LITERATURE CITED

1. A. T. Blomquist and J. A. Verdol, J. Am. Chem. Soc., 77, 1806 (1955).
2. A. P. Khitrov, Thesis, All-Union Scientific-Research Institute for Petroleum Chemistry, Leningrad (1963).
3. Ngo Zui Kyong, Yu. V. Korshak, G. N. Bondarenko, M. P. Teterina, and B. A. Dolgoplosk, Vysokomol. Soedin., B15, 375 (1973).
4. V. T. Aleksanyan and O. G. Garkusha, Izv. Akad. Nauk SSSR, Ser. Khim., 2227 (1976).
5. L. Bellamy, New Data on the Infra-Red Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 36.
6. C. C. Wu and R. W. Lenz, J. Polym. Sci., Polym. Chem. Ed., 10, 3555 (1972).
7. H. M. Frey, D. C. Montague, and I. D. R. Stevens, Trans. Faraday Soc., 63, 372 (1967).
8. Ya. M. Slobodin, and A. P. Khitrov, Zh. Obshch. Khim., 33, 2822 (1963).

HOMO- AND CODIMERIZATION OF BICYCLO[2.2.1]-HEPTA-2,5-DIENE AND ITS DERIVATIVES, CATALYZED BY RHODIUM COMPLEXES

U. M. Zhemilev, R. I. Khusnutdinov, Z. S. Muslimov,
L. V. Spirikhin, G. A. Tolstikov, and O. M. Nefedov

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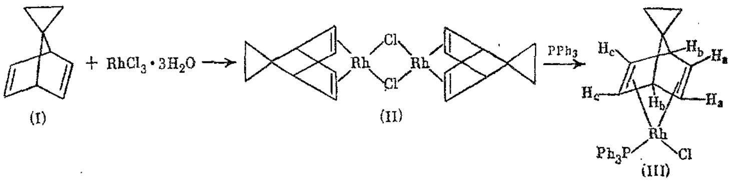
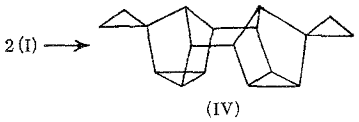
A number of articles and patents have recently appeared on the [2 + 2], [2 + 2 + 2], and [4 + 4] homodimerization of bicyclo [2.2.1] hepta-2,5-diene (norbornadiene, NBD) under the influence of compounds of Fe, Co, Ni, and Rh [1-4]. However, there is virtually no information in the literature on the participation of derivatives of NBD in this reaction. In particular, we have been unable to find any information on catalyzed reactions of spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane) (I), apparently owing to the difficulty of obtaining the latter.

To compare the reactivity of (I) with NBD, and to synthesize compounds with a new framework incorporating cyclopropane moieties, investigations have been carried out into the homodimerization of (I), and its codimerization with NBD under the influence of the new mono- and binuclear rhodium complexes (II) and (III). The binuclear rhodium complex (II), which contains the diene (I) as ligand, was synthesized according to [5] in 60% yield. Reaction of (II) with triphenylphosphine in benzene afforded the monovalent complex (III) as a yellow crystalline solid, stable in air, and sparingly soluble in organic solvents (benzene, CCl_4, $CHCl_3$, CH_2Cl_2 and acetone). The structure of (II) was confirmed by comparison of its IR spectrum with that of the analogous complex $[(NBD)RhCl]_2$ [5], and by its elemental analysis. It was not possible to obtain a PMR spectrum for (II) as a result of its limited solubility. The PMR spectrum of (III) was fully analogous to that of the complex $(NBD)RhCl(PPh_3)$ [6], except for the signals for the methylene protons of the cyclopropane ring (CPR), appearing as a multiplet at 0.05 ppm.



Complexes (II) and (III) display low activity in the homodimerization of (I) and codimerization of (I) with NBD. Addition of the reducing agent Et_2AlCl to complex (III) [ratio of (III):Al = 1:10-15] gives a highly active catalyst system, which enables the [4 + 4] dimerization of (I) to be carried out (70°C, 0.5-1 h) to give hydrocarbon (IV) in ∿95% yield.



(IV)

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2299-2303, October, 1981. Original article submitted February 11, 1981.

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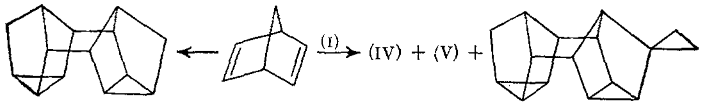


(V) (VI)

Under similar conditions, NBD gives (V) in almost quantitative yield. Codimerization of equal amounts of NBD and (I) in the presence of the (III)$-Et_2AlCl$ catalyst gives an ∿100% yield of a mixture of the codimer (VI) and the homodimers (IV) and (V) in a ratio of 2.1:1.5:1. It is noteworthy that the catalytic system (II) — PPh_3 — Et_3AlCl [(II) : P : Al = 1 : 2 : 10—15] is fully analogous in its activity and selectivity to the system (III)$-Et_2AlCl$.

The structures of (IV) and (VI) follow unambiguously from their PMR spectra (Table 1). Comparison of the PMR spectrum of (IV) with that of binor-S (V) (see Table 1) and with the data given in [7] shows that in (IV) the CPR protons at $C^{6'}$, $C^{7'}$, $C^{8'}$, $C^{11'}$, $C^{12'}$, $C^{13'}$ are nonequivalent. The signal for the protons at $C^{6'}$, $C^{13'}$ as a result of the descreening effect of the neighboring three-membered ring, are shifted to higher field (0.72 ppm), while the equivalent protons at $C^{7'}$, $C^{8'}$, $C^{11'}$, $C^{12'}$ resonate at lower field (1.32 ppm), and the signals for the $C^{6'}(C^{13'})$protons are split into a triplet as a result of interaction with the protons at $C^{7'}$, $C^{8'}$ ($C^{11'}$, $C^{12'}$), the signal for the latter appearing as a doublet with J = 6 Hz. When the signal for the protons at $C^{7'}$, $C^{8'}$, $C^{11'}$ and $C^{12'}$ are added, the triplet for protons $C^{6'}$ and $C^{13'}$ is converted into a singlet (Fig. 1). The signals for the protons at C^1 and C^4 are, as would be expected, shifted considerably to high field (β-effect, $\Delta\delta$ = 0.77 ppm), whereas the signals for the protons at $C^{2'}$, $C^{3'}$, $C^{9'}$, $C^{10'}$ occur at lower field (γ-effect, $\Delta\delta$ = 0.33 ppm).

The PMR spectrum of (VI) is a combination of the spectra of (IV) and (V), the signals of the paired nonequivalent protons at C^2, C^{10} and C^3, C^9 being split into a doublet with J = 9 Hz (Fig. 1). The IR spectra of (IV) and (VI), which contain frequencies at 786, 797, 799, and 808 (nortricyclene) and 1020, 1040, 1050, and 3070 cm^{-1} (CPR), are in complete agreement with the structures proposed for these compounds.

Compounds (IV) and (VI) are crystalline solids which are stable on heating to 250°C. Attempts to hydrogenate (IV) and (VI) under conditions typical for spirocyclopropanes [8] were unsuccessful.

EXPERIMENTAL

PMR spectra were recorded in a Tesla BS-497 (100 MHz) in C_6D_6 or $CDCl_3$ (^2H internal stabilization) relative to TMS, and IR spectra on a UR-20 instrument in vaseline or KBr.

Spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane) (I) was obtained as in [9].

Complex $[(C_9H_{10})RhCl]_2$ (II). To a solution of 1.87 g (7.1 mmole) of $RhCl_3 \cdot 3H_2O$ in 15 ml of 96% ethanol was added 2.5 g (0.21 mole) of (I), and the mixture stirred for 8 h at 25°C. The resulting yellow precipitate was crystallized from benzene to give 1.1 g (60%) of (II), mp 180°C (sealed ampul, decomp.). IR spectrum (ν, cm^{-1}); 630 w, 770 w, 790 m, 908 m, 920 s, 940 m, 980 m, 1012 w, 1030 w, 1070 m, 1150 m, 1300 s, 1420 m, 3000 s, 3070 m. Found: C 42,01; H 3,96; Cl 14,06; Rh 40,45%. $[(C_9H_{10})RhCl]_2$. Calculated: C 42,11; H 3,90; Cl 13.84; Rh 40,14%.

Complex $(C_9H_{10})RhCl(PPh_3)$ (III). To a suspension of 0.2 g (0.39 mmole) of (II) in 5 ml of benzene was added a solution of 0.21 g (0.8 mmole) of PPh_3 in 3 ml of benzene. The mixture was stirred until a homogeneous yellowish-brown solution was obtained (0.5 h), then evaporated to 3 ml and 10 ml of pentane added. On cooling the reaction mixture to ∿20°C, yellowish-brown crystals of (III) separated, yield 0.32 g (80%), mp 136-137°C (decomp.). IR spectrum (ν, cm^{-1}): 700 v.s., 750 s, 910 w, 950 w, 980 w, 1005 w, 1035 w, 1100 s, 1160 m, 1190 w, 1300 m, 1435 s, 1480 s, 1630 w, 3000 m, 3060 m. PMR spectrum (δ, ppm): 0.05 (4H, CH_2 in CPR), 2.8 (2H, H_a), 3.60-4.60 (4H, H_b, H_c), 7.06, 7.90 (15H, C_6H_5). Found: C 61,70; H 4,72; Cl 6,90; P 6,05; Rh 20,22%. $(C_9H_{10})RhCl[P(C_6H_5)_3]$. Calculated: 62,48; H 4,80; Cl 6,84; P 5,98; Rh 19,86%.

Homodimerization of (I) or Norbornadiene. To a solution of 0.02 g (0.04 mmole) of complex (III) [or 0.02 g (0.039 mmole) of (II) and 0.021 g (0.8 mmole) of PPh_3] in 3 ml of toluene was added at −5°C in a stream of argon 0.06 g (0.5 mmole) of Et_2AlCl. The mixture was stirred for 15 min, and the catalyst solution transferred to a steel autoclave of capacity 17 ml in which had previously been placed 17 mmole of (I) or NBD, and heated for 0.5-1 h at 70°C. The mixture was treated with 0.5 ml of alcohol with cooling, and filtered through 30 g of Al_2O_3. After removal of the solvent, the residue was crystallized from benzene.

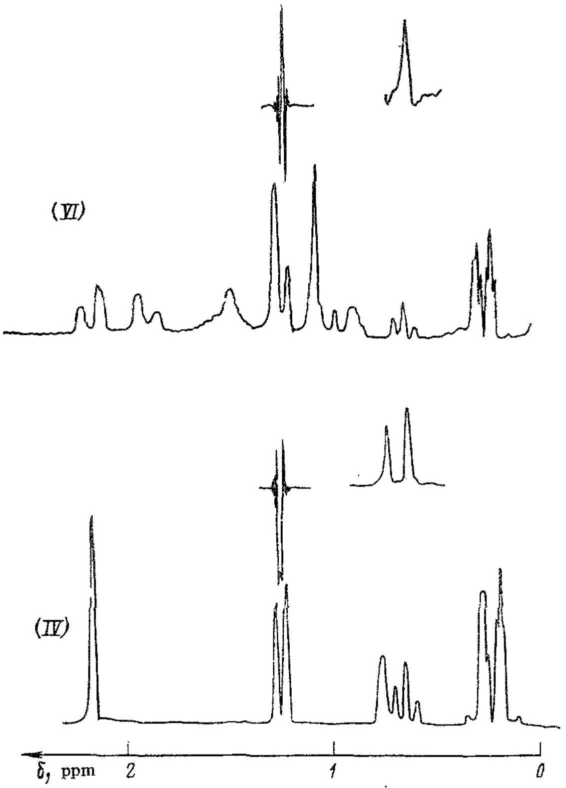
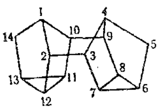
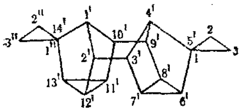
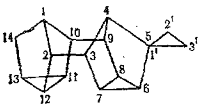


Fig. 1. PMR spectra of (IV) and (VI) in $CDCl_3$.

TABLE 1. PMR Spectral Data for Compounds (IV)-(VI)

Compound	δ, ppm	Assignment of signal	Multiplicity (J, Hz)	Number of protons
 (V)	1,06	C^6, C^7, C^8, C^{11}, C^{12}, C^{13}	Singlet	6
	1,29	C^5, C^{14}	»	4
	1,60	C^1, C^4	»	2
	1,88	C^2, C^3, C^9, C^{10}	»	4
 (IV)	0,27 0,31	C^2, C^3, $C^{2''}$, $C^{3''}$	Doublet of doublets (8; 6, 5)	8
	0.72	$C^{6'}$, $C^{13'}$	Triplet (5)	2
	0,83	$C^{1'}$, $C^{4'}$	Singlet	2
	1,32	$C^{7'}$, $C^{8'}$, $C^{11'}$, $C^{12'}$	Doublet (5)	4
	2,21	$C^{2'}$, $C^{3'}$, $C^{9'}$, $C^{10'}$	Singlet	4
 (VI)	0,28 0,32	$C^{2'}$, $C^{3'}$	Doublet of doublets (8; 6, 5)	4
	0,7	C^6	Triplet (5)	1
	0,94	C^4	Singlet	1
	1,12	C^{11}, C^{12}, C^{13}	Singlet	3
	1,28	C^7, C^8	Doublet (5)	2
	1,30	C^{14}	Singlet	2
	1,52	C^1	»	1
	1,93	C^2, C^{10}	Doublet (9)	2
	2,2	C^3, C^9	» (9)	2

The dispiro(cyclopropane-1,5'-endo-cis-endoheptacyclo [8.4.0.0.$^{2',12'}$0.$^{3',7'}$0$^{4',9'}$0.$^{6',8'}$0.$^{11',13'}$] tetradecane-14', 1''-cyclopropane) (IV) obtained in 95% yield had mp 135.5-136°C (sealed ampul). IR spectrum (ν, cm^{-1}): 786, 797 (nortricyclene), 1020, 1040, 1050, and 3070 (CPR). Found: C 91,04; H 8,50%. $C_{18}H_{20}$. Calculated: C 91,52; H 8,48%; M^+ 232.

The constants for (V) prepared here were in full agreement with those given in [7].

Codimerization of Norbornadiene with (I). Compound (I) (2 g, 17 mmole) and 1.56 g (17 mmole) of NBD in 5 ml of toluene were heated under the conditions described above in the presence of the catalyst (III)–Et_2AlCl [or (II)–PPh_3–Et_2AlCl]. There was obtained 3.5 g of a mixture of hydrocarbons containing 32% of (IV), 21% of (V), and 47% of endo-cis-endoheptacyclo $[8.4.0.0^{2,12}0.^{3,7}0^{4,9}\ 0.^{6,8}0.^{11,13}]$ tetradecane-5-spiro-1′-cyclopropane (VI). The (VI) obtained by vacuum fractionation had mp 34.5-35°C. IR spectrum (ν, cm^{-1}): 799, 808 (nortricyclene), 1015, 1040, and 3070 (CPR). Found: C 91,33; H 8,67%. $C_{16}H_{18}$. Calculated: C 91,43; H 8,57%; M^+ 210.

CONCLUSIONS

1. Mono- and binuclear rhodium complexes have been obtained which contain spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane) as ligand.

2. A study has been carried out of the catalyzed (4 + 4) homodimerization and codimerization of spiro(bicyclo-[2.2.1]hepta-2,5-diene-7,1′-cyclopropane), leading to new octa- and nonacyclic hydrocarbons.

LITERATURE CITED

1. G. N. Schrauzer, Adv. Catal., 18, 375 (1968).
2. N. Acton, R. J. Roth, T. J. Katz, J. K. Frank, C. A. Maier, and J. C. Paul, J. Am. Chem. Soc., 94, 5446 (1972).
3. US Patent No. 4094916.
4. US Patent No. 4094917.
5. E. W. Abel, M. A. Bennett, and G. Wilkinson, J. Chem. Soc., 3178 (1959).
6. K. Vrieze and H. C. Volger, J. Organomet. Chem., 11(2), 17 (1968).
7. G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, J. Am. Chem. Soc., 88, 4890 (1966).
8. M. N. Akhtar, J. J. Rooney, and W. J. Jackson, J. Chem. Soc., Perkin Trans., 1412 (1976).
9. K. Alder, H-J. Ache, and F. H. Flock, Chem. Ber., 93, 1888 (1960).

REACTION OF METHOXYPHENYLCARBENEPENTACARBONYLTUNGSTEN WITH TETRACHLOROMETHANE AND THE CATALYTIC ACTIVITY OF THE SYSTEM FORMED RELATIVE TO THE POLYMERIZATION OF CYCLOOLEFINS WITH RING OPENING

S. P. Kolesnikov, T. L. Mitenina, S. A. Radzinskii,
A. P. Sheinker, A. D. Abkin, and O. M. Nefedov

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133.541.64:547.518

According to current concepts, the polymerization sites in the polymerization of cycloolefins with ring opening are carbene complexes of transition metals [1]. Catalytic activity has been shown in these reactions for both individual carbene complexes such as $(CO)_5WCPh_2$ and $(CO)_5WC(OR)Ph$ and systems containing such complexes [2-6]. In particular, methoxyphenylcarbenepentacarbonyltungsten $(CO)_5WC(OCH_3)Ph$ (I) is capable of producing polymerization of norbornene (53% in 6 days) and cyclobutene (60% in 15 h) [2].

We have found that carbene complex (I) and its freshly prepared solution in CCl_4 is inactive in the polymerization of 1,5-cis-cis-cyclooctadiene (COD) and is converted into a catalytically active form upon brief UV irradiation of its solution in CCl_4 either after heating of this solution at 50-70°C for 2-6 h or maintenance for 2 days at about 20°C. The system formed as a result of the reaction of (I) with CCl_4 may be used for the polymerization immediately after its preparation or after removal of excess CCl_4 and volatile reaction products in vacuum.

Figure 1 illustrates the polymerization kinetics of COD in the catalytic system formed by the reaction of (I) with CCl_4 under various conditions. This figure shows that the dependence of the polymer yields on the reaction time is virtually linear to high monomer conversions. Constant UV irradiation accelerates the polymerization. However, in the

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. L. Ya. Karpov Institute of Physical Chemistry, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2303-2307, October, 1981. Original article submitted February 25, 1981.

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