

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of 1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl Haloacetates

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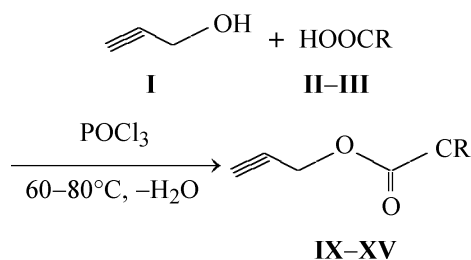
Abstract—Hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl haloacetates were prepared by [4+2]-cycloaddition of hexachlorocyclopentadiene to the corresponding propargyl haloacetates.

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Compounds of the bicyclo[2.2.1]heptene series exhibit diverse useful properties. Rigid framework structures of these compounds with fixed substituents are promising models for studying structure–property relationships [1].

Polyhalogenated bicyclic esters with other functional groups are widely used for imparting fireproof properties to polymeric materials, and also as modifiers, epoxy resin hardeners, and biologically active substances [2, 3]. Halogen-containing functionally substituted norbornenes are used as starting compounds for preparing important commercial chemicals [4–7]. Studies of reactions involving hexachlorocyclopentadiene (HCCPD) and its derivatives, along with practical significance, are of scientific interest for elucidating the mechanism of Diels–Alder reactions [8].

Proceeding with studies in the field of the synthesis of polyhalogenated bicyclic esters [9–14], we prepared and examined polyhalonorbornadienylmethyl haloacetates. First, by the esterification procedure, we prepared propargyl haloacetates **IX–XV** by the following scheme:



R = CH₂Cl (**II**, **IX**), CHCl₂ (**III**, **X**), CCl₃ (**IV**, **IX**); CH₂Br (**V**, **XII**), CHBr₂ (**VI**, **XIII**), CBr₃ (**VII**, **XIV**), CF₃ (**VIII**, **XV**).

Table 1. The physicochemical properties of the esters prepared

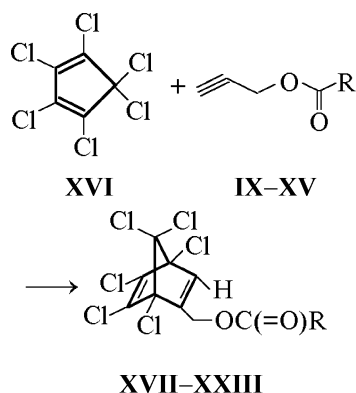
Compound	T_b , °C/P, mm Hg	n_D^{20}	d_4^{20}	Yield, %
Propargyl monochloroacetate IX	70–71/10	1.4610	1.2230	65
Propargyl dichloroacetate X	75/8	1.4730	1.3615	55
Propargyl trichloroacetate XI	75–76/9	1.4771	1.4972	50
Propargyl monobromoacetate XII	79–81/10	1.4875	1.5675	60
Propargyl dibromoacetate XIII	49–51/1	1.4566	1.7270	60
Propargyl tribromoacetate XIV	84–85/1	1.5456	2.2865	54
Propargyl trifluoroacetate XV	75/3	1.3480	1.2373	48

Table 2. Physicochemical characteristics and elemental analysis of hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl haloacetates

Compound	T_b , °C (1 mm Hg)	n_D^{20}	d_4^{20}	Found, %			Formula	Calculated, %		
				C	H	Hlg		C	H	Hlg
XVII	174	1.5500	1.6473	29.13	1.16	61.04	$C_{10}H_5Cl_7O_2$	29.63	1.24	61.23
XVIII	165–166	1.5550	1.6840	28.60	1.30	65.40	$C_{10}H_4Cl_8O_2$	27.31	0.92	64.49
XIX	178–179	1.5541	1.7146	24.85	0.44	66.53	$C_{10}H_3Cl_9O_2$	25.33	0.64	67.29
XX	161–162	1.5595	1.7515	30.46	1.04	59.26	$C_{10}H_5Cl_6BrO_2$	26.70	1.12	65.06
XXI	165–167	1.5610	1.8607	29.16	0.86	61.35	$C_{10}H_4Cl_6Br_2O_2$	22.72	0.76	70.47
XXII	180–181	1.5690	2.1480	20.06	0.44	76.20	$C_{10}H_3Cl_6Br_3O_2$	19.77	0.50	74.46
XXIII	104–105	1.5018	1.6718	27.73	0.55	63.11	$C_{10}H_3Cl_6O_2F_3$	28.27	0.71	63.49

The physicochemical properties of the esters prepared are given in Table 1.

The target products **XVII–XXIII** were prepared by the Diels–Alder reaction of HCCPD **XVI** with propargyl haloacetates **IX–XV**. The reaction follows the scheme



$\text{R} = \text{CH}_2\text{Cl}$ (**XVII**), CHCl_2 (**XVIII**), CCl_3 (**XIX**), CH_2Br (**XX**), CHBr_2 (**XXI**), CBr_3 (**XXII**), CF_3 (**XXIII**).

The reaction was performed in the temperature range 100–180°C for 2–14 h at the diene : dienophile molar ratio of 1 : 1 to 4 : 1. The physicochemical constants of the synthesized adducts **XVII–XXIII** are given in Table 2, and the influence of reaction conditions (temperature, time, reactant ratio) on the adduct yield is illustrated by Table 3.

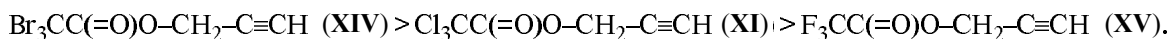
As seen from Table 3, one of the main parameters affecting the adduct formation rate is temperature. The influence of temperature was examined in the range 100–180°C, with the reaction of hexachlorocyclopentadiene with propargyl monobromoacetate **XII** as example. The yield of **XX** appeared to be strongly dependent on

temperature. Below 100°C, there is virtually no reaction. With an increase in the temperature from 100 to 160°C, the yield of adduct **XX** increases from 10 to 82%. With an increase in the diene : dienophile molar ratio from 1 : 1 to 3 : 1, the yield of adduct **XX** increases from 52 to 82%. Further increase in the molar ratio to 4 : 1 has virtually no effect on the yield: it increases to only 83%. An increase in the temperature to 180°C leads to a decrease in the yield of adduct **XX** to 71% and to partial tarring of the reaction mixture.

With propargyl mono-, di- and tribromoacetate as examples, we examined how the number of halogen atoms in dienophile molecules affects the yield of the corresponding adducts **XX–XXII**. Propargyl monobromoacetate reacts with hexachlorobutadiene more readily than do propargyl di- and tribromoacetate. The adduct yield at 160°C, reaction time of 12 h, and diene : dienophile ratio of 3 : 1 decreases from 82% for **XX** to 78% for **XXI** and 61% for **XXII**. That is, the dienophilic activity decreases with an increase in the number of halogen atoms:



To determine how the kind of the halogen atoms in the dienophile molecule affects their activity and adduct yield, we compared the reactions of [4+2]-cycloaddition of hexachlorocyclopentadiene to propargyl trihaloacetates **XI**, **XIV**, and **XV** under similar conditions (160°C, 12 h, diene : dienophile molar ratio 3 : 1). As judged from the yields, the compounds can be ranked in the following



82%

47%

40%

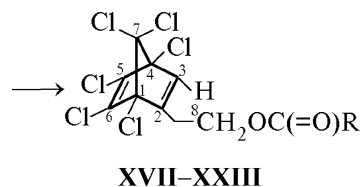
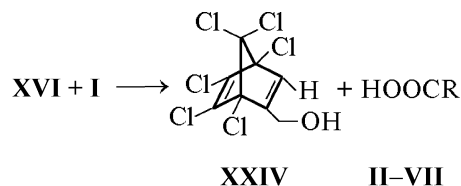
order with respect to the dienophilic activity:

This trend is apparently associated with an increase in the electronegativity of the substituent and a decrease in the nucleophilicity of the triple bond. Hexachlorocyclopentadiene reacts more readily with the more nucleophilic dienophile **XIV** (yield 83%) than with **XI** (47%) and **XV** (40%).

Thus, the optimal conditions for preparing adducts **XVII–XXIII** are 160°C, 12 h, and diene : dienophile molar ratio of 3 : 1.

The structures of the synthesized adducts **XVII–XXII** were confirmed by independent synthesis. By the reaction of hexachlorocyclopentadiene with propargyl alcohol **I**, following the procedure from [15], we prepared 2-hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hepta-2,5-diene **XXIV**. The subsequent esterification of **XXIV** with haloacetic acids **II–VIII**, performed as described in [16], yielded hexachloronorbornadiene-containing esters

XVII–XXIII:



All the physicochemical properties of compounds **XVII–XXIII** prepared by the two procedures are identical.

The structures of **XVII–XXIII** were confirmed by elemental analysis (Table 2) and by IR and ¹H NMR spectra. The purity was checked by TLC.

In the IR spectra of the compounds, there are strong absorption bands in the ranges 1760–1730 cm^{−1}, characteristic of the C=O group, and 1200–1050 cm^{−1}, characteristic of the ester C–O group. The C–Cl bands are observed at 840–650 cm^{−1}. The ethylene fragments absorb at 1600–1580 cm^{−1}, and the C–H groups at the double bond, at 3050–3045 cm^{−1}. The absorption bands of C–Br bonds in **XX–XXII** are observed at 640–600 cm^{−1}, and those of C–F bonds in **XXIII**, at approximately 1300 cm^{−1}.

In the ¹H NMR spectra of the adducts, the C=C–H protons in the norbornene ring (C³) give multiplets at δ 6.15–6.45 ppm. Two protons of the CH₂OOCR fragment give a triplet at δ 4.05–4.20 ppm, and protons of the CR substituent, a triplet at δ 3.30–3.70 ppm.

EXPERIMENTAL

The IR spectra of the compounds were recorded on a UR-20 spectrophotometer in the range 4000–400 cm^{−1}. The ¹H NMR spectra were taken on a Tesla BS-48 spectrometer (80 MHz) from solutions in CCl₄; the chemical shifts are given relative to TMS. TLC analysis was performed according to [17]. As a sorbent we used Al₂O₃ of Brockmann grade II. Heptane–acetone was

Table 3. Influence of reaction conditions on the yield of adducts **XVII–XXIII**

Dieno- phile	<i>T</i> , °C	<i>τ</i> , h	Diene : dienophile molar ratio	Yield, %
XII	100	12	3 : 1	10
XII	120	12	3 : 1	34
XII	140	12	3 : 1	75
XII	160	12	3 : 1	82
XII	180	12	3 : 1	71
XII	160	12	1 : 1	52
XII	160	12	2 : 1	65
XII	160	12	4 : 1	83
IX	160	12	3 : 1	74
X	160	12	3 : 1	59
XI	160	12	3 : 1	47
IX	160	2	3 : 1	7
IX	160	4	3 : 1	13
IX	160	6	3 : 1	24
IX	160	8	3 : 1	49
IX	160	10	3 : 1	69
IX	160	14	3 : 1	76
XIII	160	12	3 : 1	78
XIV	160	12	3 : 1	61
XV	160	12	3 : 1	40

an eluent. The plates were developed by irradiation with a mercury lamp equipped with a color filter.

Hexachlorocyclopentadiene **XVI** was prepared by the procedure described in [18], bp 104°C/9 mm Hg, n_D^{20} 1.5652, d_4^{20} 1.719.

Propargyl haloacetates **IX–XV** were prepared by the procedure described previously [16]. To 0.6 mol of haloacetic acids **II–VIII** protected from moisture, we added with vigorous stirring 0.6 mol of POCl₃ and then 0.9 mol of propargyl alcohol **I**. The mixture was stirred for 30 min. After the reaction completion, the mixture was extracted with ether. The ether solution was washed with a 5% NaHCO₃ solution and then with water to neutral reaction, after which it was dried over MgSO₄ and distilled.

Hexachloronorbornadienylmethyl haloacetates **XVII–XXIII** were prepared by the Diels–Alder reaction from HCCPD and the corresponding dienophiles **IX–XV**.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dienylmethyl monochloroacetate **XVII**. A mixture of 8.19 g (0.03 mol) of HCCPD and 1.33 g (0.01 mol) of **IX** was heated at 160°C for 12 h. Yield of adduct **XVII** 2.96 g (74%), bp 174°C/1 mm Hg, n_D^{20} 1.5500, d_4^{20} 1.6473. IR spectrum, ν , cm⁻¹: 670 (C–Cl), 1100 (C–O), 3045 (C=CH). ¹H NMR spectrum, δ , ppm: 3.40 t (2H, CH₂Cl), 4.1 t (2H, OCH₂), 6.2 (H, C=C–H). Found, %: C 29.13; H 1.16, Hlg 61.04. Calculated, %: C 29.63; H 1.24; Hlg 61.23.

Adducts **XVII–XXIII** were prepared similarly.

2-Hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene **XXIV** was prepared by the procedure described in [15]. Independent synthesis of **XVII–XXIII** was performed by esterification of alcohol **XXIV** with the corresponding haloacetic acids **II–VIII**, as described previously [16].

CONCLUSIONS

(1) Polyhalogenated norbornadienylmethyl esters were prepared by the Diels–Alder reaction of propargyl haloacetates with hexachlorocyclopentadiene.

(2) The optimal conditions for preparing the target products were found: 160°C, 12 h, diene : dienophile molar ratio 3 : 1. Under these conditions, the yield of the adducts is 40–82%.

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