Unusual formation of 7-vinylcycloheptatriene derivatives in the catalytic cyclopropanation of cyclooctatetraene with diazocarbonyl compounds in the presence of rhodium catalysts

Yu. V. Tomilov, D. N. Platonov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: tom@cacr.ioc.ac.ru

The reaction of cyclooctatetraene with methyl diazoacetate or diazoacetone in the presence of rhodium binuclear complexes gives, besides 9-substituted bicyclo[6.1.0]nona-2,4,6-trienes (mixture of *anti*- and *syn*-isomers, total yields 60—75%), isomeric β-(cyclohepta-2,4,6-trien-1-yl)acrylates or 4-(cyclohepta-2,4,6-trien-1-yl)but-3-en-2-one in 20—34% yields. In the case of methyl diazoacetate, a mixture of *E*- and *Z*-isomers in a ratio of ~3.5 : 1 was obtained, while diazoacetone gave only *E*-isomer.

Key words: cyclooctatetraene, bicyclo[6.1.0]nona-2,4,6-trienes, 7-vinylcyclohepta-1,3,5-trienes, diazo compounds, dirhodium tetracarboxylates, NMR spectra.

Catalytic cyclopropanation of cyclooctatetraene (COT) with alkyl diazoacetates is normally performed at 95—110 °C in the presence of copper powder or $CuSO_4$ and gives bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylates (**1**) in 37—62% yields; the *anti*-isomers of these products predominate.[1—5] Virtually no structural isomers were formed under the reaction conditions, although esters **1** are known to isomerize at temperatures of >110 °C to give *cis*-8,9-dihydroindene-1-carboxylates.[4,6]

In this work, we studied the reactions of COT with methyl diazoacetate (MDA) and diazoacetone (DAA) catalyzed by binuclear rhodium compounds, which ensure decomposition of diazoesters and diazoketones at a lower temperature (0—20 °C).[7] The experiments were carried out by slow addition of MDA or DAA to a 2.5—3-fold molar excess of COT in CH_2Cl_2 containing 1 mol. % of the catalyst, which was rhodium acetate, trifluoroacetate, perfluorobutyrate, or caprolactamate — $Rh_2(OAc)_4$, $Rh_2(OCOCF_3)_4$, $Rh_2(pfb)_4$, or $Rh_2(cap)_4$. The compositions of the reaction mixtures were determined by the ^1H NMR spectra; individual compounds were isolated by thin layer or column chromatography.

Even the first experiments with $Rh_2(OAc)_4$ or $Rh_2(pfb)_4$ as the catalysts for cyclopropanation of COT with MDA showed the fundamental difference between Rh and copper catalysts. It was found that under these conditions, the formation of *anti*- and *syn*-bicyclo[6.1.0]nonatriene-9-carboxylates **1** (overall yields 60—75%) is accompanied by the formation of their structural isomers, β-cyclohepta-2,4,6-trien-1-ylacrylates **2**, whose yields reached 30—34%. Irrespective of the reaction conditions and the nature of the anion in the catalyst, the *E*-isomer was formed as the major product and the yield of *Z*-**2** was no more than 9% (Table 1).

Table 1. Composition of cyclooctatetraene cyclopropanation products as a function of the nature of Rh catalysts

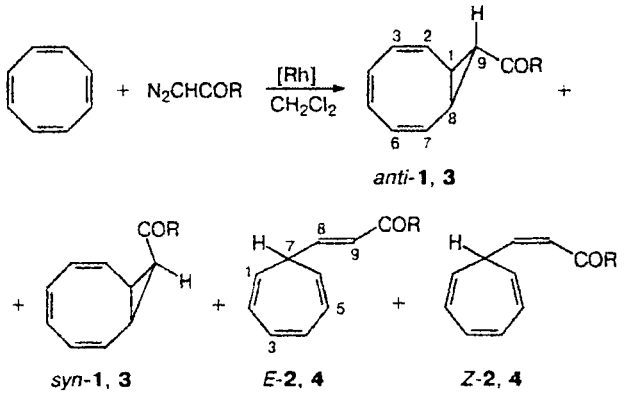
N_2CHCOR	Catalyst*	Solvent	*T*/°C	Yield (%)			Isomer ratio		
				1 or **3**	**2** or **4**	$(=CHCOR)_2$	**1**(**3**) : **2**(**4**)	*anti*/*syn*	*E*/*Z*
MDA	$Rh_2(OAc)_4$	CH_2Cl_2	20	75	18	7	4.2	1.8	3.5
(R = OMe)	$Rh_2(pfb)_4$	CH_2Cl_2	20	62	31	7	2.0	1.3	3.4
		CH_2Cl_2	40	62	34	4	1.8	1.3	3.3
		CCl_4	20	63	32	5	2.0	1.9	3.6
		CCl_4	76	45	14	41	3.2	2.0	3.7
		CH_2Cl_2	−40	45	20	35	2.3	1.6	4.0
	$Rh_2(OCOCF_3)_4$	CH_2Cl_2	20	49	31	20	1.6	1.6	2.4
	$Rh_2(cap)_4$	CH_2Cl_2	20	21	—	80		2.0	
DAA	$Rh_2(OAc)_4$	CH_2Cl_2	20	82	12**	6	6.8	1.6	
(R = Me)	$Rh_2(pfb)_4$	CH_2Cl_2	20	70	26**	4	2.7	2.5	

* pfb = $OCOC_3F_7$, cap = *cyclo*-$NCOC_5H_{10}$ (caprolactamate). ** Compound *Z*-**4** was not detected in the reaction mixture.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2204—2206, November, 1999.

1066-5285/99/4811-2178 $22.00

However, despite its lower yield, this isomer was isolated in a virtually pure state by chromatography on silica gel using benzene as the eluent (R_f ~0.8), whereas the *E*-isomer was eluted as a mixture with the structural isomer *anti*-**1** (R_f 0.6—0.7). Nevertheless, this mixture could also be separated to a large extent by using a hexane—AcOEt solvent system (24 : 1); this gave ~95% pure acrylate *E*-**2**.



R = OMe (**1**, **2**); Me (**3**, **4**)

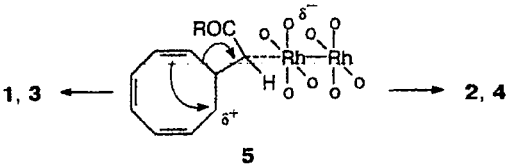
Yet another feature of Rh catalysts distinguishing them from copper compounds is manifested in the isomeric composition of the resulting bicyclic esters **1**. Thus the ratio of the *anti*- to *syn*-isomers formed upon cyclopropanation of COT with MDA in the presence of $CuSO_4$ (110 °C) was ~18 : 1 (see Ref. 5), whereas the reaction catalyzed by Rh catalysts gives *anti*- and *syn*-**1** isomers in close amounts (see Table 1); their ratio ranged from 1.3 to 2 and the greatest proportion of the *syn*-isomer was formed when the reaction was carried out in CH_2Cl_2 in the presence of $Rh_2(pfb)_4$.

The reaction of COT with DAA in the presence of $Rh_2(OAc)_4$ or $Rh_2(pfb)_4$ also resulted in a mixture of unsaturated compounds, in which the bicyclic ketone *anti*-**3** was the major product formed in ~50% yield. Cycloheptatriene vinyl ketone **4** was produced only as *E*-isomer and its amount increased from 12 to 26% on passing from $Rh_2(OAc)_4$ to $Rh_2(pfb)_4$ (see Table 1). The isomeric ketones *anti*- and *syn*-**3** and *E*-**4** were isolated by TLC on silica gel using a (24 : 1) hexane—AcOEt solvent mixture.

Bicyclic ester *anti*-**1** was identified by comparing its ^1H NMR spectra with those reported in the literature.[2,5] The structures of the other compounds were established based on ^1H and ^{13}C NMR spectra and mass spectra. It is of interest that the signal of the methine proton at C(9) in *syn*-**1** is exhibited as a doublet of doublets (J = 9.7 and 7.8 Hz) rather than a triplet as that for *anti*-**1**. Apparently, this is due to the distortion of the molecular symmetry in relation to the plane passing through C(9) and to the slight difference between the spin—spin coupling constants of the vicinal protons H(1), H(9) and H(8), H(9). A similar effect was observed for ketone *syn*-**3**; in this case, even the methyl group signal was slightly split into a doublet (J = 0.8 Hz).

The ^1H and ^{13}C NMR spectra of isomeric acrylates *E*-**2** and *Z*-**2** proved to be fairly similar; the only noticeable difference was the position of signals for H(7) (δ 2.53 and 3.66) and H(8) (δ 7.19 and 6.50). The spin—spin coupling constants of the protons of the exocyclic double bond, $J_{8,9}$ = 15.7 and 11.4 Hz, confirmed the structure of acrylates **2** as *E*- and *Z*-isomers. The attachment of the only low-field methine proton in each isomer to the olefinic protons of exo- and endocyclic double bonds was proved by {H,H}-correlation.

The reaction of COT with dimethyl diazomalonate in the presence of $Rh_2(OAc)_4$, studied previously,[8] was less efficient than the reactions with MDA and DAA and afforded dimethyl bicyclo[6.1.0]nonatriene-9,9-dicarboxylate in 32% yield; no formation of other isomers was noted. In turn, the possibility of isomerization of bicyclo[6.1.0]nonatriene into 7-vinylcyclohepta-1,3,5-trienes was demonstrated by sensitized photolysis of 9,9-(2,2′-diphenylidene)- and 9,9-diphenylbicyclo-[6.1.0]nonatrienes.[9] However, in our case, the formation of 7-vinylcycloheptatriene derivatives **2** and **4** in the reaction of COT with MDA or DAA in the presence of rhodium catalysts seems to occur simultaneously with the formation of normal cyclopropanation products, bicyclo[6.1.0]nona-2,4,6-trienes. Indeed, it was found in special experiments that refluxing of solutions of *anti*- and *syn*-**1** in CH_2Cl_2 in the presence of $Rh_2(OAc)_4$ or $Rh_2(pfb)_4$ does not give any noticeable amount of isomers **2**. In addition, since the proportion of cycloheptatrienylacrylates somewhat increased in the presence of rhodium perfluorocarboxylates, having a greater charge on the metal atom, it can be suggested that the first step of the addition of the carbene fragment to the double bond of COT results in an intermediate of type **5** with a substantial positive charge on C(2). Apparently, in this case, the standard formylation of the cyclopropane fragment is accompanied by skeletal rearrangement with contraction of the eight-membered ring, resulting in the formation of 7-vinylcyclohepta-1,3,5-triene structure.



5

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 (300 and 75.5 MHz) spectrophotometers in $CDCl_3$ containing 0.05% of TMS as the internal standard. The mass spectra were recorded on

a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct injection). Cycloocta-1,3,5,7-tetraene (Ferak Berlin) was distilled *in vacuo* prior to use.

Cyclopropanation of cyclooctatetraene (COT) (general procedure). A solution of methyl diazoacetate (0.33 g, 3.3 mmol) or diazoacetone (0.28 g, 3.3 mmol) in 8 mL of a solvent was added with stirring over a period of 2 h to a solution of COT (1.04 g, 10 mmol) in 10 mL of CH_2Cl_2 or CCl_4 containing 1 mol. % of the catalyst. The reaction mixture was stirred for an additional 30 min and passed through a layer of silica gel (0.5—1 cm) to separate the catalyst. Then the solvent was separated *in vacuo* and the residue was analyzed by ^1H NMR spectroscopy and separated on a column with silica gel (Silica Woelm, 32—63 μm).

Methyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (1). Isomer *anti*-1. TLC, hexane—AcOEt, 24 : 1, as the eluent, R_f = 0.7. ^1H NMR ($CDCl_3$), δ: 5.99 (m, 4 H); 5.90 (m, 2 H); 3.73 (s, 3 H, OMe); 2.12 (d, 2 H, H-1, H-8, $J_{1,9} = J_{8,9}$ = 5.6 Hz); 1.40 (t, 1 H, H-9, $J_{1,9}$ = 5.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 173.7 (CO); 129.2 (C-3, C-6); 127.0 (C-2, C-7); 125.5 (C-4, C-5); 51.9 (OMe); 28.6 (C-9); 27.9 (C-1, C-8).

Isomer *syn*-1. TLC, benzene as the eluent, R_f = 0.45. ^1H NMR (C_6D_6), δ: 6.05 (m, 2 H, H-3, H-6, $J_{2,3} = J_{6,7}$ = 10.9 Hz, $J_{3,4} = J_{5,6}$ = 2.2 Hz); 5.96 (br.d, 2 H, H-2, H-7, $J_{2,3} = J_{6,7}$ = 10.9 Hz); 5.85 (dt, 2 H, H-4, H-5, $J_{3,4} = J_{5,6}$ = 2.2, J = 1.0 Hz); 3.48 (s, 3 H, OMe); 1.81 (dd, 1 H, H-9, $J_{1,9}$ = 9.7 Hz, $J_{8,9}$ = 7.8 Hz); 1.70 (br.d, 2 H, H-1, H-8). ^{13}C NMR ($CDCl_3$), δ: 170.8 (CO); 129.5 (C-3, C-6); 125.7 (C-4, C-5); 125.5 (C-2, C-7); 51.1 (OMe); 23.6 (C-1, C-8); 23.1 (C-9). Partial MS, m/z (I_{rel} (%)): 176 (12) $[M]^+$, 144 (14), 117 (100), 116 (46), 115 (81), 91 (50).

Methyl β-(cyclohepta-2,4,6-trien-1-yl)acrylate (2). Isomer *E*-2. TLC, hexane—AcOEt, 24 : 1, as the eluent, R_f = 0.5. ^1H NMR ($CDCl_3$,), δ: 7.19 (dd, 1 H, H-8, $J_{8,9}$ = 15.7 Hz, $J_{7,8}$ = 7.0 Hz); 6.67 (dd, 2 H, H-3, H-4, J = 3.6 Hz, J = 2.8 Hz); 6.27 (m, 2 H, H-2, H-5); 5.99 (dd, 1 H, H-9, $J_{8,9}$ = 15.7 Hz, $J_{7,9}$ = 1.4 Hz); 5.24 (dd, 2 H, H-1, H-6, $J_{1,2} = J_{5,6}$ = 8.9 Hz, $J_{1,7} = J_{6,7}$ = 5.9 Hz); 3.77 (s, 3 H, OMe); 2.53 (m, 1 H, H-7, $J_{1,7} = J_{6,7} \approx J_{7,8}$ = 5.9 Hz, $J_{7,2} = J_{7,5} \approx J_{7,9}$ = 1.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 167.0 (CO); 148.5 (C-8); 131.0 (C-3, C-4); 125.5 (C-2, C-5); 121.2 (C-9); 121.0 (C-1, C-6); 51.6 (OMe); 40.8 (C-7). Partial MS, m/z (I_{rel} (%)): 176 (26) $[M]^+$, 161 (20), 144 (41), 117 (51), 116 (47), 115 (100), 91 (38).

Isomer *Z*-2. TLC, benzene as the eluent, R_f = 0.75. ^1H NMR ($CDCl_3$), δ: 6.67 (br.dd, 2 H, H-3, H-4, J = 3.5, J = 2.9 Hz); 6.50 (dd, 1 H, H-8, $J_{8,9}$ = 11.4 Hz, $J_{7,8}$ = 9.4 Hz); 6.26 (m, 2 H, H-2, H-5); 5.89 (dd, 1 H, H-9, $J_{8,9}$ = 11.4 Hz, $J_{7,9}$ = 1.2 Hz); 5.17 (br.dd, 2 H, H-1, H-6, $J_{1,2} = J_{5,6}$ = 9.4 Hz, $J_{1,7} = J_{6,7}$ = 6.0 Hz); 3.71 (s, 3 H, OMe); 3.66 (m, 1 H, H-7). ^{13}C NMR ($CDCl_3$), δ: 166.2 (CO); 150.4 (C-8); 130.8 (C-3, C-4); 125.1 (C-2, C-5); 121.0 (C-1, C-6); 120.0 (C-9); 51.2 (OMe); 38.0 (C-7). Found (%): C, 74.67; H, 6.96. $C_{11}H_{12}O_2$. Calculated (%): C, 74.98; H, 6.86.

9-Acetylbicyclo[6.1.0]nona-2,4,6-triene (3). Isomer *anti*-3. TLC, hexane—AcOEt, 24 : 1, as the eluent, R_f = 0.8. ^1H NMR (C_6D_6), δ: 5.91 (m, 2 H, H-3, H-6, $J_{2,3} = J_{6,7}$ = 11.3 Hz, $J_{3,4} = J_{5,6} \approx$ 2.5 Hz); 5.82 (br.d, 2 H, H-2, H-7, $J_{2,3} = J_{6,7}$ = 11.3 Hz); 5.81 (narr.m, 2 H, H-4, H-5); 2.27 (br.d, 2 H, H-1, H-8, $J_{1,9}$ = 5.5 Hz); 1.93 (s, 3 H, COMe); 1.54 (t, 1 H, H-9, $J_{1,9} = J_{8,9}$ = 5.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 203.6 (CO); 129.1 (C-3, C-6); 127.1 (C-2, C-7); 125.4 (C-4, C-5); 37.7 (C-9); 30.7 (Me); 30.6 (C-1, C-8). Partial MS, m/z (I_{rel} (%)): 160 (43) $[M]^+$, 145 (36), 127 (8), 117 (81), 116 (25), 115 (100), 91 (40). Found (%): C, 82.31; H, 7.64. $C_{11}H_{12}O$. Calculated (%): C, 82.46; H, 7.55.

Isomer *syn*-3. TLC, hexane—AcOEt, 24 : 1, as the eluent, R_f = 0.55. ^1H NMR ($CDCl_3$), δ: 6.03 (m, 2 H, H-3, H-6, $J_{2,3} = J_{6,7}$ = 11.2 Hz, $J_{3,4} = J_{5,6} \approx$ 2.4 Hz); 5.86 (narr.m, 2 H, H-4, H-5); 5.75 (br.d, 2 H, H-2, H-7, $J_{2,3} = J_{6,7}$ = 11.2 Hz); 2.28 (m, 1 H, H-9); 2.23 (d, 3 H, COMe, J = 0.9 Hz); 2.10 (br.d, 2 H, H-1, H-8, $J \approx$ 8.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 205.1 (CO); 129.8 (C-3, C-6); 126.0 (C-2, C-7); 125.8 (C-4, C-5); 33.1 (C-9); 31.2 (Me); 26.3 (C-1, C-8). Partial MS, m/z (I_{rel} (%)): 160 (23) $[M]^+$, 145 (31), 117 (80), 116 (22), 115 (94), 91 (40), 43 (100).

***E*-4-(Cyclohepta-2,4,6-triene-1-yl)but-3-en-2-one (*E*-4).** Hexane—AcOEt, 24 : 1, as the eluent, R_f = 0.7. ^1H NMR ($CDCl_3$), δ: 6.88 (dd, 1 H, H-8, $J_{8,9}$ = 15.8 Hz, $J_{7,8}$ = 7.0 Hz); 6.57 (br.t, 2 H, H-3, H-4, J = 3.1 Hz); 6.17 (m, 2 H, H-2, H-5); 6.15 (dd, 1 H, H-9, $J_{8,9}$ = 15.8 Hz, $J_{7,9}$ = 1.3 Hz); 5.14 (dd, 2 H, H-1, H-6, $J_{1,2} = J_{5,6}$ = 8.8 Hz, $J_{1,7} = J_{6,7}$ = 6.0 Hz); 2.47 (m, 1 H, H-7, $J_{1,7} = J_{6,7} \approx J_{7,8}$ = 6.0 Hz, $J_{7,2} = J_{7,5} \approx J_{7,9}$ = 1.2 Hz); 2.18 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$), δ: 198.4 (CO); 147.0 (C-8); 131.0 (C-3, C-4); 130.8 (C-9); 125.6 (C-2, C-5); 120.5 (C-1, C-6); 40.8 (C-7); 27.2 (Me). Partial MS, m/z (I_{rel} (%)): 160 (13) $[M]^+$, 145 (11), 127 (7), 117 (63), 115 (84), 91 (45), 43 (100). Found (%): C, 82.28; H, 7.61. $C_{11}H_{12}O$. Calculated (%): C, 82.46; H, 7.55.

References

1. D. D. Phillips, *J. Am. Chem. Soc.*, 1955, **77**, 5179.
2. G. Boche and D. Martens, *Chem. Ber.*, 1979, **112**, 175.
3. S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, 1955, **77**, 2476.
4. K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, 1964, **86**, 905, 1159.
5. M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Am. Chem. Soc.*, 1970, **92**, 3118.
6. M. B. Sohn, M. Jones, Jr., and B. Fairless, *J. Am. Chem. Soc.*, 1972, **94**, 4774.
7. A. J. Hubert, A. F. Noels, A. J. Anciaux, and Ph. Teyssie, *Synthesis*, 1976, 600; A. de Meijere, S. I. Kozhushkov, T. Spaeth, and N. S. Zefirov, *J. Org. Chem.*, 1993, **58**, 502.
8. M. von Birkhahn, E. V. Dehmlow, and H. Bögge, *Angew. Chem.*, 1987, **99**, 80.
9. T. Miyashi, Y. Takahashi, A. Konno, T. Mukai, H. D. Roth, M. L. Schilling, and C. J. Abelt, *J. Org. Chem.*, 1989, **54**, 1445.

Received May 12, 1999