NEW CONVERSIONS OF SUBSTITUTED VINYLCYCLOPROPANES UNDER THE EFFECT OF COMPLEXES OF RHODIUM AND PALLADIUM

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Methods have been developed for the synthesis of the dimethyl ester of 1carboxysorbic acid, 2-methyl-3-acetyl-5-vinyl- and 2-methyl-3-ethylcarboxy-5-vinyldihydrofurans by isomerization, respectively, of 1,1-dimethylcarboxy-2-vinyl-, 1,1-diacetyl-2-vinyl-, and 1-acetyl-1-ethylcarboxy-2-vinylcyclopropanes under the effect of Rh- and Pd-containing catalysts promoted with AcOH or CF₃COOH.

Numerous examples of the thermal rearrangements of vinylcyclopropanes (VCPs) with formation of cyclopentenes are well known [1]. Under the effect of homogeneous metal complex catalysts the very simple VCPs undergo cyclopropylallyl isomerization [2, 3].

In this paper we investigate the isomerization of VCPs that contain two electronacceptor substituents, under the effect of complexes of Rh and Pd.

1,1-Di(methoxycarbonyl)-2-vinylcyclopropane (I) in the presence of Rh-containing catalytic systems undergoes isomerization with the formation of the dimethyl ester of dienic diacid (II).

 $\overset{H_{3}CO_{2}C}{\underset{(I)}{\overset{CO_{2}CH_{3}}{\xrightarrow{[Rh]}}}} \xrightarrow{CO_{2}CH_{3}}$

The yield of (II) is dependent on the valence state of the rhodium, the nature of the ligands, and the reaction conditions (Table 1). Thus, in the presence of catalyst prepared in situ in the system $Rh(acac)_3$ -AlEt_3-1,2-bis(diphenylphosphino)ethane (BPE), (II) was obtained with a yield to 80% and conversion of (I) of 74%. The isomerization of (I) to (II) occurs more selectively under the effect of the Wilkinson complex $Rh(PPh_3)_3C1$ in THF solution (experiments 6, 7). The activity of this complex increases sharply when catalytic quantities of AcOH or CF₃COOH are added to the system. At a [Rh]:acid mole ratio of 1:25, which is optimum, the reaction time is reduced to 10 minutes. It must be emphasized that CH_3COOH (or CF_3COOH) without additions of the rhodium complex do not catalyze isomerization of (I) to diene (II). The promoting action of the acids when complexes of Pd(0) are used is less pronounced (Table 2, experiments 14, 15). It turned out that the presence of even one acetyl group in the VCP molecule changes its properties and directs isomerization toward formation of dihydrofuran derivatives (V) and (VI)



1,1-Diacetylcyclopropane (VII) isomerizes by an analogous scheme

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No.	Catalytic system	ing	т, °С	Time, h	Solvent	ver- n of %	ld (II),	ld of ner gomers,
	• •	Pro mot: age				Conv sior (I)	Yie of %	Yie high %
1	$Rh(acac)_3 - BPE - AlEt_3$	-	100	10	Benzene	74	80	20
$\frac{2}{2}$	(1, 1, 5, 5) $Rh(acac)_3 - BPE - AlEt_3$ (1, 3, 5)	-	100	10	»	59	33	67
3	(1:3:5) Rh(acac) ₃ - PPh ₃ - AlEt ₃ (1:2:5)		100	20	*	75	25	75
4	Rh (PPh ₃) ₃ Cl	-	70	10	THF	60	100	0
5	× ×	()	80	10	•	75	· 100	0
6	»	-	80	20	»	100	100	0
7	»	-	100	10	.»	100	100	0
8	*	AcOH	100	1/6	»	100	100	0
9	*	»	80	1	×	100	100	0
-10	*	»	100	1/6)»	100	100	0
11	*) »	80	1	'»	100	100	0
12	$\begin{array}{c} \mathbf{Pd_2}(\mathbf{DBA})_{3}\mathbf{CHCl_3}:\mathbf{PPh_3} *\\ 1:1 \end{array}$	-	80	8	Benzene	21	100	0
13	»	-	100	10	×	53	[100	0
14	Pd(DBA) ₃ CHCl ₃ : PPh ₃	AcOH	100	10	×	88	93	7
	(1:1)				»	98	96	4
15	»		100	10	1			[
16	No catalyst	AcOH	100	1 10	»	0	-	-

TABLE 1. Catalytic Isomerization of (I) PPh₃[Rh] ([Pd]: acid = 1:25)

*DBA) dibenzylidene acetone.



1,1-(Dimethoxycarbonyl)cyclopropane (IX) is very resistant to the action of the catalyst $Rh(PPh_3)_3Cl-CH_3COOH$. Only under severe conditions (200°C, 4 h) and with an increase of the concentration of AcOH to concentrations stoichiometric to (IX) does the latter undergo the unusual conversion with the formation of cyclopropane, CO_2 , and methyl acetate

$$\bigcup_{\substack{\text{CO}_2\text{CH}_3\\\text{CO}_2\text{CH}_3\\\text{(IX)}}} \frac{[\text{Rh}]-2\text{CH}_3\text{CO}_2\text{H}}{200^\circ, 4\text{ h}, \text{ THF}} \xrightarrow{\text{CO}_2} + \xrightarrow{\text{CO}_2} + 2\text{CH}_3\text{OAc}$$

The structure of the synthesized compounds was demonstrated by comparison with samples of (V) and (VI) obtained by a different method [4], by the spectral data, and also by chemical conversions. Sorbic acid (XI) was obtained with a fotal yield of ~80% in two steps from diester (II).



EXPERIMENTAL

Monomers with 99% purity synthesized in accordance with [5] were used. The PMR spectra were recorded on a Tesla BS-497 instrument (180 MHz) in $CDCl_3$ relative to TMS; the IR spectra were recorded on a UR-20 instrument (film). The ¹³C NMR spectrum was recorded on a Jeol FX-90 instrument (22.5 MHz, TMS as standard). GLC was done on a Khrom-4 instrument with column 3.5 m × 3 mm, 15% SE-30 on Chromaton N-AW-HMDS, vaporizer temperature 300°C, column 50-350°C.

<u>Methoxycarbonyl-2,4-hexadienic Acid.</u> To a solution of 0.1 g (0.28 mmole) of $Rh(acac)_3$, 0.17 g (0.42 mmole) of BPE in 5 ml anhydrous benzene at 0°C in a stream of Ar was added by

drops to 0.16 g (1.4 mmoles) AlEt₃ and the mixture was stirred at this temperature for 0.5 h. Then the resulting solution was transferred to a steel microautoclave (V = 17 ml), which contained 5.1 g (28 mmoles) of (I) and the contents were heated for 10 h at 100°C. The cooled reaction mixture was treated with 2 ml ethanol, washed with water, the organic layer was filtered through 50 g Al₂O₃ and eluted with hexane. After evaporation of the solvent and distillation, 3.0 g of ester (II) was obtained, b.p. 65°C (2 mm), np²⁰ 1.4515, UV spectrum: λ_{max} 272 nm, $\varepsilon = 19,200$. IR spectrum (ν , cm⁻¹): 910, 930, 970, 1590, 1620, 1630, 1720, 3020. PMR spectrum (δ , ppm): 1.86 (3H, CH₃), 5.50-6.15 (3H, CH=CH), 3.90 (6H, OCH₃). ¹³C NMR spectrum (δ , ppm): 18.93 q (CH₃), 52.04 q (OCH₃), 122.56 s (C¹), 127.08 d (C⁵), 144.85 d (C⁴), 145.86 d (C³), 164.54 s (C¹). Mass spectrum: 184 (M⁺). The experiments with PPh₃ as activator and also with the complexes of Pd were carried out by an analogous technique.

Isomerization of (I) with Additions of Acids. In a steel autoclave (17 ml) in an Ar atmosphere was placed 0.086 g (0.1 mmole) $Rh(PPh_3)_3Cl$ in 5 ml anhydrous THF, 0.15 g (2.5 mmoles) AcOH (or 2.5 mmoles CF_3COOH), 4.6 g (25 mmoles) vinylcyclopropane (I) was added, and the mixture was heated for 10 minutes at 100°C. After cooling the THF was evaporated out and the residue was vacuum distilled. The product was 4.55 g (99%) of (II).

Isomerization of 1,1-diacetyl-2-vinylcyclopropane (III) under the effect of the catalytic system $Rh(PPh_3)_3Cl-AcOH$ (100°C, 1 h, THF) produced with ~100% yield 2-methyl-3-acetyl-5-vinyl-4,5-dihydrofuran (V), b.p. 70°C (1 mm), $n_D^{2^0}$ 1.5025 [4]. IR spectrum (v, cm⁻¹): 910, 990, 1705. PMR spectrum (δ , ppm): 2.6 (CH₃-CO), 2.15 (CH₃-C=), 2.66-3.03 (2H, C⁴, CH₂), 4.88 (1H, C⁵, CH), 5.11-5.90 (-CH=CH₂). ¹³C NMR spectrum (δ , ppm): 15.01 q (CH₃), 29.31 q (CH₃-CO), 37.66 t (C⁴), 82.69 d (C⁵), 111.89 s (C³), 116.85 t and 136.62 d (vinyl group), 167.70 s (C²), 194.72 s (C=O). Mass spectrum: 152 (M⁺).

Under the same conditions the substituted cyclopropane (IV) was converted with a yield of ~100% to 2-methyl-3-ethoxycarbonyl-5-vinyl-4,5-dihydrofuran (VI), b.p. 128°C (15 mm), nD²⁰ 1.4748 [4]. IR spectrum (v, cm⁻¹): 915, 990, 1720. PMR spectrum (δ , ppm): 1.21 (3H, CH₃-C-), 2.11 (3H, CH₃-C-), 2.33-3.00 (2H, C³H₂), 4.08 (2H, -CH₂-O), 4.56-6.10 (4H, -C⁵H-, -C⁵H

 $CH=CH_2$). Mass spectrum: 182 (M⁺).

2-Methyl-3-acetyl-4,5-dihydrofuran (VIII), b.p. $50^{\circ}C$ (1 mm), $n_D^{2^{\circ}}$ 1.4922 was obtained from 1,1-diacetylcyclopropane (VII) (100°C, 1 h, Rh:CH₃COOH = 1:25) with yield of ~100%. IR spectrum (v, cm⁻¹): 1720. PMR spectrum (δ , ppm): 2.01 (CH₃-CO), 1.95 (CH₃-C=), 2.48-2.86 (2H, C⁴H₂), 4.03-4.36 (2H, C⁵H₂). ¹³C NMR spectrum (δ , ppm): 15.01 q (CH₃), 29.31 q (CH₃-CO), 30.35 t (C⁴), 70.43 t (C⁵), 112.41 s (C³), 169.00 s (C²), 194.98 s (C=O). Mass spectrum: 126 (M⁺).

<u>The Reaction of 1,1-Di(methoxycarbonyl)cyclopropane (IX) with AcOH in the Presence</u> of an Rh Catalyst. A mixture containing 0.18 g (0.2 mmole) $Rh(PPh_3)_3Cl$, 6 g (50 mmoles) AcOH, 10 ml THF, and 7.8 g (50 mmoles) substituted cyclopropane (IX) was heated in a steel autoclave (100 ml) for 4 h at 200°C. The pressure in the autoclave rose to 25 atm. Cyclopropane, propylene, CO_2 , and methyl acetate were identified among the reaction products from the GLC and mass spectrometry data.

Synthesis of Sorbic Acid. After saponification of 4.5 g diester (II) with a solution of 9 g KOH in 20 g MeOH at ~25°C the resulting reaction mixture was poured into cold water, neutralized with 10% H₂SO₄, extracted with benzene (3 × 10 ml), dried under MgSO₄, and the solvent was evaporated out. The residue (3.75 g, 99%) without further purification was put into a round-bottom flask with reflux condenser, 50 ml pyridine was added and the mixture was heated until CO₂ ceased to evolve. After cooling, the reaction mixture was poured into a mixture of ice and 30% HCl, then extracted with ether and the solvent was evaporated out. The sample recrystallized from a benzene-ether (1:1) mixture melts at 133-134°C, does not give a melting point depression with pure sorbic acid and has spectral characteristics identical to it.

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REACTION OF CYCLIC KETONES WITH KOH-DMSO

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Upon reaction of cycloalkanones with a KOH-DMSO system 2-methylenecycloalkanols are formed, the yield (10-37%) of which decreases in the series: cyclohexanone > cycloheptanone > cyclooctanone > cyclododecanone.

It was shown [1-4] recently that the simple superbasic system KOH-DMSO can serve as a source of dimsyl anions for obtaining allyl alcohols from ketones by the sequence



In spite of moderate yields of allyl alcohols (XI)-(XV) (<40%), this reaction has obvious advantages over the known four-step method of obtaining allyl alcohols from ketones [5-7], based on the use of less accessible reagents (phenylsulfinylmethyllithium, trimethylsilylimidazole, lithium diisopropylamide, KH).

The goal of this work was to explore the possibility of using the above reaction for preparative synthesis of allyl alcohols and sulfoxides from cyclic and macrocyclic ketones, and especially the influence of ketone ring size on product yield. In the investigation the following ketones were used: cyclopentanone (I), cyclohexanone (II), 4-methylcyclohexanone (III), cycloheptanone (IV), cyclooctanone (V), and cyclododecanone (VI). It turned out (see Table 1) that with increase of the starting ketone ring size, beginning with cycloheptanone, the yield of the corresponding allyl alcohol decreases and in order to maintain it within 10-30% it is necessary to increase the relative amount of alkali and the reaction time. For example, under comparable conditions (110°C, starting ketone concentration: 0.5-0.6 mole/liter, KOH: 1.0-1.5 mole/liter) after 1 h the following amounts of ketones are found in the reaction mixture (GLC) (%): (II) traces, (IV) 46, (V) 67. The content of ketone (V) in the reaction mixture changes with time as follows: after 2 h 58%, after 4 h 50%. Apparently, addition of dimsyl anion to the carbonyl group is very sensitive to steric effects as is also the competing aldol condensation. From a preparative point of view, the best balance in favor of the first process is observed with six- and sevenmembered cyclic ketones.

In the case of cyclopentanone (I) no 2-methylenecyclopentanol was observed in the reaction products. Instead a fraction was obtained (bp 98-101°C at 1 mm Hg), consisting mainly of 2-cyclopentylidenecyclopentanone (XVI) (IR, PMR) - the product of aldol condensation.

Kinetic experiments (Fig. 1) confirm the participation of ketones (II) and (IV) in a competing process. The rate of their disappearance [curves (II) and (IV)] exceeds significantly the formation rate of allyl alcohols (XI) and (XV). The concentration increase of the latter over 40-50 min stops at 35-40% of the theoretical value.

Curves a and b, constructed from the difference between the initial concentration of starting ketones (II) and (IV) (100%) and the sum of the current concentrations of these

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