

## Diels–Alder Reaction of Polychlorocyclopentadienes with Vinyl- and Allylacetylene Dienophiles

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**Abstract**—Diels–Alder reactions of 1,2,3,4-tetrachloro-, 1,2,3,4-tetrachloro-5,5-dimethoxy-, and hexachlorocyclopentadienes with vinyl- and allylacetylene dienophiles were studied. Kinetic parameters of these reactions were determined, and the cycloaddition processes were assigned to the “neutral” type involving symmetric arrangement of the highest occupied and lowest unoccupied molecular orbitals of the diene and dienophile. Vinylacetylene derivatives were found to be more reactive than allylacetylenes. Increase in the number of chlorine atoms in the bicycloheptene fragment of the adduct favors its acetylene–allene isomerization.

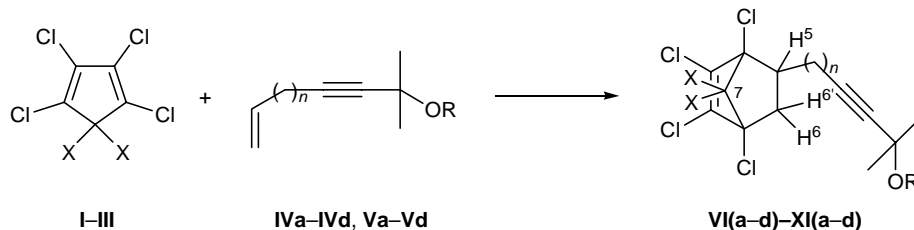
High reactivity of conjugated and nonconjugated enynes is widely utilized in organic synthesis [1–4], in particular for the synthesis of new cyclic adduct via Diels–Alder reaction [5–9]. However, their behavior in cycloaddition processes has been studied insufficiently, while information on the relative reactivity of 1,3- and 1,4-enynes in Diels–Alder reactions (except for 1,3-cyclohexadiene [10]) is absent at all.

We previously studied Diels–Alder reactions of some vinyl- and allylacetylene derivatives with 1,3-cyclohexadiene, hexachlorocyclopentadiene (**I**), and tetrachloro-5,5-dimethoxycyclopentadiene (**II**) [10–13]. We found that these reactions occur regioselectively at the double bond of enynes to afford the corresponding *endo* adducts. The kinetics of the reactions of allylacetylene compounds with diene **I** were studied, their activation parameters were determined, and analysis in terms of the molecular orbital perturbation theory was performed. 1,3-Cyclohexadi-

ene was found to be less reactive in the diene condensation with vinylacetylene and its derivatives than with allylacetylene and the corresponding derivatives. It was also shown that the reactivity of the above systems depends not only on donor–acceptor properties but also on the localization energy [12] and that 1,3-cyclohexadiene reacts according to the “normal” Diels–Alder pattern while reactions of allylacetylene and its derivatives with diene **I** follow the “neutral” scheme [13].

In continuation of our studies on the reactivity of conjugated and nonconjugated enynes in Diels–Alder reactions with electron-donor [12] and electron-acceptor dienes [13], in the present work we examined the relative reactivity of polychlorinated cyclic dienes, hexachlorocyclopentadiene (**I**), 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**II**), and 1,2,3,4-tetrachlorocyclopentadiene (**III**) toward vinyl- and allylacetylene dienophiles **IV** and **V**, as well as some

Scheme 1.



**I, VI, IX**, X = Cl; **II, VII, X**, X = OMe; **III, VIII, XI**, X = H; R = H (**a**), Me (**b**), COMe (**c**), CH<sub>2</sub>CH<sub>2</sub>CN (**d**);  
**IV, VI–VIII**, n = 0; **V, IX–XI**, n = 1.

**Table 1.** Yields, physical constants, and elemental analyses of compounds **VIb–VIIIb**, **XIa–XId**, **XIIb**, **XIIIa**, and **XIVa–XIVc**<sup>a</sup>

Comp. no.	Yield, %	bp, °C ( <i>p</i> , mm)	$n_D^{20}$	$d_4^{20}$	Found, %			Formula	Calculated, %		
					C	H	Cl		C	H	Cl
<b>VIb</b>	86.3	167–168 (2)	1.5335	1.4068	39.45	3.10	53.40	C <sub>13</sub> H <sub>12</sub> Cl <sub>6</sub> O	39.33	3.05	53.59
<b>VIIIb</b>	90.2	160–161 (1)	1.5143	1.2877	46.30	4.59	36.63	C <sub>15</sub> H <sub>18</sub> Cl <sub>4</sub> O <sub>3</sub>	46.42	4.67	36.54
<b>VIIIb</b>	95	139–140 (1.5)	1.5177	1.2919	47.68	4.26	43.18	C <sub>13</sub> H <sub>14</sub> Cl <sub>4</sub> O	47.59	4.30	43.23
<b>XIa</b>	85.0	160–162 (1)	1.5625	1.4815	48.74	4.64	44.23	C <sub>13</sub> H <sub>14</sub> Cl <sub>4</sub> O	47.56	4.30	43.23
<b>XIb</b>	90.3	138–140 (1)	1.4880	1.3865	48.95	4.83	42.10	C <sub>14</sub> H <sub>16</sub> Cl <sub>4</sub> O	49.16	4.72	41.46
<b>XIc</b>	74.5	144–146 (1)	1.5005	1.4140	49.10	4.40	37.95	C <sub>15</sub> H <sub>16</sub> Cl <sub>4</sub> O <sub>2</sub>	48.65	4.36	38.32
<b>XId</b>	68.3	153–154 (2)	1.5295	1.4630	51.10	4.55	37.11	C <sub>16</sub> H <sub>17</sub> Cl <sub>4</sub> NO	50.40	4.50	37.22
<b>XIIb</b>	87.0	128–129 (1)	1.5644	1.4196	44.69	3.12	52.20	C <sub>10</sub> H <sub>8</sub> Cl <sub>4</sub>	44.48	2.99	52.53
<b>XIIIa</b>	75.5	135–136 (1.5)	1.5465	1.3696	44.54	3.16	52.28	C <sub>10</sub> H <sub>8</sub> Cl <sub>4</sub>	44.48	2.99	52.53
<b>XIVa</b>	85.5	136–137 (1.5)	1.5533	1.4454	41.77	3.62	49.06	C <sub>10</sub> H <sub>10</sub> Cl <sub>4</sub> O	41.70	3.50	49.24
<b>XIVb</b>	81.0	156–157 (1)	1.5499	1.4414	41.50	4.11	40.60	C <sub>12</sub> H <sub>14</sub> Cl <sub>4</sub> O <sub>3</sub>	41.41	4.05	40.75
<b>XIVc</b>	74.4	152–153 (1)	1.5616	1.5979	33.76	2.35	59.48	C <sub>10</sub> H <sub>8</sub> Cl <sub>6</sub> O	33.65	2.26	59.60

<sup>a</sup> The physical constants and spectral parameters of compounds **VIa**, **VIc**, **VId**, **VIIa**, **VIIc**, **VIIId**, **VIIIa**, **VIIIc**, **VIIIId**, **IXa–IXd**, **Xa–Xd**, **XIIa**, and **XIIb–XIIIe** were reported previously [8, 9, 13, 20].

chemical transformations of the polychlorinated bicyclic adducts having a terminal triple bond in the side chain.

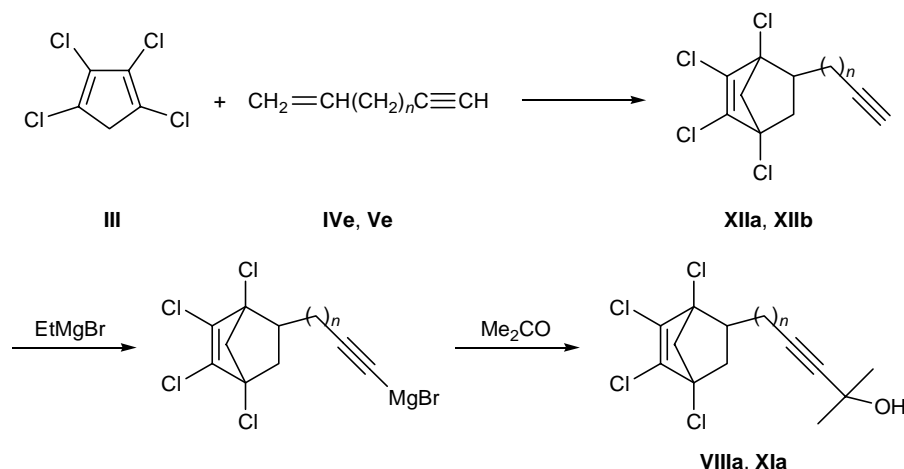
Polychlorocyclopentadienes **I–III** readily reacted with an equimolar amount of compounds **IVa–IVd** and **Va–Vd** at 100–120°C to give the corresponding bicyclic *endo*-adducts **VI–XI** (Scheme 1). The reactions occurred regioselectively at the double bond of dienophiles **IV** and **V** while the triple bond was not involved, and it appeared in the side chain, as in the adducts obtained previously [7–10].

The purity of the products was checked by TLC, and their structure was confirmed by the data of elemental analysis (Table 1) and IR and <sup>1</sup>H NMR spectroscopy. The *endo* configuration of the adducts obtained from dienes **I** and **II** was established on the basis of the <sup>1</sup>H NMR spectra by comparing spin–spin coupling constants with those found for structurally related bicyclic compounds. The adducts derived from tetrachlorocyclopentadiene **III** were rigorously assigned *endo* configuration by analysis of proton signals with a long-range coupling constant ( $J_{endo-6,-syn-7} = 2.15$  Hz). The coupling constants for the *endo*-6-H, *exo*-6'-H, and 5-H protons unambiguously indicate that the substituent occupies the *endo* position [14–17]. The *endo*-6-H proton (upfield signal) is coupled with *exo*-

6'-H ( $J_{6,6'} = 12.5–12.7$  Hz) and 5-H ( $J_{5,6} = 3.9–4.0$  Hz) in the spectra of adducts **VIa–VId**, **VIIa–VIIId**, **IXa–IXd**, and **Xa–Xd**, which is in complete agreement with published data [14, 15]. An additional support for the assumed stereochemical structure of adducts **VI**, **VIIa**, **IX**, and **X** is given by the vicinal coupling constant  $J_{5,6'} = 9.0–9.6$  Hz for 5-H, 6-H, and 6'-H,  $\delta$ , ppm: 2.8–3.0 m (*exo*-5-H), 2.5–2.6 d.d (*exo*-6'-H), 1.70–1.85 d.d (*endo*-6-H). The IR spectra of bicyclic acetylenic alcohols **VIa** and **IXa** contained strong absorption bands in the region of 3400 cm<sup>-1</sup>, which are typical of hydroxy group. In addition, absorption bands at 2240 (C≡C) and 1600 cm<sup>-1</sup> (C=C) were present [16].

It should be noted that Diels–Alder reactions of diene **III** with dienophiles of the vinylacetylene series were studied poorly, as compared to dienes **I** and **II** [7, 18, 19], while its reactions with allylacetylene dienophiles were not reported at all. We have found that, like other polychlorinated cyclopentadienes [10–13], diene **III** reacts with vinylacetylene at 50–60°C and with allylacetylene at 80–100°C, affording the corresponding adducts exclusively at the double bond. Products **XIIa** and **XIIb** with a terminal triple bond were thus obtained in up to 80% yield (Scheme 2). Compounds **XII** attract interest from the viewpoint of their further transformations. For

Scheme 2.



**IVe, XIIa**,  $n = 0$ ; **Ve, XIIb**,  $n = 1$ .

example, treatment of **XIIa** and **XIIb** with organo-magnesium reagents gives the corresponding Iotsitch compounds. Reactions of the latter with acetone lead to formation of polychlorinated bicyclic acetylenic alcohols **VIIIa** and **XIa**. This transformation confirms the structure of adducts **VIIIa** and **XIa** (Table 1) obtained directly by the Diels–Alder reaction.

The structure of compounds **XIIa** and **XIIb** was confirmed by the IR and  $^1\text{H}$  NMR spectra. In the IR spectra we observed absorption bands at 3300, 2130, and 1600  $\text{cm}^{-1}$ , which are characteristic of  $\equiv\text{C-H}$ ,  $\text{C}\equiv\text{C}$ , and  $\text{C}=\text{C}$  bonds, respectively [16]. Alcohols **VIIIa** and **XIa** showed in the IR spectra strong absorption bands at 3400  $\text{cm}^{-1}$  due to hydroxy group. Proton at the terminal triple bond in **XIIa** and **XIIb** gives a singlet at  $\delta$  2.50 ppm in the  $^1\text{H}$  NMR spectra.

It is known that the main electronic factor responsible for the reactivity of addends in Diels–Alder

reactions includes intermolecular interactions which stabilize the transition state and depend on donor–acceptor properties of the diene and dienophile [20, 21]. In addition, the energy of localization (1,4 for dienes and 1,2 for dienophiles) is taken into account. It destabilizes the transition state and depends on the ease of rupture of the initial  $\pi$ -systems of the diene and dienophile upon formation of the adduct.

In order to estimate the reactivity of vinyl- and allylacetylene derivatives we examined the kinetics of their Diels–Alder reactions with dienes **II** and **III** and compared the results with those found for diene **I** [13]. We also analyzed the reactions of diene **III** with such dienophiles as butadiene, pentadiene, vinylacetylene, and allylacetylene in terms of the molecular orbital perturbation theory. For this purpose, we performed MINDO-3 quantum-chemical calculations [22] of the above molecules and determined the energies of the

**Table 2.** Energies of the lowest unoccupied (LUMO) and highest occupied molecular orbitals (HOMO) of 1,2,3,4-tetrachlorocyclopentadiene (**III**, **A**) and some dienophiles **B**

Diene ( <b>A</b> ) and dienophiles ( <b>B</b> )	$E_{\text{HOMO}}$ , eV	$E_{\text{LUMO}}$ , eV	$E_1 = E_{\text{LUMO}(\text{B})} - E_{\text{HOMO}(\text{A})}$ , eV	$E_2 = E_{\text{LUMO}(\text{A})} - E_{\text{HOMO}(\text{B})}$ , eV	$E_3 = E_{\text{LUMO}(\text{B})} - E_{\text{HOMO}(\text{B})}$ , eV
1,2,3,4-Tetrachlorocyclopentadiene ( <b>A</b> )	−8.983	−0.670	8.313 <sup>a</sup>	–	–
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ( <b>B</b> )	−8.853	1.125	10.108	8.183	9.978
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ ( <b>B</b> )	−9.526	1.699	10.673	8.856	11.221
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ ( <b>B</b> )	−9.261	1.466	10.449	8.591	10.727
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$ ( <b>B</b> )	−9.758	1.737	10.740	10.428	11.495

<sup>a</sup>  $E_{\text{LUMO}(\text{A})} - E_{\text{HOMO}(\text{A})}$  ( $E_4$ ).

**Table 3.** Kinetic parameters of the Diels–Alder reactions of vinylacetylenes **IVa–IVd** with dienes **I–III**

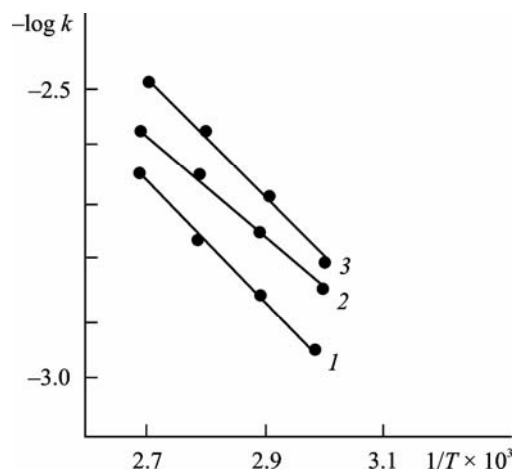
Substituent R in <b>IVa–IVd</b>	$k \times 10^{-4}, \text{l mol}^{-1} \text{min}^{-1} (80^\circ\text{C})$			$E_a, \text{kJ/mol}$			$-\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$		
	<b>I</b>	<b>II</b>	<b>III</b>	<b>I</b>	<b>II</b>	<b>III</b>	<b>I</b>	<b>II</b>	<b>III</b>
CH <sub>3</sub>	23.1	45.6	59.1	16.8	28.3	36.4	278.3	202	185
H	22.8	41.3	48.5	23.0	34.2	45.1	261.2	196	179
CH <sub>2</sub> CH <sub>2</sub> CN	22.4	40.8	43.9	18.1	40.8	51.2	252.0	182	168
COCH <sub>3</sub>	18.0	33.9	38.2	23.8	35.4	49.3	241.0	176	159

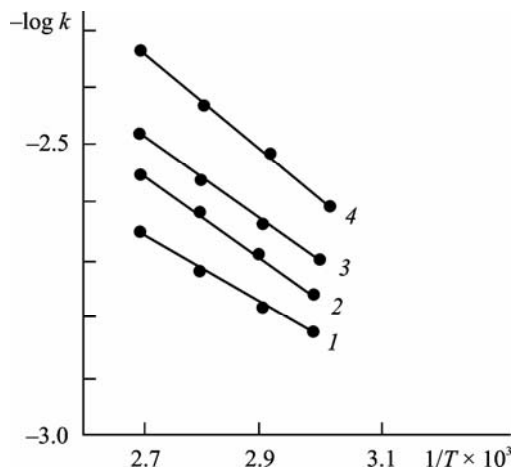
corresponding highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). The differences  $\Delta E$  between the LUMO energy of the diene and HOMO energy of the dienophile are given in Table 2. The obtained data suggest that Diels–Alder reactions between vinyl- and allylacetylene derivatives and diene **III** can follow the neutral pattern. Introduction of a methylene unit between the vinyl and ethynyl moieties (in going from vinylacetylene to allylacetylene) leads to increase of the LUMO energy and decrease of the HOMO energy, which implies reduction of the dienophilic activity of the double bond in allylacetylene. In fact, allylacetylene reacts with diene **III** at 80–100°C, while the reaction with vinylacetylene occurs at a lower temperature (50–60°C). The data in Table 2 indicate that vinyl- and allylacetylene derivatives are stronger electron donors than diene **III**. Therefore, the reactivity of dienophiles **IVa–IVd** and **Va–Vd** should increase with rise in their electron-donor properties.

In order to compare the reactivity of dienes **I–III** with regard to the nature and size of the geminal substituents we studied the kinetics of their condensation with vinyl- and allylacetylene dienophiles **IVa–IVd** and **Va–Vd**. The kinetic measurements were performed by GLC, following decrease in the diene concentration in the reaction mixture. The rate constants were calculated from the experimental kinetic curves for diene consumption using the second-order equation. The logarithms of the rate constants were linear in the reciprocal temperature. From the slopes of the semilog straight lines we calculated the corresponding energies of activation (Table 3) [23]. The energies of activation and rate constants thus determined clearly indicate the general trend in variation of the diene reactivity which decreases in the series **III** > **II** > **I**: the rate constants at 80°C are  $59.1 \times 10^{-4}$ ,  $45.6 \times 10^{-4}$ , and  $23.1 \times 10^{-4} \text{l mol}^{-1} \text{min}^{-1}$ , respectively. As might be expected, diene **I** is less reactive than **II** and **III**.

The presence of electronegative chlorine atoms in diene **I** makes the system electron-deficient. Replacement of the geminal chlorine atoms by methoxy groups partially compensates deficit of electron density in the cyclopentadiene ring, favoring formation of intermediate complex and its subsequent stabilization via formation of the final product. Insofar as diene **II** contains two electron-donor groups, it reacts with dienophiles having electron-acceptor substituents much more readily than does diene **I**, and the diene reactivity changes in the series **III** > **II** > **I** (Fig. 1).

Study of the reactions of vinyl- (**IVa–IVd**) and allylacetylene dienophiles (**Va–Vd**) with polychlorinated dienes **I–III** showed that the former are more reactive (Fig. 2) [13], which is consistent with the results of quantum-chemical calculations (Table 2). The effect of substituents in vinylacetylenes **IVa–IVd** is the same as in allylacetylene derivatives [13]: the reactivity decreases in the following series of substituents R: CH<sub>3</sub> > H > CH<sub>2</sub>CH<sub>2</sub>CN > COCH<sub>3</sub>. The energy of activation  $E_a$  for the Diels–Alder reactions of 2-dimethyl-5-hexen-3-yn-2-ol (**IVa**) with dienes **I–III**

**Fig. 1.** Semilog temperature dependences of the rate constants for Diels–Alder reactions of dienes (1) **I**, (2) **II**, and (3) **III** with 2-methyl-5-hexen-3-yn-2-ol (**IVa**).



**Fig. 2.** Semilog temperature dependences of the rate constants for Diels-Alder reactions of diene **I** with vinyl-acetylene dienophiles  $\text{CH}_2=\text{CHC}\equiv\text{CCMe}_2\text{OR}$ : (1)  $\text{R} = \text{COMe}$ , (2)  $\text{R} = \text{CH}_2\text{CH}_2\text{CN}$ , (3)  $\text{R} = \text{H}$ , (4)  $\text{R} = \text{OMe}$ .

ranges from 16.8 to 51.2 kJ/mol, and the entropy of activation ( $-\Delta S^\ddagger$ ) changes from 159 to 278.3  $\text{J mol}^{-1} \times \text{K}^{-1}$  (Table 3). The high negative values of  $\Delta S$  correspond to a highly ordered transition state, in agreement with the assumption that these reactions follow a concerted mechanism involving a cyclic transition state [18].

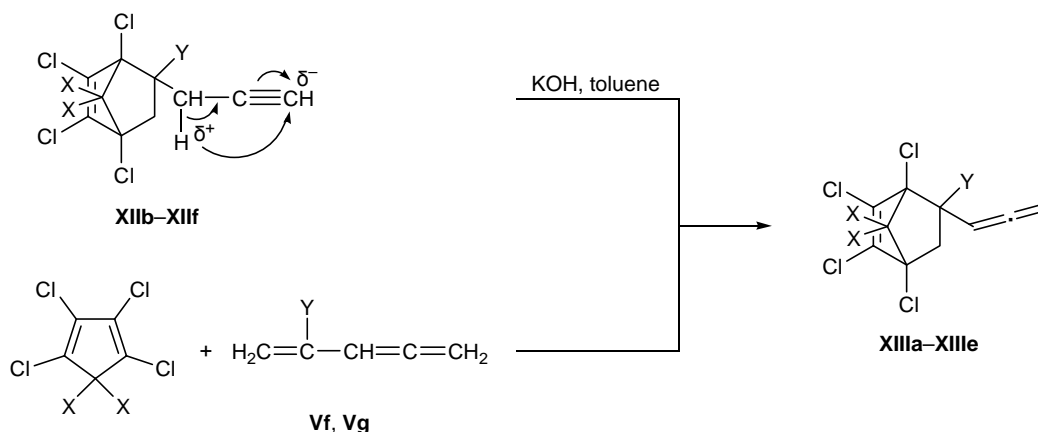
We previously showed that polychlorinated bicyclic adducts with a triple carbon-carbon bond in the  $\beta$ -position of the side chain (derived from 5-hexen-2-yn-1-ol [8, 13]), unlike those obtained from 4-penten-2-yn-1-ol [5, 24] (in which the triple bond appears in the  $\alpha$ -position of the side chain), undergo acetylene-allene isomerization in the presence of alkali. While

studying the synthetic potential of polychlorinated adducts with a side-chain acetylenic moiety we found that compounds **XIIb–XII f** having a terminal triple bond (in the  $\beta$ -position of the side chain) are converted into the corresponding allene derivatives **XIIIa–XIII e** in up to 75–95% yield on heating in toluene (100°C) in the presence of powdered potassium hydroxide (Scheme 3). Increase in the number of electronegative chlorine atoms in the bicycloheptene fragment facilitates the acetylene-allene isomerization. This follows from the yields of allenyl derivatives **XIIIa–XIII e**. The latter were also synthesized by Diels-Alder reaction of polychlorocyclopentadienes with vinyl-allenes **Vf** and **Vg** at 80–100°C (the reactions occurred at the vinyl group; Scheme 3).

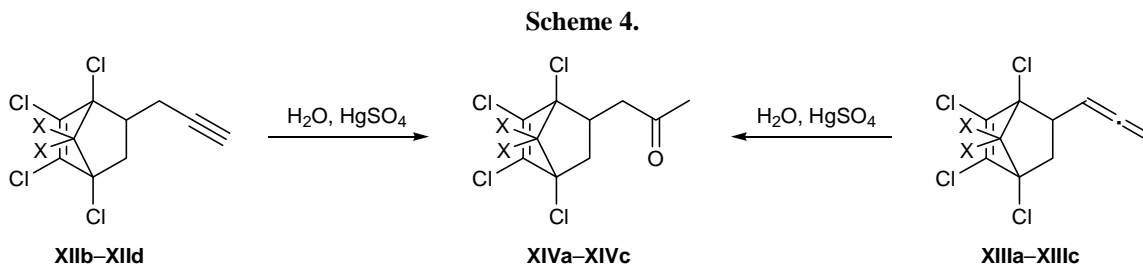
The IR spectra of compounds **XIIIa–XIII e** contained absorption bands at 1960, 1595, 1615, and 730–850  $\text{cm}^{-1}$ , which belong to stretching vibrations of the  $\text{C}=\text{C}=\text{C}$ ,  $\text{C}=\text{C}$ , and  $\text{C}-\text{Cl}$  bonds, respectively. No absorption typical of triple bond was observed. Protons of the allene fragment appeared in the  $^1\text{H}$  NMR spectra of **XIIIa–XIII e** at  $\delta$  5.0 (m,  $\text{CH}=\text{}$ ), and 4.70 ppm (m,  $=\text{CH}_2$ ). The physical constants and IR and  $^1\text{H}$  NMR spectra of compounds **XIIIa–XIII e** obtained by the two methods were identical.

By hydration of polychlorinated bicyclic acetylene and allene derivatives **XIIb–XII d** and **XIIIa–XIII c** according to Kucherov ( $\text{HgSO}_4$ , 80–85°C, 10 h) we obtained the corresponding ketones **XIVa–XIV c** in 75–85% yield (Scheme 4). Ketones **XIVa–XIV c** displayed in the IR spectra strong carbonyl absorption bands in the region 1725–1735  $\text{cm}^{-1}$ , while absorption typical of  $\text{C}\equiv\text{C}$  or  $\text{C}=\text{C}=\text{C}$  moiety was absent. The  $^1\text{H}$

**Scheme 3.**



**V**, **Y** = H (**f**), Cl (**g**); **XIIb**, **XIIIa**, **Y** = H, **X** = H; **XIIc**, **XIIIb**, **Y** = H, **X** = OMe; **XII d**, **XIIIc**, **Y** = H, **X** = Cl; **XIIe**, **XIII d**, **Y** = Cl, **X** = OMe; **XII f**, **XIII e**, **Y** = Cl, **X** = Cl.



NMR spectra of **XIVa–XIVc** contained no signals assignable to a terminal acetylene or allene moiety, but a sharp singlet from the methyl protons appeared at  $\delta$  1.98 ppm; protons of the side-chain  $\alpha$ -methylene group gave a multiplet at  $\delta$  2.0–2.3 ppm.

Thus the above chemical transformations open the way to difficultly accessible polychlorinated bicyclic allenes and ketones which can be used in organic synthesis for the preparation of new classes of compounds.

#### EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained on Tesla BS-487B (80 MHz) and Bruker M-250 (250 MHz) spectrometers from solutions in carbon tetrachloride using HMDS as internal reference. The purity of products was checked by TLC on Silufol UV-254 plates. Their yields, physical constants, and elemental analyses are given in Table 1.

The kinetics of the Diels–Alder reactions of vinylacetylene dienophiles with polychlorocyclopentadienes **I–III** were studied by GLC using an LKhM-8MD chromatograph (200  $\times$  0.4-cm column packed with 3% of SE-30 on Chromaton-W, carrier gas flow rate 30 ml/min). The progress of reactions was monitored following the consumption of dienes **I–III** [23]. The reactions were carried out in toluene with equimolar amounts of the reactants at 60–100°C (in ampules).

**Polychlorobicycloheptenes VIa–VIId, VIIa–VIIId, VIIIa–VIIIId, IXa–IXd, Xa–Xd, XIa–XIId, XIIa, and XIIb (general procedure).** *a.* A mixture of 0.1 mol of diene **I–III**, 0.1 mol of dienophile **IVa–IVe** or **Va–Ve**, and 0.05 g of hydroquinone was heated for 6–10 h at 90–120°C in a sealed ampule. The mixture was separated by vacuum distillation. Unreacted initial compounds were distilled off first, and the product was subjected to repeated distillation.

*b.* Acetone, 0.05 mol, was added dropwise to the Iotsitch compound prepared from 0.05 mol of metallic magnesium, 0.05 mol of ethyl bromide, and 0.05 mol of compound **XIIa** or **XIIb**. The mixture was heated for 4–5 h, decomposed with 5% hydrochloric acid (or with water), and extracted with diethyl ether. The extract was dried over  $\text{MgSO}_4$ , the solvent was distilled off, and the residue was subjected to vacuum distillation to isolate compound **VIIIa** or **XIa** (75 and 80%, respectively).

**Allenyl-substituted polychlorobicycloheptenes XIIIa–XIIIe (general procedure).** *a.* A mixture of 0.025 mol of compound **XIIb–XIIId**, 2 g of powdered potassium hydroxide, and 20 ml of toluene was stirred for 3 h at 110–115°C. The mixture was treated with water and extracted with diethyl ether. The extract was dried over  $\text{MgSO}_4$ , the solvent was distilled off, and the residue was subjected to vacuum distillation to isolate compounds **XIIIa–XIIIe** (Table 1).

*b.* A mixture of 0.05 mol of vinylallene **Vf** or **Vg**, 0.05 mol of diene **I–III**, and 0.05 g of hydroquinone was heated for 16 h at 80–90°C in a sealed ampule. The resulting mixture was subjected to fractional distillation under reduced pressure to isolate compounds **XIIIa–XIIIe** in 60–70% yield.

**Ketones XIVa–XIVc (general procedure).** A mixture of 0.018 mol of adduct **XIIb–XIIId** or **XIIIa–XIIIc**, 0.4 ml of concentrated sulfuric acid, 0.2 g of  $\text{HgSO}_4$ , and 10 ml of water was heated for 10–12 h at 80–85°C under vigorous stirring. The products were extracted into diethyl ether, the extract was dried over  $\text{CaCl}_2$ , and evaporated, and the residue was subjected to vacuum distillation.

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