not occur under the conditions studied.

Thus, MVK dimerizes much more readily than acrylonitrile and methyl acrylate in the presence of Rh(I) complexes. The direction of the dimerization ("head-to-tail" or "tail-to-tail")

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TABLE 1. Catalytic Dimerization of Methyl Vinyl Ketone[a]

Catalyst	Solvent	MVK conversion, %	Yield of dimer (I)	
			rel. to converted MVK, %	mole/g,atom Rh
$RhCl(PMe_3)_3$	Acetone	42	89	20
Same	2-Pentanone	37	96	18
»	Propylene oxide	32	88	16
»	Toluene	57	53	15
»	Acetonitrile	18	41	4
$RhCl(PPh_3)_3$	Acetone	5	—	2
$[RhCl(C_8H_{14})_2]_2$	Acetone	26	12	2 [b]
PPh_3	Acetone	9	27	1
$RhCl(PMe_3)_3$	Toluene	3	—	1 [c]
Same	Acetone	18	95	9 [c,d]
»	Acetone	67	90	28 [e]

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[a] 0.7 g (10 mmoles MVK, 0.1 mmole catalyst, 3 ml solvent at 60°C for 5 h.

[b] The dimerization product was diketone (II).

[c] Acrylonitrile was the starting unsaturated compound. The yields of dinitrile (III) are given.

[d] At 80°C.

[e] The reaction time was 10 h.

is a function of the ligands attached to the metal.

EXPERIMENTAL

The PMR spectra were taken on Bruker WM-250 and Tesla BS-467 spectrometers in $CDCl_3$ with TMS as the internal standard. The IR spectra were taken on a Specord M-80 spectrometer. The gas–liquid chromatographic analysis was carried out on an LKhM-8MD(5) spectrometer with flame ionization detector on a 300 × 0.3 cm column packed with 5% E-301 on Inertone N-AW with 30 cm^3 nitrogen gas carrier flow rate.

All the operation were carried out in an argon atmosphere. The solvents and starting reagents were dried and degassed. $RHCl(PMe_3)_3$ [8], $RhCl(PPh_3)_3$ [9] and $[RhCl(C_8H_{14})_2]_2$ [10] were obtained according to reported procedures.

Dimerization of Methyl Vinyl Ketone. A sample of 0.037 (0.1 mmole) $RhCl(PMe_3)_3$, 0.7 g (10 mmoles) MVK and 3 ml acetone were placed in a glass ampul. The mixture obtained was heated in the sealed ampul for 5 h at 60°C. Unreacted MVK and acetone were distilled off. The residue was extracted with ether and the extract was evaporated to give 0.25 g 3-methylene-2,6-heptanedione (I), bp 105-107°C (17 mm). PMR spectrum (δ, ppm): 2.15 s, 2.36 s (2 CH_3), 2.58 s (2 CH_2), 5.85 s (CH=C), 6.05 s (CH=C). IR spectrum (ν, cm^{-1}): 1632 (C=C), 1680 (C=O), 1715 (C=O).

The other experiments were run analogously. The results obtained are given in Table 1.

trans-3-Octene-2,7-dione (II). PMR spectrum (δ, ppm): 2.17 s, 2.22 s (2 CH_3), 2.48 m, 2.61 m (2 CH_2), 6.07 d. t (CH=C, J_1 = 1.625, J_2 = 1.6 Hz), 6.79 d. t (CH=C, J_1 = 16.25, J_2 = 6.75 Hz). IR spectrum (ν, cm^{-1}): 1630 (C=C), 1675 (C=O), 1718 (C=O).

Dinitrile of 2-Methyleneglutaric acid (III). PMR spectrum (δ, ppm): 2.65 s (2 CH_2), 5.95 s (CH=C), 6.05 s (CH=C). IR spectrum (ν, cm^{-1}): 1625 (C=C), 2245 (C≡N), 2265 (C≡N).

CONCLUSION

1. Methyl vinyl ketone was dimerized with catalysis by Rh(I) phosphine complexes.

2. The dimerization of methyl ketone catalyzed by $RhCl(PMe_3)_3$ proceeds regioselectively by "head-to-tail" addition, while the corresponding dimerization catalyzed by $[RhCl(C_8H_{14})_2]_2$ proceeds by "tail-to-tail" addition with the formation of 3-methylene-2,6-heptanedione and 3-octene-2,7-dione, respectively.

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ADDITION OF 1,1,1-TRICHLOROALKANES TO VINYLTRIMETHYLSILANE IN THE PRESENCE OF $Fe(CO)_5$ SYSTEMS

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The addition of polychloromethanes to vinyltrimethylsilane (VTMS) with initiation by a system containing $Fe(CO)_5$ and a nucleophilic coinitiator (NC) [1] or complex $(R_3SiCH{=}CH_2)\cdot Fe(CO)_4$ [2] is a method for the preparation of polychloroalkyltrimethylsilanes.

In order to prepare polychloroalkyltrimethylsilanes with an alkyl group longer than three carbon atoms, we studied the previously uninvestigated reaction of 1,1,1-trichloroethane (TCE) and 1,1,1,3-tetrachloropropane (TCP) with VTMS in the presence of $Fe(CO)_5$ in conjunction with NC such as Ph_3P, DMF, HMPTA, and 2-propanol. The reaction proceeds according to the following scheme:

$$RCCl_3 + CH_2{=}CHSiMe_3 \xrightarrow[HC]{Fe(CO)_5} \underset{(I),(II)}{RCCl_2CH_2CHClSiMe_3} \qquad (1)$$

R = Me (I), CH_2CH_2Cl (II).

The reaction of TCE with VTMS using $Fe(CO)_5$ in conjunction with Ph_3P, DMF or HMPTA gives adduct (I) in high yields (Table 2, experiments 1-3). The maximum yield was obtained with $Fe(CO)_5 + Ph_3P$ at 105°C (experiment 1). The use of 2-propanol instead of Ph_3P at this temperature leads to a decrease in the yield of (I) to 3%. An increase in the temperature leads to an improvement in the yield of (I) (experiment 4). Despite a twofold excess of the telogen, the telomer homolog with two monomer units, namely, $CH_3CCl_2(CH_2CHSiMe_3)_2Cl$ (T_2), is formed in 3-4% yield (experiments 1-4).

These systems also initiate the addition of TCP to VTMS at 130°C, i.e., at a higher temperature than in the case of TCE (experiments 6-9). In this case, the maximum yield was also obtained with the $Fe(CO)_5 + PPh_3$ system (experiment 6). In the absence of a nucleophilic coinitiator, $Fe(CO)_5$ virtually does not initiate the reaction (experiment 5). An increase in the reaction time or reaction temperature leads to a decrease in the yield of adduct (II) due to its dehydrochlorination. Thus, a special experiment shows that heating (II) with the $Fe(CO)_5 + PPh_3$ system in $(CHCl_2)_2$ at 150°C leads to the formation of a mixture of unsaturated compounds (III) and (IV) by the scheme:

$$(II) \xrightarrow[Ph_3P]{Fe(CO)_5} \underset{(III)}{ClCH_2CH{=}CClCH_2CHClSiMe_3} + \underset{(IV)}{ClCH_2CH_2CCl{=}CHCHClSiMe_3} \qquad (2)$$

The conversion of (II) over 1.5 h is 92% and the yield of isomers (III) and (IV) is 71%. The major product is (III) and the (III)/(IV) ratio ranges from 3.5 to 4.5 as indicated by

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