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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Hexachlorobicyclo[2.2.1]hept-5-enylmethyl Haloacetates

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Abstract—The possibility of preparing hexachlorobicyclo[2.2.1]hept-5-enylmethyl haloacetates by reactions of hexachlorocyclopentadiene with allyl haloacetates was examined. The optimal conditions for preparing the esters were found. The structures of the compounds prepared were proved by IR and ^{1}H NMR spectroscopy.

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Hexachlorocyclopentadiene (HCCPD) and related compounds are peculiar objects in the modern organic chemistry. Studies of HCCPD gave an impetus to the development of the theory of X-philic reactions in theoretical organic chemistry, and the theory of pericyclic reactions was supplemented by the reverse Diels–Alder reaction. The *syn–anti* isomerism of adducts of diene condensation involving HCCPD derivatives was substantiated [1]. Hexachlorocyclopentadiene and related compounds are of scientific interest for understanding the mechanism of the Diels–Alder reaction [2].

Halogen-containing bicyclic esters are widely used for imparting the fire resistance to polymeric materials, as modifiers and curing agents for epoxy resins, as modifiers for biologically active substances [3], and as synthetic precursors of halogen-substituted sterically hindered phenols [4–6] and α-diketones [7, 8].

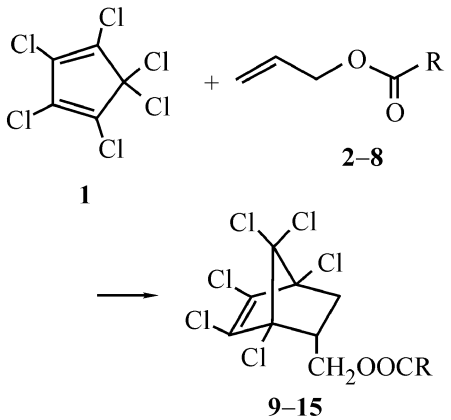
Proceeding with studies in the field of synthesis of polyhalogenated norbornene esters [9–11], we examined the reactions of formation of hexachlorobicyclo[2.2.1]-heptenylmethyl haloacetates. These compounds were prepared by the Diels–Alder reaction of HCCPD with allyl haloacetates **2–8** following Scheme 1.

The physicochemical characteristics of adducts **9–15** are given in Table 1.

The reaction was performed in the temperature range 100–160°C for 2–14 h. The diene : dienophile molar ratio was varied from 1 : 1 to 4 : 1. We examined the effect of the above parameters on the yield and isomeric composition of the final products. The results are given in Table 2.

Studies of the influence of the reaction temperature on the adduct yield, performedby the condensation of HCCPD with allyl monochloroacetate as an example, showed that the yield of adduct **9** increased from 21.6 to 85.1% with increasing temperature from 100 to 160°C. With an increase in the diene : dienophile molar ratio from 1 : 1 to 2 : 1, the yield of adduct **9** increased from 48.2 to 85.1%. Further increase in the molar ratio to 3 : 1 and 4 : 1 is unfavorable for the yield, which decreased to 79.6%.

Scheme 1.



R = CH_2Cl (**2**, **9**), $CHCl_2$ (**3**, **10**), CCl_3 (**4**, **11**), CH_2Br (**5**, **12**), $CHBr_2$ (**6**, **13**), CBr_3 (**7**, **14**), CF_3 (**8**, **15**).

Table 1. Physicochemical characteristics of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-enylmethyl haloacetates **9–15**

Compd.	T_b, °C/P, mm Hg	n_D^{20}	D_4^{20}	Found, %			Formula	Calculated, %		
				C	H	halogen		C	H	halogen
9	154–155/1	1.5510	1.6453	29.14	1.68	60.72	$C_{10}H_7O_2Cl_7$	29.45	1.72	60.98
10	175–180/1	1.5530	1.6780	26.85	1.11	64.94	$C_{10}H_6O_2C1_8$	27.15	1.36	64.25
11	178–181/1	1.5538	1.7093	24.65	0.97	66.73	$C_{10}H_5O_2C1_9$	25.18	1.05	67.05
12	167–168/1	1.5572	1.7658	26.22	1.34	63.89	$C_{10}H_7O_2C1_6Br$	26.65	1.55	64.82
13	176–179/1	1.5596	1.8991	29.06	1.23	61.05	$C_{10}H_6O_2C1_6Br_2$	29.34	1.47	61.37
14	186–188/1	1.5762	2.099	19.42	0.63	73.88	$C_{10}H_5O_2C1_6Br_3$	19.67	0.81	74.26
15	105–106/1	1.5010	1.6705	27.63	0.89	62.95	$C_{10}H_5O_2Cl_6F_3$	28.10	1.17	63.23

As seen from Table 2, appreciable effect on the yield of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-enylmethyl trifluoroacetate **15** synthesized by the reaction of HCCPD with allyl trifluoroacetate **8** is exerted by the reaction time: With an increase in the reaction time from 2 to 10 h, the yield of **15** increases from 18.1 to 46.5%. Further increase in the reaction time to 14 h does not lead to an increase in the product yield.

With allyl mono-, di-, and trichloroacetates (**2–4**) as examples, we examined how the number of halogen atoms in the acid moiety affects the yield of adducts (9–11). The other conditions being the same (160°C, 10 h, diene : dienophile ratio 2 : 1), the adduct yield decreased with increasing number of chlorine atoms: 85.1% for 9, 80.1% for 10, and 75.3% for 11. Thus, under these conditions the dienophile activity decreases with an increase in the number of halogen atoms: $CH_2Cl > CHCl_2 > CCl_3$.

This order of the dienophilic activity is apparently associated with an increase in the electronegativity of radical R and hence in the electrophilicity of the dienophile. HCCPD, as a diene with a decreased electron density, will add more readily to less electrophilic dienophile **2**, and with **4** the addition will be relatively hindered.

To elucidate how the nature of halogen atoms in dienophile molecules affects their activity and the yield of the adducts, we examined under similar conditions (120°C, 10 h, diene : dienophile molar ratio 2 : 1) the Diels–Alder reactions of allyl trihaloacetates **4**, **7**, and **8** with HCCPD. Judging from the adduct yields, the dienophilic activity of the esters decreases in the following order:

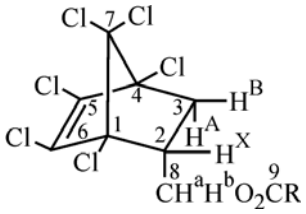
$Br_3CCOO–CH_2–CH=CH_2$ (**7**)
57.1 %
> $Cl_3CCOO–CH_2–CH=CH_2$ (**4**)
48.2%
> $F_3CCOO–CH_2–CH=CH_2$ (**8**)
39.3%

This trend is apparently due to an increase in the electronegativity of the radical and to a decrease in the nucleophilicity of the double bond in the dienophile molecule. However, this trend is broken at 160°C [in going from 4 to 7, the yield of the corresponding adduct (**11**, **14**) decreases from 75.3 to 59.3%], which may be

Table 2. Influence of the conditions of [4+2]-cycloaddition of hexachlorocyclopentadiene **1** to allyl haloacetates **2–8** on the yield of adducts **9–15**

Dieno-phile	*T*, °C	Diene : dienophile molar ratio	τ, h	Yield of adducts 9–15, %
2	100	2:1	10	21.6
	120	2:1	10	51.2
	140	2:1	10	80.2
	160	2:1	10	85.1
	160	1:1	10	48.2
	160	3:1	10	81.4
	160	4:1	10	79.6
3	160	2:1	10	80.1
4	160	2:1	10	75.3
5	160	2:1	10	87.4
6	160	2:1	10	78.2
7	160	2:1	10	69.3
8	160	2:1	10	46.5
	160	2:1	2	18.1
	160	2:1	4	23.7
	160	2:1	6	29.6
	160	2:1	8	35.8
	160	2:1	12	46.5
	160	2:1	14	47.1
4	120	2:1	10	48.2
7	120	2:1	10	57.1
8	120	2:1	10	39.3

Table 3. 1H NMR spectra of compounds **9–15**



Compd.	R	Chemical shift, δ, ppm						Coupling constant J, Hz			
		H^A m	H^B m	H^X m	H^{8a} t	H^{8b} t	H^9 q	J_{AB}	J_{BX}	J_{AX}	$J_{a,b}$
9	CH_2C1	2.42	3.26	3.7	4.27	4.65	4.2 (2H)	–11.9	8.0	4.8	–10.8
10	$CHC1_2$	2.51	3.25	3.8	4.35	4.70	4.9 (H)	–11.9	8.1	4.1	–10.7
11	$CC1_3$	1.93	2.73	3.27	4.50	4.65	–	–12.7	8.9	4.7	–10.9
12	CH_2Br	2.3	3.15	3.60	4.30	4.55	4.3 (2H)	–11.23	8.19	4.5	–10.8
13	$CHBr_2$	2.35	3.20	3.65	4.40	4.50	4.95 (H)	–11.9	8.11	5.0	–11.9
14	CBr_3	1.90	2.53	2.91	4.35	4.60	–	–12.3	7.5	4.0	–11.1
15	CF_3	2.1	3.08	3.45	4.65	4.80	–	–12.0	9.0	5.0	–11.8

due to partial decomposition of allyl tribromoacetate **7** at this temperature.

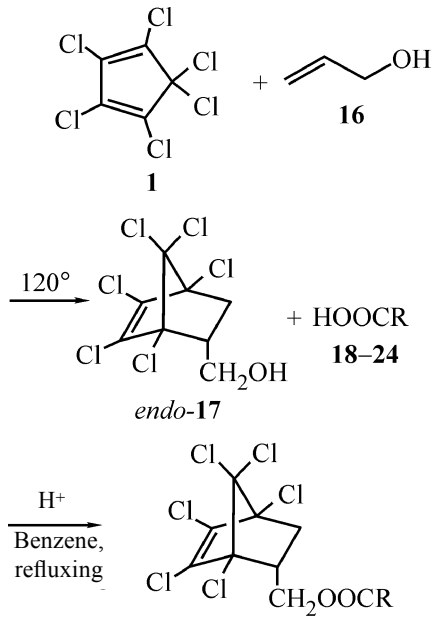
Thus, we found that the optimal conditions for preparing adducts **9–15** are 160°C, 10 h, and diene : dienophile molar ratio of 2 : 1.

The structures of adducts **9–15** were proved by independent synthesis. First, by the reaction of HCCPD with allyl alcohol **16** we prepared 2-*endo*-hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene 17 [12]. The subsequent esterification of **17** with haloacetic acids **18–24** according to Scheme 2 yielded the corresponding bicyclic esters **9–15**.

All the physicochemical constants of compounds **9–15** prepared by both procedures are identical. The structures of the adducts were confirmed by elemental alalysis (Table 1) and by IR and 1H NMR spectroscopy (Table 3). The purity was checked by TLC. All the reactions we performed are stereospecific and yield exclusively the endo isomers.

Hexachloronorbornene derivatives **9–15** exhibit ABX patterns in the 1H NMR spectra. The low-field signal is assigned to the proton adjacent to the electronegative substituent R (HX). As indicated in [13], the coupling constants of the HX proton with the other protons differ by a factor of approximately 2. The endo orientation of the substituent at C_2 is confirmed by the ^{1}H NMR spectra (Table 3) whose parameters are in agreement with the available data for the known chlorinated analogs [14], hexabromonorbornenes [15], and 1,4,5,6-tetrabromo-7,7-dimethoxynorbornenes [16]. The endo orientation of the CN substituent at the C_2 atom of the hexabromonorbornene core was confirmed by comparison of the experimental and calculated dipole moments [13]. In addition, it is known that the parameters of the ^{1}H NMR spectrum of pentachloronorbornene with the exo orientation of the CN substituent at the C_2 atom are essentially different

Scheme 2.



R = CH_2Cl (**18**), $CHCl_2$ (**19**), CCl_3 (**20**), CH_2Br (**21**), $CHBr_2$ (**22**), CBr_3 (**23**), CF_3 (**24**).

[17]. The *endo* configuration of 2*S*-(–)-menthyl hexachloronorborn-5-ene-2-carboxylic acid was proved by single crystal X-ray diffraction [18], and the 1H NMR data for this compound are in full agreement with those obtained in our study.

In the IR spectra of **9–15**, characteristic absorption bands are observed of the C=O group at 1720–1740 cm^{-1}, ester C–O group at 1000–1200 cm^{-1}, and C–Cl bonds at 750 cm^{-1}. The absorption band of the C–Br bonds in **12–14** is observed at 650–600 cm^{-1}, and that of the C–F bonds in **15**, at 1300 cm^{-1}.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hept-5-enylmethyl trichloroacetate **11** was tested for the flame-extinguishing activity with respect to medium-density polyethylene (MDPE). We found that this compound as an effective fire retardant for MDPE. In particular, addition of **11** to MDPE in a 5 : 95 proportion (by weight) imparts self-extinction to the polymer and improves its physicomechanical parameters and dielectric properties.

Compounds **9–15** were tested as bactericides toward sulfate-reducing bacteria. 1,4,5,6,7,7-Hexachlorobic yclo[2.2.1]hept-5-enylmethyl dibromoacetate **13** and trifluoroacetate **15** appeared to be the most effective. Both compounds in a concentration of 0.025% fully suppress the development of sulfate-reducing bacteria.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer, and the ^1H NMR spectra, on a Tesla BS-48 spectrometer (80 MHz) in CCl_4, internal reference hexamethyldisiloxane. The TLC analysis was performed according to [19] using Al_2O_3 (Brockmann grade II) as sorbent and heptane–acetone as eluent. The spots were visualized by UV irradiation from a mercury lamp equipped with a light filter.

Hexachlorocyclopentadiene **1** was prepared according to [20]: bp 109–111°C/11 mm Hg, $n_D^{20} = 1.5654$, $d_4^{20} = 1.7210$ (published data [20]: bp 110–111°C/11 mm Hg, $n_D^{20} = 1.5652$, $d_4^{20} = 1.7213$).

Hexachlorobicyclo[2.2.1]hept-5-enylmethyl haloacetates 9–15 were prepared by the Diels–Alder reaction from HCCPD and the corresponding dienophiles **2–8**.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hept-5-enylmethyl monochloroacetate 9. A mixture of 5.46 g (0.02 mol) of HCCPD and 1.34 g (0.01 mol) of 2 was heated at 160°C for 12 h. Vacuum distillatoin yielded 3.453 g (85.1%) of the liquid product.

Compounds **10–15** were prepared similarly.

Independent synthesis. endo-2-Hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene **17** was prepared according to [12]. Independent synthesis of **9–15** was performed by esterification of **17** with the corresponding haloacetic acids **18–24**.

CONCLUSIONS

(1) Hexachlorobicyclo[2.2.1]hept-5-enylmethyl haloacetates were prepared by the Diels–Alder reaction of hexachlorocyclopentadiene with the corresponding allyl haloacetates.

(2) The influence of the reaction parameters on the yield and isomeric composition of the adducts was examined. The optimal conditions for preparing the target products were found: 160°C, 10 h, hexachlorocyclopentadiene : allyl ester molar ratio 2 : 1. Under these conditions, the product yield is 46–87%. The products consist exclusively of the endo isomers.

(3) Hexachlorinated bicyclic esters dibromoacetic and trifluoroacetic acids in a concentration of 0.025% fully suppress the development of sulfate-reducing bacteria. (4) Hexachlorobicyclo[2.2.1]hept-5-enylmethyl trifluoroacetate is an effective fireproofing agent for medium-density polyethylene. Its addition to polyethylene in a 5 : 95 proportion (by weight) imparts to the polymer self-extinction and improves its physicomechanical and dielectric properties.

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