[2+2+2] Cycloaddition reaction with the participation of unsaturated ketones catalyzed by an Rh(I)-Sn(II) system

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Codimerization of vinyl ketones with metallylacetone or metallylacetophenone in the presence of $[RhCl(C_2H_4)_2]_2$ —SnCl₂ affords substituted *endo*-2-acyl-8-oxabicyclo[3.2.1]octanes, the products of the formal [2+2+2] cycloaddition.

Key words: cycloaddition, codimerization, unsaturated ketones, rhodium catalyst.

Complex compounds of Rh(1) catalyze a wide range of reactions of the formation of a carbon—carbon bond proceeding with the participation of unsaturated compounds.¹ Thus, for example, the $[RhCl(C_2H_4)_2]_2$ —SnCl₂ system catalyzes the codimerization between allylacetone and vinyl ketones in the course of which only C=C bonds of vinyl ketones undergo changes.² As a result, unsaturated linear 1,7- and branched 1,5-diketones are formed.

We established that when the methyl substituent is introduced at the γ position of allylacetone, the direction of the codimerization reaction principally changes. Thus, the reaction of vinyl ketones (1) with metallylacetone (2, R² = Me) affords monoketones, the derivatives of 8-oxabicyclo[3.2.1]octane (3). The reaction of metallylacetophenone 2 (R² = Ph) with 1 proceeds in a similar manner.

Scheme 1



This reaction can be formally considered as [2+2+2] cycloaddition with the participation of the carbonyl group of compound 2 and two C=C bonds of compounds 1 and 2. Unlike reactions discussed previously,² this reaction proceeds regioselectively and stereoselectively and gives e 'usively *endo*-2-acyl-substituted isomers **3a**-e in 14-39 % yield for the converted 2 (Table 1).

The structures of compounds 3b-e were confirmed by the spectral data (Tables 2-4).



Proton *a* has one vicinal spin-spin interaction constant with protons, in *trans* positions, ${}^{3}J_{ac}$ (~12.5 Hz), which is indicative of an equatorial position of the COR substituent.¹ However, this does still not confirm the fact that the six-membered cycle has a chair con-

Table 1. Synthesis of substituted 8-oxabicyclo[3.2.1]octanes

R ¹	R ²	Conversion	Yield of 3 calculated per					
		of 2 (%)	converted 2 (%)	mol g-atom Rh				
Me	Me	31	39 (3a)	12				
Ph	Me	54	26 (3b)	11				
Bu ^t	Me	26	14 (3c)	4				
5-(2-Me- thylfuryl)	Me	47	33 (3d)	15				
Me	Ph	64	20 (3e)	13				

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Com- pound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	R ¹	R ²
3b	52.10	83.08	34.05	37.02	81.40	37.02	24.56	204.02	26.93	138.78 (<i>i</i>) 129.12 (<i>o</i>) 129.35 (<i>m</i>) 133.98 (<i>p</i>)	26.21 (CH ₃)
3c	51.62	83.20	34.69	37.22	81.37	37.09	26.24	219.44	26.88	45.97 (C) 26.63 (CH ₃)	26.42 (CH ₃)
3d	52.63	82.89	34.06	37.04	81.48	36.98	23.95	191.00	26.95	152.87 (C-1') 121.34 (C-2') 109.92 (C-3') 159.50 (C-4') 14.03 (CH ₃)) 26.13 (CH ₃)))
3e	60.21	86.33	32.46	36.41	81.41	36.86	23.24	210.71	27.09	32.37 (CH ₃)	146.21 (i) 126.91 (o) 128.87 (m) 127.95 (p)

Table 2. Chemical shifts of ¹³C NMR signals of compounds 3b-e (ppm)*

* The ¹H, ¹³C, and ¹⁷O NMR spectra of compound **3a** are given in Ref. 8.

Table 3. Chemical shifts of ¹H NMR of compounds 3b-e (ppm)

Com- pound	а	Ь	с	d	е	f	g	h	i	С(9)— <u>Н</u>	R ¹	R ²
3b	3.653	1.779	1.917	1.542	1.590	1.857	1.668	2.618	1.503	1.26	8.01 (o) 7.45 (m) 7.55 (p)	1.12 (Me)
3c	3.094	1.765	1.671	1.467	1.479	1.811	1.633	2.812	1.453	1.23	1.11 (Bu ^t)	1.09 (Me)
3d	3.281	1.703	1.961	1.535	1.533	1.856	1.651	2.578	1.464	1.25	7.28 (C(2')H) 6.25 (C(3')H) 2.36 (Me)	1.13 (Me)
3e	2.97	1.97	1.68	1.61	1.57	1.97	1.71	2.85	1.96	1.30	1.38 (Me)	7.2-7.4 (Ph)

Table 4. ${}^{1}H^{-1}H$ Spin-spin interaction constants in compounds 3b-e (Hz)

Com- pound	a—b	a—c	a—i	b—c	b—e	b-d	с—е	c—d	d−e d−f	e—f	fg	f—h	f—i	g—h	g—i	h—i
3b	4.51	12.57	0.77	-13.85	5.33	1.88	12.95	5.33	-13.02 0.4	0.7	-12.27	10.15	4.83	5.03	13.08	-12.94
3c	4.29	12.32	0.9	-13.52	5.91	1.29	11.80	6.17	-13.91		-12.15	10.09	5.03	5.03	13.18	-13.00
3d	4.49	12.50	0.88	-13.73	5.17	2.07	13.17	5.32	-13.00 0.3	0.7	-12.28	10.11	5.01	4.95	13.11	-12.90
3e	4.44	12.85	0.92	_	-				_ ~~		-12.62	9.99	4.88	4.91	13.28	-12.74

Note. We failed to calculate completely the spin-spin interaction constants of the ¹H NMR spectrum of compound **3e** because of a strong overlapping of most signals.

formation, because when a boat conformation occurs, proton a also should have a large spin-spin interaction constant with proton b, which is in a *trans* position. We chose a chair conformation based on a long-range (separated by four bonds) constant between protons aand i. Only in the case of a chair conformation of the six-membered ring are four chemical bonds between protons a and i approximately in the same plane in the so-called sequence W, which favors the transfer of a spin-spin interaction through four bonds.

Experimental

All initial and final compounds were analyzed by the GLC method on an LKhM-80 chromatograph with a flame ionization detector; 3000×3 mm column; 10 % PEGS on Chromaton N-AW-HMDS; nitrogen as carrier gas. IR spectra were recorded on a Specord M-80 spectrometer using KBr pellets or cast films.

NMR spectra of compounds 3b-e were obtained on Bruker AM 300 and Bruker AMX 400 spectrometers. Chemical shifts were measured relative to TMS signals (¹H) and an acetonitrile-d₃ solvent (${}^{13}C$ 1.30 p.p.m.). High-resolution ¹H NMR spectra were analyzed using the PANIC (Bruker) and CALM (the Rezonans small enterprise. Moscow) iteration programs. The average accuracy of determination of variable parameters was 0.05 Hz. The spectra of compounds **3b** and **3d** were analyzed as 9-spin systems; the spectra of compounds **3c** and **3e** were analyzed as weakly coupled 4- and 5-spin systems. The complete assignment of signals in ¹³C NMR spectra was made using two-dimensional correlation ¹H-¹³C NMR spectra based on direct and long-range spin-spin interactions.

5-Methyl-5-hexen-2-one.⁴ vinyl ketones 1 (see Ref. 5) and $[RhCl(C_2H_4)_2]_2$ (see Ref. 6) were obtained according to the known procedures.

4-Methyl-1-phenyl-4-penten-1-one $(2, \mathbb{R}^2 = \mathbb{P}h)$. Benzoylacetic ester (31.1 g, 0.162 mol) was added dropwise to a solution of Na (3.73 g. 0.162 mol) in 80 mL of anhydrous alcohol, and then metallyl chloride (15.6 g, 0.172 mol) was added with weak heating over 40 min. After the solution was kept for 1 h, alcohol was distilled off with weak boiling, ice water was added until the precipitate was dissolved, the organic layer was separated, and the aqueous layer was extracted with ether. Combined organic layers were evaporated, a solution of NaOH (7.8 g) in 150 mL of water was added, and after boiling for 6.5 h, the mixture was again extracted with ether. The mixture was dried with Na₂SO₄, the ether was evaporated, and the mixture was distilled at 140-141 °C (15 Torr). 4-Methyl-1-phenyl-4-penten-1-one was obtained in 56 % yield (15.8 g). ¹H NMR (CDCl₃, δ): 1.79 (s, 3 H), 2.45 (t, 2 H, J =7.5 Hz), 3.12 (t, 2 H, J = 7.5 Hz), 4.72 (s, H), 4.77 (s, H), 7.43-7.55 (m, 3 H), 7.95-7.98 (m, 2 H). ¹³C NMR (CDCl₃, δ): 199.58, 144.58, 136.90, 132.89, 128.51, 127.95, 110.13, 36.76, 31.61, 22.65 (cf. Ref. 7).

Derivatives of 8-oxabicyclo[3.2.1]octane. General procedure. A mixture of $[RhCl(C_2H_4)_2]_2$ (0.1 mmol), $SnCl_2 \cdot 2H_2O$ (0.4 mmol), vinyl ketone (20 mmol), and γ , δ -unsaturated ketone (20 mmol) in a degasified solvent was heated in a sealed glass ampule under an argon atmosphere at 80 °C for 10 h. The solvent was distilled off, and then the residue was extracted with heptane and evaporated. The residue was chromatographed on a column with SiO₂.

endo-2-Acetyl-1,5-dimethyl-8-oxabicyclo[3.2.1]octane (3a). Compound 3a was obtained from a solution of 1a (0.65 g) and 5-methyl-5-hexen-2-one (1.04 g, 9.26 mmol) in 3.0 mL of acetone in a yield of 0.20 g. Hexane—ether (2 : 1) was used as an eluent. IR (ν/cm^{-1}): 1706 (C=O). Mass spectrum, m/z: 182 [M]⁺. endo-2-Benzoyl-1,5-dimethyl-8-oxabicyclo[3.2.1]octane (3b). Compound 3b was obtained form a solution of 1b (2.04 g) and 5-methyl-5-hexen-2-one (1.74 g, 15.5 mmol) in 4.0 mL of acetone in a yield of 0.42 g. Hexane—ether (4 : 1) was used as an eluent. IR (ν/cm^{-1}): 1670 (C=O). Mass spectrum, m/z: 244 [M]⁺.

endo-2-(tert-Butylcarbonyl)-1,5-dimethyl-8-oxabicyclo[3.2.1]octane (3c). Compound 3c was obtained from a solution of 1c (0.89 g) and 5-methyl-5-hexen-2-one (0.89 g, 8.0 mmol) in 2.2 mL of acetone in a yield of 0.07 g. Hexane ether (2 : 1) was used as an eluent. Benzene—ether (6 : 1) was used as an eluent. IR (v/cm⁻¹): 1698 (C=O). Mass spectrum, m/z: 224 [M]⁺.

endo-1,5-Dimethyl-2-(5-methylfuroyl)-8-oxabicyclo[3.2.1]octane (3d). Compound 3d was obtained from a solution of 1d (2.05 g) and 5-methyl-5-hexen-2-one (1.68 g, 15.1 mmol) in 4.0 mL of acetone in a yield of 0.56 g. Heptane-ether (4 : 1) was used as an eluent. IR (ν/cm^{-1}): 1654 (C=O). Mass spectrum, m/z: 248 [M]⁺.

endo-2-Acetyl-5-methyl-1-phenyl-8-oxabicyclo[3.2.1]octane (3e). Compound 3e was obtained from a solution of 1a (0.37 g) and 4-methyl-1-phenyl-4-penten-1-one (0.93 g, 5.35 mmol) in 1.5 mL of THF in a yield of 0.169 g. Heptane-acetone (15 : 1) was used as an eluent. IR (v/cm⁻¹): 1704 (C=O). Mass spectrum, m/z: 244 [M]⁺.

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References

- R. S. Dickson, Homogeneous Catalysis with Compounds of Rhodium and Iridium. D. Reidel Publ. Co., Dordrecht (Neth.), 1985.
- 2. G. I. Nikishin, T. E. Klimova, A. V. Ignatenko, and I. P. Kovalev, *Tetrahedron Lett.*, 1991, **32**, 1077.
- 3. I. P. Kovalev, V. V. Ipatkin, Y. A. Strelenko, A. V. Ignatenko, and G. I. Nikishin, *Tetrahedron Lett.*, 1992, 33, 1791.
- 4. G. Rosini, E. Marotta, M. Petrini, and R. Ballini, Tetrahedron, 1985, 41, 4633.
- 5. G. Mannich and G. Heilner, Berichte, 1922, 55, 356.
- 6. Inorg. Synth., 1974, XV, 14.
- E. W. Thomas and J. R. Szmuszkovich, J. Org. Chem., 1990, 55, 6054.

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