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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of 1,4,5,6-Tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl Haloacetates

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Abstract—The possibility of preparing 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl haloacetates by the reaction of tetrachlorodimethoxycyclopentadiene with allyl haloacetates was examined. The effect of various factors on the product yield was studied, and the optimal synthesis conditions were found.

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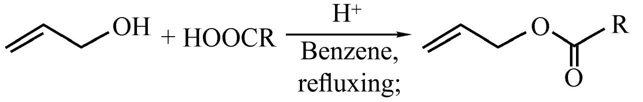
Halogenated bicyclic compounds containing various substituents are widely used as fire retardants for commercially important polymeric materials [1] and are convenient starting compounds for preparing halogen-substituted sterically hindered phenols [2–4] and α-diketones [5, 6]. Therefore, the development of synthesis procedures and study of properties of new polyhalogenated bicyclic compounds of the norbornene series are topical problems.

Here we report on the synthesis of 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl haloacetates by the Diels–Alder reaction of tetrachlorodimethoxycyclopentadiene with allyl haloacetates. The initial allyl esters **IX–XV** were prepared by common esterification of haloacetic acids **II–VIII** with allyl alcohol I:

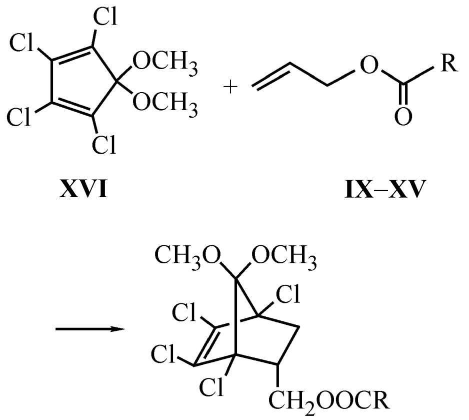


I **II–VIII** **IX–XV**

where R = CH_2Cl (**II, IX**), $CHCl_2$ (**III, X**), CCl_3 (**IV, XI**), CH_2Br (**V, XII**), $CHBr_2$ (**VI, XIII**), Br_3 (**VII, XIV**), CF_3 (**VIII, XV**).

The physicochemical data for **IX–XV** are given in Table 1.

Target products **XVII–XXIII** were prepared by the following scheme:



XVI **IX–XV** **XVII–XXIII**

where R = CH_2Cl (**XVII**), $CHCl_2$ (**XVIII**), CCl_3 (**XIX**), CH_2Br (**XX**), $CHBr_2$ (**XXI**), CBr_3 (**XXII**), CF_3 (**XXIII**).

The physicochemical characteristics of the synthesized adducts XVII–XXIII are given in Table 2.

The reaction was performed in the temperature interval 80–160°C for 2–14 h. The diene : dienophile molar ratio was 1 : 1 to 4 : 1. We examined the effect of these parameters on the product yield. The results are given in Table 3.

With allyl mono-, di-, and trichloroacetates as examples, we examined how the number of halogen atoms in dienophile molecules affects the yield of the adducts (**XVII, XVIII, XIX**, respectively). We found that, with an increase in the number of chlorine atoms

Table 1. Physicochemical characteristics of allyl haloacetates **IX–XV**

Comp.	Acid	T_b, °C/P, mm Hg	n_D^{20}	d_4^{20}	Yield, %
IX	Monochloro-acetic	43–44/5	1 .4460	1.1469	85
X	Dichloroacetic	63–64/10	1 .4544	1.3996	70
XI	Trichloroacetic	68–69/10	1.4632	1 .4648	75
XII	Monobromoacetic	73/10	1.4729	1.4329	65
XIII	Dibromoacetic	66–67/0	1.4704	1.4500	60
XIV	Tribromoacetic	80–82/1	1.5470	2.0061	45
XV	Trifluoroacetic	78–79	1.3364	1.1764	60

in dienophile molecules, at equal reaction temperature (160°C), time (10 h), and diene : dienophile ratio (3 : 1), the product yield increases (73.2% for **XVII**, 78.1% for **XVIII**, 95.1% for **XIX**), i.e., the dienophilic activity increases with an increase in the number of chlorine atoms. As seen from Table 3, the reaction time strongly affects the yield of 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl monochloroacetate **XVII** in the reaction of **XVI** with allyl monochloroacetate **IX**. As the reaction time is increased from 2 to 10 h, the yield of **XVII** increases from 13.4 to 73.2%. Further increase in the reaction time to 14 h does not lead to a significant increase in the yield (75.1%).

A study of the effect of the reaction temperature on the adduct yield, with the reaction of **XVI** with allyl trichloroacetate **XI** as example, showed that the yield of **XIX** strongly depended on temperature and increased from 11.2 to 95.1% with an increase in the temperature from 80 to 160°C. With an increase in the diene : dienophile molar ratio from 1 : 1 to 3 : 1, the yield of **XIX** increased from 71.4 to 95.1%. Further increase in the molar ratio to 4 : 1 adversely affected the yield: it decreased to 80.2%.

Thus, the optimal conditions for the synthesis of adducts **XVII–XXIII** are as follows: temperature 160°C, time 10 h, and diene : dienophile molar ratio 3 : 1.

The structure of adducts **XVII–XXIII** was proved by independent synthesis. By the reaction of tetrachlorodimethoxycyclopentadiene with allyl alcohol I, following the procedure from [7], we prepared 2-endo-hydroxymethyl-1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-ene **XXIV**. Its subsequent esterification with haloacetic acids **II–VIII** yielded bicyclic esters **XVII–XXIII** (see Scheme

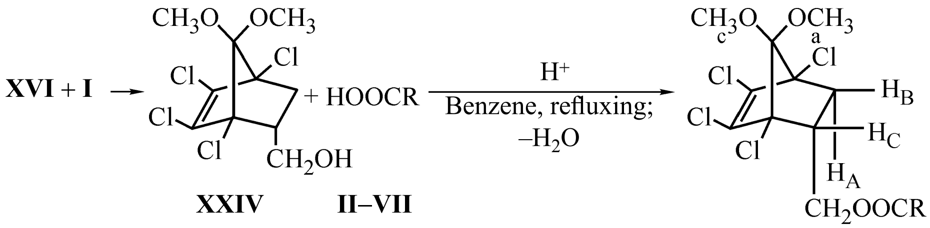
All the physicochemical characteristics of compounds **XVII–XXIII** prepared by alternative routes are identical.

The structures of **XVII–XXIII** were confirmed by elemental analysis (Table 2) and by IR and 1H NMR

Table 2. Properties of 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl haloacetates **XVII–XXIII**

Compound	T_b, °C/P, mm Hg	n_D^{20}	d_4^{20}	Found, %/Calculated, %			Formula
				C	H	Gas	
XVII	167-168/1	1.5299	1.5014	35.87 36.14	3.04 3.26	44.21 44.54	$C_{12}H_{13}C1_{5}0_{4}$
XVIII	172-173/1	1.5340	1.5368	33.2 32.4	2.8 2.6	49.1 48.2	$C_{12}H_{12}C1_{6}0_{4}$
XIX	176-179/1	1.5349	1.5840	30.64 30.80	2.01 2.35	52.74 53.16	$C_{12}H_{11}C1_{7}0_{4}$
XX	164-172/1	1.5370	1.5401	32.11 32.51	2.65 2.93	49.83 50.11	$C_{12}H_{13}C1_{4}Br0_{4}$
XXI	169-174/1	1.5415	1.7226	27.89 27.58	3.02 3.26	58.53 57.87	$C_{12}H_{12}C1_{4}Br_{2}0_{4}$
XXII	189-191/1	1.5592	1.9270	23.68 23.96	1.67 1.83	63.14 63.56	$C_{12}H_{11}C1_{4}Br_{3}0_{4}$
XXIII	150-152/1	1.4822	1.4557	34.05 34.45	2.18 2.63	47.43 47.61	$C_{12}H_{11}C1_{4}Br_{3}0_{4}$

Scheme.



XXIV **II–VII** **XVII–XXIII**

spectra. The purity was checked by TLC. We found that the reactions yield exclusively endo isomers of the adducts.

In the IR spectra of **XVII–XXIII**, there are strong absorption bands at 1760–1770 cm^{-1}, characteristic of the carbonyl group, and bands at 1275–1050 cm^{-1} characteristic of the ester C–O–C fragment. The C–Cl vibration bands are observed at 850–650 cm^{-1}. In the IR spectra of the bromo derivatives, there are strong C–Br absorption bands at 660–550 cm^{-1}. The ν(C–F) band in the spectrum of **XXIII** is observed at 1040 cm^{-1}. The ethylene moiety of the norbornene ring gives rise to vibration bands at 1556–1550 [ν(C=C)] and 3050–3045 cm^{-1} [ν(C–H) at double bond].

Table 3. Influence of the conditions of the Diels–Alder reaction of tetrachlorodimethoxycyclopentadiene **XVI** with allyl haloacetates **IX–XV** on the yield of adducts **XVII–XXIII**

Dienophile	*m*, °C	Diene : dienophile molar ratio	τ, h	Yield of adducts **XVII–XXIII**, %
IX	160	3:	10	73.2
X	160	3:	10	78.1
XI	160	3:	10	95.1
	80	3:	10	11.2
	100	3:	10	52.7
	120	3:	10	65.4
	140	3:	10	85.4
	160	1:	10	71.4
	160	2-	10	82.1
	160	4:	10	80.2
IX	160	3:	2	13.4
	160	3:	4	21.8
	160	3:	6	38.8
	160	3:	8	57.9
	160	3:	12	74.8
	160	3:	14	75.1
XII	160	3:	10	70.3
XIII	160	3:	10	71.4
XIV	160	3:	10	81.4
XV	160	3:	10	97.2

In the 1H NMR spectra of the adducts, in the high-field region, there are signals at 1.60–1.65 and 2.40–2.50 ppm, corresponding to HA and HB protons, with the geminal coupling constant *J* = –12 Hz. The vicinal coupling constants are J_{AC} = 4 and JBC = 9 Hz. The HC proton gives a multiplet at 3.0–3.1 ppm. Two strong singlets of syn- (s) and anti- (a) OCH_3 groups are observed at 3.40–3.45 and 3.55–3.60 ppm, respectively. Two protons of the $–CH_2OOCR$ group give a multiplet at 3.62–4.3 ppm.

The synthesized halogenated bicyclic esters were tested for fireproofing activity toward high-density polyethylene (HDPE). We found that these compounds impart to HDPE self-extinction and improve its physicomechanical and dielectric properties.

To make HDPE fireproof, we mainly used the halogenated compounds with synergistic additives (Sb_2O_3). Samples of polymeric materials were prepared by mixing the components on laboratory rolls (10–15 min at 150–160°C), followed by pressing into plates at 150°C.

The fire resistance of polymeric compounds was evaluated by the fire pipe method. Compounds were rated as self-extinguishing if after double ignition with flame for 10 s the combustion ceased before reaching the depth of 120 mm. No self-extinction was observed without synergistic additive (Sb_2O_3). Introduction of Sb_2O_3 into HDPE as the only additive did not enhance the fire resistance, either. However, the use of Sb_2O_3 in combination with **XVII–XXIII** gave rise to the fireproofing effect. The self-extinction may be due to formation of antimony trihalide in the combustion zone.

The results of testing 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl trichloroacetate **XIX** for the flame-extinguishing activity are given in Table 4. With the other adducts, the results were similar. The new fireproofing compounds can find use in electronics, cable industry, and other fields.

Table 4. Properties of polymeric compounds based on adduct **XIX**

Composition, %			Time before start of combustion	Self-extinction time	Weight loss, %	MFI,* g/10 min	Ultimate tensile strength, kg mm^{-2}	Relative elongation, %
HDPE	fireproofing compound **XIX**	Sb_2O_3,	s					
100	–	–	45–50	Burns	–	1.42	300	900
95	5	–	55–57	"		1.35	300	400
95	–	5	55–60	"	–	1.85	300	500
94	3	3	100	10–12, flows	10–20	0.68	263	189
92	3	3	130	15–20, drops	18–8.5	1.03	252	180
90	5	5	135	Ceases to burn and strongly drops, 5	25–30	1.31	255	200
80	10	10	150	Ceases to burn and strongly drops, 5	15.5	1.97	278	100
75	15	10	150	"	16.2	1.70	240	80

* The melt flow index (MFI) was determined according to GOST (State Standard) 11645-73/78–93.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in the range 4000–400 cm^{-1}, and the 1H NMR spectra, on a Tesla BS-48 spectrometer (80 MHz) in CCl_4, internal reference HMDS. The TLC analysis was performed according to [8], with Al_2O_3 (Brockmann grade II) as sorbent and heptane–acetone as eluent. The spots were developed by UV irradiation from a mercury lamp equipped with a color filter.

5,5-Dimethoxytetrachlorocyclopenta-1,3-diene **XVI** was prepared by the procedure described in [9] from hexachlorocyclopentadiene, bp 108–110°C (11 mm Hg), $n_D^{20} = 1.5288$, $d_4^{20} = 1.5010$.

Allyl haloacetates **II–VIII** were prepared by the common procedure, esterification in the presence of an acid catalyst (H_2SO_4, 5% of the reaction mixture volume) in refluxing benzene. After the reaction completion (when the water release ceased), the mixture was washed and dried over MgSO4. The benzene was distilled off, and the residue was distilled in a vacuum. The physicochemical properties of esters **IX–XV** are given in Table 1.

1,4,5,6-Tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-enylmethyl monochloroacetate **XVII**. A mixture of 7.92 g (0.03 mol) of tetrachlorodimethoxycyclopentadiene **XVI** and 1.34 g (0.01 mol) of allyl monochloroacetate **IX** was heated at 160°C for 10 h. After vacuum distillation, we obtained 2.91 g of adduct **XVII**; yield 73.2%, bp 167–168°C (1 mm Hg), $n_D^{20} = 1.5299$, $d_4^{20} = 1.5014$. IR spectrum, ν, cm^{-1}: 1760 (C=O), 1110 (C–O), 800 (C–Cl).

Found, %:	C 35.87; H 3.04; Cl 44.21
Calculated, %:	C 36.14; H 3.26; Cl 44.54

Adducts **XVII–XXIII** were prepared similarly (the synthesis conditions and results are given in Table 3, and the physicochemical characteristics, in Table 2).

Independent synthesis of **XVII–XXIII** was performed by esterification of bicyclic alcohol **XXIV** with appropriate carboxylic acids **II–VIII**, following the standard procedure.

2-*endo*-Hydroxymethyl-1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-ene **XIV** was prepared by Diels–Alder reaction of tetrachlorodimethoxycyclopentadiene with allyl alcohol, as described in [7].

CONCLUSIONS

(1) Polyhalogenated norbornenylmethyl esters were prepared by [4+2]-cycloaddition of tetrachlorodimethoxycyclopentadiene to allyl haloacetates.

(2) The optimal conditions for preparing target products are as follows: 160°C, 10 h, diene : dienophile ratio 3 : 1. Under these conditions, the adducts (exclusively endo isomers) are obtained in 73–92% yield.

(3) Polychlorobicyclic esters of haloacetic acids in combination with a synergistic additive (Sb_2O_3), when

compounded with polymers, impart to them self-extinction and improve their physicomechanical properties.

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