

Diene Condensation of Polychlorocyclic Dienes with Dienophiles of Allylacetylene Series

M. G. Veliev, A. Z. Chalobieva, M. I. Shatirova, E. Sh. Mamedov, and I. M. Mamedov

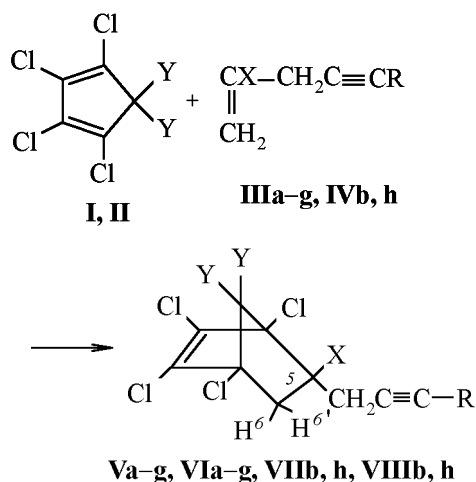
Institute of Petrochemical Processes, Azerbaidzhan Academy of Sciences, Baku, 370025 Azerbaidzhan

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Abstract—Diene condensations of hexachlorocyclopentadiene and 5,5-dimethoxytetrachlorocyclopentadiene were carried out with dienophiles of allylacetylene series. The reaction was demonstrated to proceed stereospecifically yielding adducts of the *endo*-configuration. The reactivity of functionalized allylacetylene compounds in the diene synthesis with hexachlorocyclopentadiene was studied, and the reaction was established to occur by the type of a “neutral” diene synthesis. It was established that the Faworsky decomposition of polychlorobicyclic alcohols containing in the side chain a triple bond adjacent to a methylene group occurred with acetylene–allene isomerization.

Conjugated and unconjugated enynes can be used as dienophiles for preparation of cyclic compounds, especially norbornene and halo-substituted derivatives that may serve as monomers and modifiers in the polymer chemistry [1-3] and as synthons in the organic synthesis [3-5].

We reported formerly [6, 7] on diene condensation of certain vinyl- and allylacetylene compounds with cyclopentadiene, hexachlorocyclopentadiene, and 5,5-dimethoxytetrachlorocyclopentadiene. It was demonstrated that the reaction occurred at vinyl group and yielded the corresponding adducts. The structure



III-VIII, R = H (a), C(CH₃)₂OH (b), C(CH₃)₂OCH₃ (c), C(CH₃)₂OCOCH₃ (d), C(CH₃)₂OCH₂CH₂CN (e), C(CH₃)₂Cl (f), C(CH₃)₂Br (g), CH₂OH (h); X = H (V, VI), Cl (VII, VIII); Y = Cl (I, V, VII), OCH₃ (II, VI, VIII).

of the adducts prepared and some chemical reactions thereof were studied. In extension of the investigation on the unconjugated enyne systems reactivity as influenced by functional groups in the Diels–Alder reactions with electron-donor dienes [8] we studied the diene condensation of hexachloropentadiene (II) with polyfunctional compounds of allylacetylene series (IIIa-g, IVb, h).

We demonstrated that polychlorocyclic dienes **I, II** cleanly react with dienophiles of allylacetylene series (IIIa-g, IVb, h) at heating to 90–120°C yielding by diene condensation the corresponding adducts, chlorinated bicyclo[2.2.1]heptenes **V-VIa-g, VII-VIIIb, h**.

Elemental analyses, GLC and TLC confirm the composition and homogeneity of the adducts **V-VIa-g, VII-VIIIb, h**, and IR and ¹H NMR spectra unambiguously prove their structure. The coupling constants of the three interacting protons C⁶H^{endo}, C⁶H^{exo}, and C⁵H (Table 3) in adducts **Vd-g, VIId-g** uniquely determine that the substituent acquires *endo*-configuration.

Adducts **Vb, VIb, VIIb, VIIIb, h** originating from allylacetylene carbinols **IIIb-IVb** with the dienes **I, II** under study may be used for preparation of versatile polychlorobicycloheptene derivatives. In particular, we carried out the reversed Faworsky reaction and the stepwise hydrogenation. It was established that in the reversed Faworsky reaction of polychlorobicyclic alcohols **Vb-VIIIb** unlike the behavior of bicyclooctene alcohols [8] alongside

Table 1. Physical properties and elemental analyses of compounds **Vd–g**, **VId–g**, **VIIb**, **VIIIb, h**, **X**, **XII–XIX**^a

Compd. no.	Yield, %	bp, °C (<i>p</i> , mm Hg), mp, °C	n_D^{20}	d_4^{20}	Found, %				Formula	Calculated, %			
					C	H	Cl(Br)	N		C	H	Cl(Br)	N
Vd	82.8	185–186(2)	1.5429	1.4318	41.10	3.22	48.51		C ₁₅ H ₁₄ Cl ₆ O ₂	41.04	3.22	48.45	
Ve	86.0	203–204(2)	1.5362	1.3877	42.77	3.39	47.41	3.01	C ₁₆ H ₁₅ Cl ₆ NO	42.70	3.36	47.27	3.10
Vf	54.6	161–162(1)	1.5676	1.4798	39.23	2.71	58.00		C ₁₃ H ₁₁ Cl ₇	40.69	2.64	59.80	
Vg	60.8	170–172(1)	1.5700	1.6074	45.40	3.92	42.00		C ₁₃ H ₁₁ Cl ₆ Br	44.40	3.90	43.70	
VId	83.4	193–194(3)	1.5235	1.3154	47.35	4.69	33.10		C ₁₇ H ₂₀ Cl ₄ O ₄	47.46	4.68	32.96	
VIe	88.5	217–219(2.5)	1.5190	1.2872	49.06	4.81	32.12	3.20	C ₁₈ H ₂₁ Cl ₄ NO ₃	49.00	4.79	32.14	3.17
VI f	72.8	164–165(1)	1.5412	1.3562	45.40	4.92	42.00		C ₁₅ H ₁₆ Cl ₅ O	44.40	3.90	43.70	
VI g	69.5	184–185(1)	1.5505	1.4602	41.71	4.10	48.12		C ₁₅ H ₁₆ Cl ₄ BrO ₂	40.03	3.50	49.26	
VIIb	25.0	104–105			36.30	2.67	57.41		C ₁₃ H ₁₁ Cl ₇ O	36.19	2.57	57.53	
VIIIb	29.6	82–83			32.80	1.70	61.58		C ₁₅ H ₁₇ Cl ₅ O ₃	32.76	1.75	61.53	
VIIIh	24.8	184–185(1)	1.5620	1.5165	39.42	3.38	44.69		C ₁₃ H ₁₃ Cl ₅ O ₃	39.58	3.32	44.93	
X	81.6	74–75			32.24	1.24	66.53		C ₁₀ H ₅ Cl ₇	32.17	1.35	66.48	
XII	85.4	55–56			39.66	3.12	48.51		C ₁₂ H ₁₁ Cl ₅ O ₂	39.54	3.04	48.63	
XIII	90.7	145–146(2)	1.5626	1.5474	35.45	1.90	62.91		C ₁₀ H ₆ Cl ₆	35.39	1.77	62.84	
XIV	80.3	155–156(2)	1.5810	1.6352	32.26	1.28	66.65		C ₁₀ H ₅ Cl ₇	32.17	1.35	66.49	
XV	96.0	145–146(1.5)	1.5319	1.3502	43.55	3.70	43.15		C ₁₂ H ₁₂ Cl ₄ O ₂	43.63	3.63	43.03	
XVI	84.6	152–153(1.5)	1.5605	1.4916	39.68	2.89	48.70		C ₁₂ H ₁₁ Cl ₅ O ₂	39.54	3.04	48.63	
XVII	72.0	185–188(1)	1.5542	1.6010	38.20	3.63	49.10		C ₁₃ H ₁₄ Cl ₆ O	39.13	3.53	48.75	
XVIII	79.0	183–185(1)	1.5332	1.3877	45.78	5.70	39.90		C ₁₅ H ₂₀ Cl ₄ O ₃	46.18	5.16	36.34	
XIX	55.6	70–71(12)	1.4770	0.8800	74.80	11.40			C ₈ H ₁₄ O ₆	75.50	11.09		

^a Physical properties and spectral data of compounds **Va–c**, **VIa–c** not included into Tables 1–3 were published in [4, 6].

Table 2. IR and ¹H NMR spectra of bicyclo[2.2.1]heptenes **Vd–g**, **VId–g**, **VIIb, h**, **VIIIb, h**

Compd. no.	Proton signals, δ, ppm					IR spectra, ν, cm ⁻¹		
	X ⁵	H ^{6'}	H ⁶ (H ⁷)	H ⁸ H ^{8'}	R	C≡C	C=C	C–Hlg
Vd	2.90 m	2.56 d.d	1.90 d.d	2.45 m	1.50 s, 1.90 s	2265	1625	660
Ve	2.92 m	2.60 d.d	1.78 d.d	2.40 m	1.30 s, 3.60 t (OCH ₂), 2.40 t (CH ₂ CN)	2250	1630	710
Vf	3.15 m	2.54 d.d	1.70 d.d	2.48 m	1.95 s	2260	1620	670
Vg	2.80 m	2.45 d.d	1.69 d.d	2.58 m	1.90 s	2255	1640	660
VId	2.60 m	2.25 d.d	1.60 d.d (3.52 d)	2.40 m	1.48 s, 1.90 s	2230	1630	650
VIe	2.65 m	2.52 d.d	1.60 d.d (3.50 d)	2.35 m	1.25 s, 3.35 t (OCH ₂), 2.40 t (CH ₂ CN)	2240	1630	650
VI f	3.05 m	2.45 d.d	1.58 d.d (3.30 d)	2.34 m	1.80 s	2260	1620	655
VI g	2.72 m	2.33 d.d	1.52 d.d (3.25 d)	2.45 m	1.75 s	2245	1635	650
VIIb		2.54 d	1.72 d	3.10 s	1.33 s, 1.70 s	2240	1630	665
VIIIb		2.45 d	1.81 d	2.95 s	4.35 t, 2.70 s	2245	1635	640
VIIIb		2.50 d	1.69 d (3.45 d)	3.10 s	1.27 s, 3.05 s	2250	1640	670
VIIIh		2.40 d	1.77 d (3.40 d)	2.90 s	4.30 t, 3.15 s	2255	1625	655

terminal acetylene compounds were also obtained allene derivatives **XIII–XVI**.

We developed a procedure for preparation in high yield of polychlorobicyclic compounds with the terminal acetylene (**IX–XII**) and allene (**XIII–XVI**) bonds. The structure of compounds **IX–XVI** was confirmed by IR and ^1H NMR spectra (Table 4). In the IR spectra of the compounds clearly appear the bands from monosubstituted acetylene ($3310\text{--}3320\text{ cm}^{-1}$) (**IX–XII**) and allene ($1950\text{--}1965\text{ cm}^{-1}$) bonds (**XIII–XVI**).

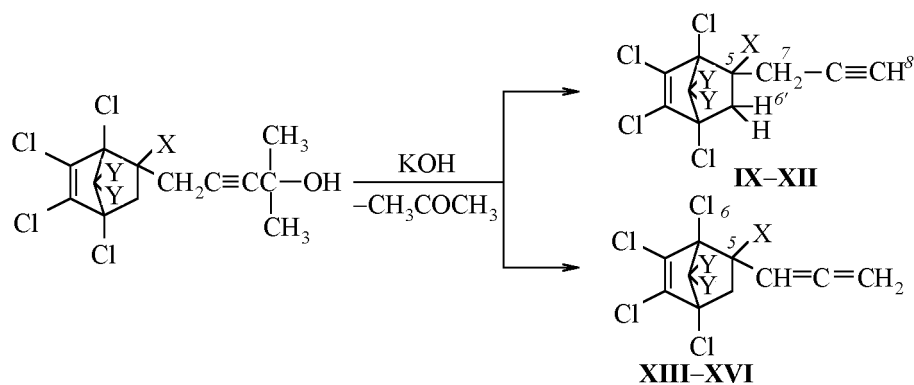
In the ^1H NMR spectra are present the signals from the hydrogen of the terminal acetylene bond $\text{--C}\equiv\text{CH}$ (**IX–XII**) [δ , ppm, 2.50 s ($\equiv\text{CH}$)] or the signals from the hydrogens belonging to allene system (**XIII–XVI**) $\text{--CH}=\text{C}=\text{CH}_2$ [δ , ppm, 5.80 t ($=\text{CH}$) and 5.15 d ($=\text{CH}_2$)].

The reduction of the triple bond in the side chain of the adducts **Vb**, **VIb** (polychlorobicycloheptene alcohols) is easily performed by treating them with

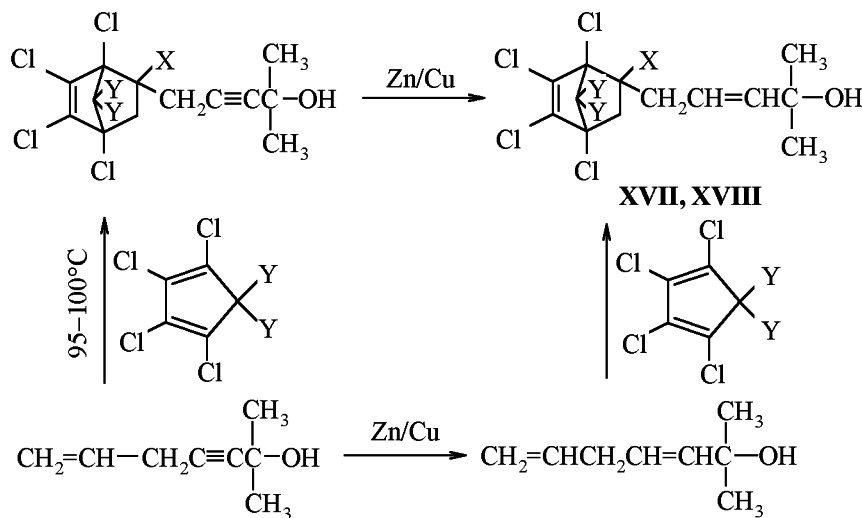
Table 3. Coupling constants in polychlorobicycloheptene adducts **Vd–g**, **VI d–g**

Compd. no.	$J_{6,6'}$, Hz	$J_{5,6}$, Hz	$J_{5,6'}$, Hz
Vd	11.5	4.1	9.3
Ve	12.6	4.2	9.1
Vf	13.2	4.3	9.6
Vg	12.1	3.9	9.1
VI d	12.1	3.8	9.3
VI e	12.5	3.5	9.5
VI f	12.6	3.7	9.0
VI g	11.7	3.7	9.2
Publ. data [9, 10]	10.4–13.7	2.5–5.0	9–10

coppered zinc powder in water–ether medium resulting in formation of the corresponding diene alcohols **XVII–XIX**.



Y = Cl, X = H (**IX**, **XIII**), Cl (**X**, **XIV**); Y = OCH₃, X = H (**XI**, **XV**), Cl (**XII**, **XVI**).



Y = Cl (**XVII**), OCH₃ (**XVIII**).

Table 4. IR and ^1H NMR spectra of compounds **XIII–XVI**

Compd. no.	IR spectra, ν , cm^{-1}	Proton signals, δ , ppm					
		H^5	$J_{6,6'}$ Hz	H^6	$\text{H}^{6'}$	H^7	H^8 $\text{H}^{8'}(\text{OCH}_3)_2$
XIII	1960, 1615, 955, 765	3.10 m	11.8	2.60 d.d	1.90 d.d	5.90 t	5.15 d
XIV	1955, 1605, 960, 780	3.05 m	12.1	2.75 d.d	1.80 d.d	5.85 t	5.20 d 3.55 d
XV	1965, 1610, 950, 770		11.7	2.64 d	1.68 d	5.95 t	5.12 d
XVI	1960, 1615, 955, 760		12.2	2.58 d	1.74 d	5.93 t	5.17 d 3.50 d

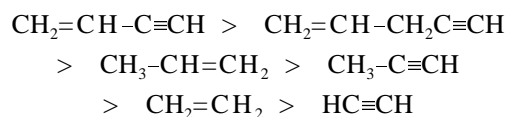
The data of ^1H NMR and IR spectra showed that hydrogenation of polychlorobicyclic alcohols **Vb**, **VIb** and allylethynyl dimethylcarbinol occurred regioselectively, exclusively at the triple bond yielding diene alcohols of *trans*-configuration (coupling constants at the double bond amounted to 16–18 Hz). The dienes obtained undergo diene condensation with polychlorocyclic dienes to afford *endo*-adducts where the double bond also has *trans*-configuration.

The stepwise hydrogenation proceeds for 45–50 h at 40–45°C; the increase of reaction time to 100 h does not result in higher yield of compounds **XVIII**, **XIX**. Under similar conditions the reduction of allylethynyl dimethylcarbinol occurs with formation of a 1,4-diene alcohol **XIX** in a fair yield (60%). It is known that to the treatment of various aspects of diene synthesis is applied the analysis of orbital interactions between the reacting systems [11, 12]. To elucidate the dependence on the functional groups character of the reactivity of the allylacetylene compounds in reaction with dienes of acceptor nature we studied in this work the kinetics of dienophiles **IIIa–e** condensation with diene **I**. We also analyzed from the viewpoint of the theory of molecular orbitals interaction the highly unsaturated dienophiles (vinyl-

acetylene, allylacetylene, ethylene, acetylene, propylene, and methylacetylene). The quantum-chemical calculation of the molecules was carried out along MINDO/3 method [13–15], LUMO and HOMO energy levels were estimated (Table 5).

As seen from Table 5, the dienophiles are better electron donors than hexachlorocyclopentadiene. These data suggest that the reactivity of dienophiles **IIIa–e** will grow with increasing electron-donor character.

The comparison of calculation results for the dienophiles under consideration (Table 5) permits a conclusion that in going from vinyl- and allylacetylenes to acetylene proper increases HOMO energy and decreases that of LUMO, therefore vinylacetylene should be the most reactive.



Note that in the molecules of highly unsaturated dienophiles containing both double and triple bonds, e.g. in vinyl- and allylacetylene, the contribution of

Table 5. Characteristics and difference between energy levels of diene HOMO (A) and LUMO of some dienophiles (B)

Compound	HOMO, eV	LUMO, eV	LUMO–HOMO, E_B-E_A (E_1)	LUMO–HOMO, E_A-E_B (E_2)	LUMO–HOMO, E_B-E_B (E_3)
Hexachlorocyclopentadiene (A) ^a	-9.268	-1.423			
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$	29.261	1.466	10.734	8.16	10.727
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$	-9.758	1.737	11.01	8.34	11.50
$\text{CH}_3-\text{C}=\text{CH}$	-10.153	2.324	11.59	8.73	12.48
$\text{CH}_2=\text{CH}_2$	-10.390	2.199	11.47	8.97	12.59
$\text{HC}=\text{CH}$	-10.800	2.287	11.55	9.38	13.09
$\text{CH}_3-\text{CH}=\text{CH}_2$	-9.865	1.768	11.04	8.44	11.63

^a The energy difference of LUMO and HOMO of hexachlorocyclopentadiene E_4 7.84 eV.

Table 6. Kinetic and thermodynamic characteristics of the Diels–Alder reaction between hexachlorocyclopentadiene and allylacetylene and its derivatives

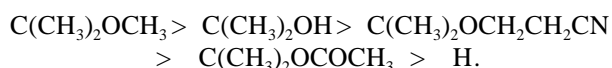
Dienophile no.	Rate constant $k \times 10^4$, $1 \text{ mol}^{-1} \text{ min}^{-1}$ at temperature, $^{\circ}\text{C}$				E_A , kJ mol^{-1}	ΔH^{\ddagger} , kJ mol^{-1}	$-\Delta S^{\ddagger}$, $\text{J mol}^{-1} \text{ deg}^{-1}$	ΔG^{\ddagger} , kJ mol^{-1}
	60	70	80	90				
IIIc	10.8	15.5	20.0	23.3	15.7	8.82	273.0	100.7
IIIb	9.1	13.3	19.1	23.1	22.0	15.15	253.6	101.0
IIIe	8.3	13.0	16.6	22.5	17.2	10.33	267.6	102.8
III d	6.6	8.3	12.5	18.7	22.6	15.77	255.96	104.5
IIIa	6.0	8.1	11.6	15.0	27.5	20.67	241.4	105.8

ethylene fragment is greater, and diene condensation should occur just at this bond (Table 5). This result is consistent with the experimental data.

The reaction kinetics was measured by GLC monitoring the consumption of diene in the reaction mixture with time (molar ratio diene–dienophile 1 : 1, reaction time 4–12 h, temperature range 60–90 $^{\circ}\text{C}$, solvent toluene). For quantitative evaluation of dienophiles reactivity as a function of their structure the experimental results were processed according to the second order equation. The rate constants were calculated from decrease in diene concentration in the reaction mixture according to the equation of a bimolecular reaction at equimolar ratio of the reacting addends [8, 16]. The average values of the rate constants are given in Table 6.

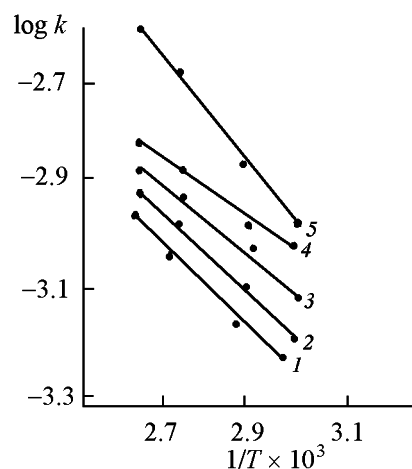
It follows from Table 6 that the reaction rate is affected both by the temperature and the character of the functional groups in dienophile. It is an additional evidence of the fact that the reactivity of allylacetylene and its derivatives depends on the donor-acceptor interaction between the components. Since the hexachloropentadiene in the reactions plays the part of electron-acceptor then the electron-donor groups in the dienophile increase its dienophilic reactivity.

With all dienophiles **IIIa–d** the plot of $\log K$ versus reciprocal temperature (in Arrhenius coordinates) is linear (see Figure). From the slope of the plots to the abscissa axis were determined the apparent activation energies (E_A) of hexachlorocyclopentadiene condensation with allylacetylenes used to calculate the thermodynamical parameters of the reactions (Table 6). The values of the rate constants obtained permitted to set the activity series of dienophiles **IIIa–e** in reaction with diene **I**:



The reaction studied is characterized by large negative values of activation entropy and relatively low activation energy common to concerted reaction of diene synthesis [17, 18].

Proceeding from the analysis of donor-acceptor characteristics of the addends and from the viewpoint of the theory of molecular orbitals interaction the observed dependence of alkenyne reactivity on the nature of the functional groups may be understood as caused by effect of donor-acceptor interaction and by localization energy similar to the reaction with electron-donor diene, 1,3-cyclohexadiene [8]. Thus the data obtained allow a conclusion that the diene synthesis of allylacetylene and its derivatives with hexachlorocyclopentadiene belongs to the “neutral” diene synthesis type where both diene and dienophile may play part of HOMO and LUMO components.



Plot of log rate constants versus reciprocal temperature for the reaction between hexachlorocyclopentadiene and allylacetylenes: (1) $\text{CH}_2=\text{CH}-\text{CH}_2\text{C}\equiv\text{CR}$. $\text{R} = \text{H}$, (2) $\text{C}(\text{CH}_3)_2\text{OCOCH}_3$, (3) $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CN}$, (4) $\text{C}(\text{CH}_3)_2\text{OH}$, (5) $\text{C}(\text{CH}_3)_2\text{OCH}_3$.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers UR-10 and UR-20 in 600–4000 cm^{-1} region with KBr, NaCl, and LiF prisms from mulls in mineral oil. ^1H NMR spectra were registered on spectrometers Tesla B-487 B (80 MHz) and Bruker M-250 (250 MHz) from solutions in carbon tetrachloride, internal reference HMDS. The purity of the products obtained was checked by TLC on Silufol UV-254 plates with fixed silica gel layer, eluent benzene-ether, 3:2, development in iodine vapor. Yields, physical constants, and elemental analyses are listed in Table 1. The kinetic experiments on diene condensation were carried out in ampules at molar ratio diene:dienophile equal to 1:1, solvent toluene. The reaction monitoring was carried out by GLC with the use of LKhM-8MD chromatograph [column 200×0.4 cm, stationary phase SE-30 on Chromaton-W (3%), flow rate of carrier gas 30 ml min^{-1}]. The rate constants of the second order process were calculated from consumption of diene in time with accuracy $\pm 5\%$. The values given are averages from three parallel runs. In the kinetic experiments were used the freshly prepared samples of diene and dienophile. Compounds **Va-c**, **VIa-c** were prepared before [4, 6] and their constants were consistent with those published.

General procedure for preparation of polychlorobicyclic adducts of acetylene series Vd-g, VI d-g, VIIb, h. A mixture of 0.1 mol of diene **I**, **II** and 0.1 mol of dienophile **IIIa-g**, **IVb, h** was heated for 6–10 h in the presence of 0.05 g of hydroquinone in a sealed ampule at 90–120°C. The products were subjected to vacuum distillation.

1,2,3,4,5,7,7-heptachloro-5-(propyn-2-yl)bicyclo[2.2.1]heptene-2 (X). A mixture of 4.3 g (0.01 mol) of 1,2,3,4,5,7,7-heptachloro-5-(4-methyl-4-hydroxypentynyl)bicyclo[2.2.1]heptene-2 and 0.15 g of potassium hydroxide powder was subjected to a vacuum distillation. The heating rate ensured slow distilling off of decomposition products (the acetone obtained was collected in a coiled trap). IR spectrum (ν , cm^{-1}): 3320 ($\equiv\text{C-H}$), 2125 ($\text{C}\equiv\text{C}$), 1610 ($\text{C}=\text{C}$), 765 (C-Cl). ^1H NMR spectrum (δ , ppm): 2.66 d (1H, H^6), 1.72 d (1H, H^6), 3.05 s (2H, $\text{H}^{7,7'}$), 2.18 t (1H, H^8); $J_{6,6'}$ 12.3.

Similarly from compound **VIIIb** was obtained compound **XII**. IR spectrum (ν , cm^{-1}): 3330 ($\equiv\text{C-H}$), 2130 ($\text{C}\equiv\text{C}$), 1615 ($\text{C}=\text{C}$), 760 (C-Cl). ^1H NMR spectrum (δ , ppm): 2.61 d (1H, H^6), 1.69 d (1H, H^6), 2.95 s (2H, $\text{H}^{7,7'}$), 2.15 t (1H, H^8), 3.52 d [6H, (OCH_3)₂]; $J_{6,6'}$ 11.9.

1,2,3,4,7,7-Hexachloro-5-(propadien-1,2-yl)bicyclo[2.2.1]heptene-2 (XIII). A mixture of 3.9 g (0.01 mol) of 1,2,3,4,7,7-hexachloro-5-(4-methylhydroxy-2-pentynyl)bicyclo[2.2.1]heptene-2, 1.5 g of powdered potassium hydroxide, and 20 ml of toluene was heated to 110–115°C for 3 h. Then the reaction mixture was washed with water, extracted with ether, and dried with magnesium sulfate. The solvents were distilled off, the residue was distilled in a vacuum to afford compound **XIII**. IR spectrum (ν , cm^{-1}): 1960, 1615, 955, 765. ^1H NMR spectrum (δ , ppm): 3.10 m (1H, H^5), 2.60 d.d (1H, H^6), 1.90 d.d (1H, H^6), 5.90 t (1H, H^7), 5.15 d (2H, $\text{H}^{8,8'}$); $J_{6,6'}$ 11.8.

In a similar way from adducts **VIIb**, **VIIIb**, **VIIIb** were obtained respectively the following allenes.

Compound XIV. IR spectrum (ν , cm^{-1}): 1955, 1605, 960, 780. ^1H NMR spectrum (δ , ppm): 2.64 d (1H, H^6), 1.68 d (1H, H^6), 5.95 t (1H, H^7), 5.12 d (2H, $\text{H}^{8,8'}$); $J_{6,6'}$ 11.7.

Compound XV. IR spectrum (ν , cm^{-1}): 1965, 1610, 950, 770. ^1H NMR spectrum (δ , ppm): 3.05 m (1H, H^5), 2.75 d.d (1H, H^6), 1.80 d.d (1H, H^6), 5.85 t (1H, H^7), 5.20 d (2H, $\text{H}^{8,8'}$), 3.55 d [6H, (OCH_3)₂]; $J_{6,6'}$ 12.1.

Compound XVI. IR spectrum (ν , cm^{-1}): 1960, 1615, 955, 760. ^1H NMR spectrum (δ , ppm): 2.58 d (1H, H^6), 1.74 d (1H, H^6), 5.93 t (1H, H^7), 5.17 d (2H, $\text{H}^{8,8'}$), 3.50 d [6H, (OCH_3)₂]; $J_{6,6'}$ 12.2.

1,1-Dimethyl-2,5-hexadien-1-ol (XIX). To a solution of 12.4 g (0.1 mol) of allylethynyl dimethylcarbinol in 30 ml of ether was added 4 ml of water and 7.4 g of coppered zinc dust. The suspension was stirred under reflux for 11 h at 40–54°C. Then was again added a portion of the coppered zinc dust with water, and the stirring was continued for 23 h. The third portion of the coppered zinc dust and water was added, and the stirring was continued for another 10 h at the same temperature. After appropriate workup we obtained 6.1 g (55.6%) of the diene alcohol.

Similarly to dienol **XIX** from alcohols **Vb**, **VIIb** were obtained compounds **XVII**, **XVIII**. Compound **XVII**, IR spectrum (ν , cm^{-1}): 3640, 1640, 760; ^1H NMR spectrum (δ , ppm, CCl_4): 4.50 m (H^5), 1.51 m (H^6), 2.55 m (H^6), 2.40 m (H^8), 4.90 m (H^9), 5.0 m (H^{10}), 1.10 s and 1.15 s (H^{11}), 1.72 s (1H, OH). Compound **XVIII**, IR spectrum (ν , cm^{-1}): 3620, 1660, 750; ^1H NMR spectrum (δ , ppm): 3.95 m (H^5), 1.58 m (H^6), 3.0 m (H^6), 3.28 s (H^7), 2.45 m (H^8), 4.85 m (H^9), 5.52 d (H^{10}), 1.32 m (H^{11}), 3.20 s (1H, OH).

REFERENCES

1. Grigor'ev, A.A., Ioffe, A.E., and Sadovskaya, T.P., *Khim. Prom.*, 1983, no. 7, pp. 393-398.
2. Motsarev, G.V. and Moskovtsev, V.V., *Khim. Prom.*, 1981, no. 8, pp. 17-19.
3. Feld'blyum, V.Sh., *Sintez i primeneniye nepredel'nykh tsiklicheskiykh uglevodorodov* (Synthesis and Application of Unsaturated Hydrocarbons), Moscow: Khimiya, 1982, pp. 17-44, 134-165.
4. Veliev, M.G., Guseinov, M.M., Yanovskaya, L.A., and Gakhramanov, R.F., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, no. 11, pp. 2586-2589.
5. Veliev, M.G., Chalabieva, A.Z., Gakhramanov, R.F., and Shatirova, M.I., *Zh. Org. Khim.*, 1993, vol. 29, no. 9, pp. 1798-1904.
6. Veliev, M.G., Guseinov, M.M., Yanovskaya, L.A., Mamedov, E.Sh., and Bairamov, A.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 16, pp. 1358-1362.
7. Veliev, M.G., Guseinov, M.M., Yanovskaya, L.A., and Burstein, K.Ya., *Tetrahedron*, 1985, vol. 41, no. 4, pp. 749-761.
8. Veliev, M.G., Chalabieva, A.Z., Gakhramanov, R.F., and Mustafaev, A.M., *Zh. Org. Khim.*, 1994, vol. 30, no. 1, pp. 40-54.
9. Marchand, R. and Rose, E., *J. Am. Chem. Soc.*, 1968, vol. 90, no. 14, pp. 3724-3728.
10. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, New York: Wiley & Sons, 1974.
11. Samuilov, Ya.D. and Konovalov, A.I., *Usp. Khim.*, 1984, vol. 53, no. 4, pp. 566-582.
12. Sustmann, R.A., *Tetrahedron Lett.*, 1971, no. 29, pp. 2721-2724.
13. Bingham, R.C., Demar, M., and Lo, D.H., *J. Am. Chem. Soc.*, 1975, vol. 97, no. 6, pp. 1285-1293.
14. Sharygin, P.P. and Burshtein, K.Ya., *Usp. Khim.*, 1981, vol. 56, no. 8, pp. 1345-1375.
15. Burshtein, K.Ya., Anikin, N.A., Yanovskaya, L.A., Veliev, M.G., and Guseinov, M.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, no. 8, pp. 1909-1912.
16. Denisov, E.T., *Kinetika gomogenykh khimicheskikh reaktsii* (Kinetics of Homogeneous Chemical Reactions), Moscow: Vysshaya shkola, 1978.
17. Wasserman, A., *Diels-Alder Reactions*, New York: Elsevier, 1965.
18. Konovalov, A.I., *Usp. Khim.*, 1983, vol. 52, no. 11, pp. 1852-1878.