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ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Photostabilizing Properties of Hexachlorobicyclo[2.2.1]hept-5-enylmethyl Esters of Substituted Benzoic Acids

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Abstract—Polychlorinated bicyclic esters of *p*-substituted benzoic acids were prepared by the Diels–Alder reaction of hexachlorocyclopentadiene with allyl esters of *p*-substitutted benzoic acids. Some of the adducts synthesized were tested as photostabilizers for polyethylene-based polymer formulations.

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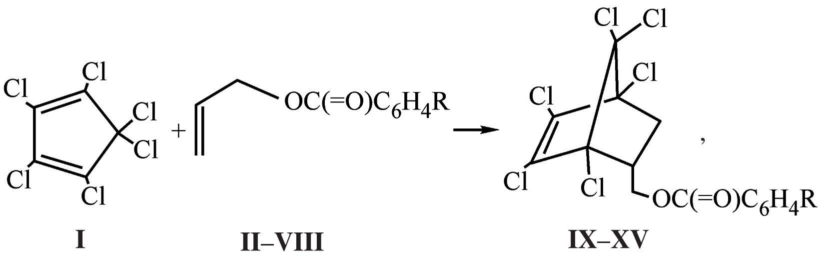
Hexachlorocyclopentadiene (HCCPD, **I**) and related compounds are among unusual objects of the modern organic chemistry. Thanks to HCCPD, the theory of X-philic reactions was developed, and the theory of pericyclic reactions was supplemented by the reversed Diels–Alder reaction. The *syn–anti* isomerism of diene condensation adducts was substantiated using data for HCCPD derivatives [1]. Simple synthesis of dihomocubane compounds from polyhalogenated cyclopentadienes attracts attention. Hexachlorocyclopentadiene and related compounds, along with practical significance, are of interest for elucidating the mechanism of the Diels–Alder reaction [2].

Halogen-containing bicyclic esters with other unique fragments are widely used for imparting flame resistance to polymeric materials, and also as modifiers and curing agents for epoxy resins and biologically active substances [3].

Synthesis of various polyhalogenated bicyclic esters from unsaturated esters of substituted benzoic acids attracts researchers' attention [4, 5].

Proceeding with studies in the field of synthesis of polyhalogenated bicyclic esters [6–9], we prepared, identified, and examined polyhalonorbornenylmethyl esters of *p*-substituted benzoic acids. First, we prepared by a common esterification procedure allyl esters of *p*-substituted benzoic acids **II**–**VIII**. Their physicochemical properties are given in Table 1.

Target products **IX**–**XV** were prepared by diene condensation of HCCPD **I** with allyl esters of *p*-substituted benzoic acids **II**–**VIII**. The reaction follows the scheme



where R = H (**II**, **IX**), CH_3 (**III**, **X**), HO (**IV**, **XI**), MeO (**V**, **XII**), Cl (**VI**, **XIII**), Br (**VII**, **XIV**), NO_2 (**VIII**, **XV**).

The reaction was performed in the temperature range 100–160°C for 4–12 h; the diene : dienophile molar ratio was from 1 : 1 to 4 : 1. The physicochemi-

Table 1. Constants of allyl esters of *p*-substituted benzoic acids

Compound	T_b, °C (1 mm Hg)	n_D^{20}	d_4^{20}	Yield, %
Allyl benzoate (**II**)	74–75	1.5156	1.056	80
Allyl *p*-methylbenzoate (**III**)	90–92	1.4940	0.8861	58
Allyl *p*-hydroxybenzoate (**IV**)	85–87	1.5040	1.0348	60
Allyl *p*-methoxybenzoate (**V**)	90–92	1.5010	1.0115	60
Allyl *p*-chlorobenzoate (**VI**)	85–89	1.6343	1.2055	78
Allyl *p*-bromobenzoate (**VII**)	95	1.5546	1.3305	82
Allyl *p*-nitrobenzoate (**VIII**)	128–132	1.5420	1.1218	58

Table 2. Properties and elemental analyses of polychloronorbornenyl esters of substituted benzoic acids

Compound	T_b, °C (P, mm Hg) or T_m, °C	n_D^{20}	d_4^{20}	Found, %			Formula	Calculated, %		
				C	H	Hlg		C	H	Hlg
IX	193–194 (1), T_m 50	1.5775	1.4625	41.38	2.30	48.97	$C_{15}H_{10}Cl_6O_2$	41.02	2.15	48.64
X	207–208 (1)	1.5750	1.6340	42.36	2.55	47.06	$C_{16}H_{12}Cl_6O_2$	42.76	2.67	47.44
XI	188–190 (1)	1.5800	1.4986	38.4	1.80	46.4	$C_{15}H_{10}Cl_6O_3$	40.0	2.2	47.2
XII	185–186 (2)	1.5820	1.5010	39.6	1.92	38.7	$C_{16}H_{12}Cl_6O_3$	41.03	2.58	45.08
XIII	97–98	–	–	38.34	1.92	52.56	$C_{15}H_9Cl_7O_2$	38.09	1.67	52.56
XIV	126	–	–	35.02	1.75	57.0	$C_{15}H_9Cl_6BrO_2$	34.86	1.46	56.74
XV	126	–	–	38.06	1.90	30.02	$C_{15}H_9Cl_6O_4$	37.64	1.58	29.88

cal properties of **IX**–**XV** are given in Table 2.

We examined the effect of reaction conditions (temperature, time, reactant ratio) on the yield of the adducts (Table 3).

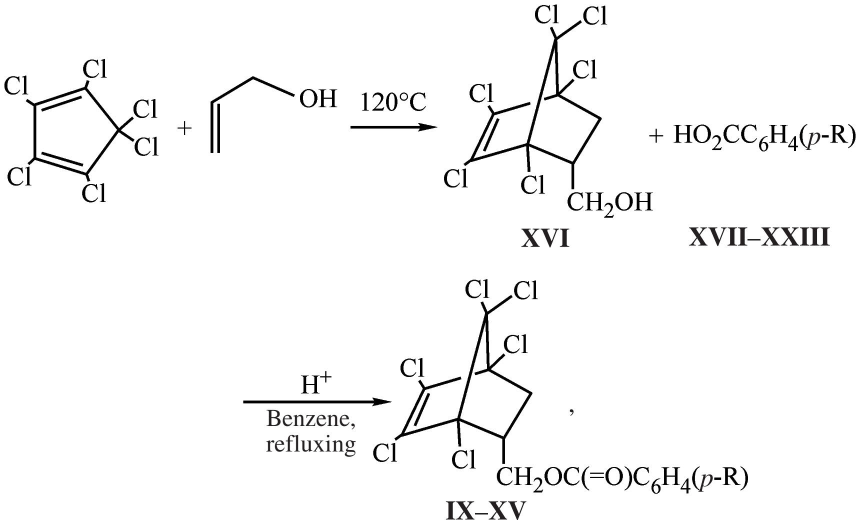
As can be seen, with an increase in the temperature from 100 to 150°C the yield of adduct **IX** increases from 58.2 to 82.4%. Further increase in the temperature (160°C) only slightly affects the yield of **IX**. The data obtained also show that the optimal conditions of adduct formation (with the reaction **I** + **II** → **IX** as example) are as follows: 150°C, 12 h, diene : dienophile ratio 2 : 1.

Under similar optimal conditions (150°C, 12 h, diene : dienophile molar ratio 2 : 1), we performed the condensation of HCCPD with allyl esters of other *p*-substituted benzoic acids **III**–**VIII**. The yields of adducts **X**–**XII** vary within 65.4–90.7%, with the lowest yield observed with allyl halobenzoates **VI** and **VII** (78.8 and 65.4%, respectively). On introducing *p*-hydroxy, *p*-methoxy, and *p*-nitro groups into the aromatic ring, the yield of the adducts increases (90.7, 88.6, and 82.7%, respectively).

The compositions and structures of **IX**–**XV** were proved by independent synthesis: preparation of 2-*endo*-hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene **XVI** by the reaction of **I** with allyl alcohol according to [10], followed by esterification of alcohol **XVI** with *p*-substituted benzoic acids **XVII**–**XXIII** to obtain the corresponding bicyclic esters **IX**–**XV**:

Table 3. Influence of reaction conditions on the yield of adducts **IX**–**XV**

Dienophile	T, °C	τ, h	Diene : dienophile molar ratio	Yield of adducts **IX**–**XV**, %
II	100	12	2 : 1	58.2
II	120	12	2 : 1	65.3
II	150	12	2 : 1	82.4
II	160	12	2 : 1	84.2
II	150	12	1 : 1	64.2
II	150	12	4 : 1	69.4
II	150	4	2 : 1	43.3
II	150	8	2 : 1	49.2
II	150	16	2 : 1	85.1
III	150	12	2 : 1	64.1
IV	150	12	2 : 1	73.2
V	150	12	2 : 1	90.7
VI	150	12	2 : 1	78.8
VII	150	12	2 : 1	65.4
VIII	150	12	2 : 1	82.7



where R = H, CH_3, HO, MeO, Cl, Br, NO_2.

All the physicochemical characteristics of compounds **IX**–**XV** prepared by both procedures are identical.

The compositions and structures of **IX**–**XV** are confirmed by IR and ^1H NMR spectra. The purity was checked by TLC. In the IR spectra of **IX**–**XV**, there are characteristic bands of the C=O bond at 1720–1740, ester C–O bond at 1000–1200, and C–Cl bonds at 750 cm^{-1}. The C=C vibrations have somewhat decreased frequency, 1575–1685 cm^{-1}, because of the presence of chlorine atoms at the double bond. The ^1H NMR data for **IX**–**XV** are given in Table 4.

The ^1H NMR spectra of polychlorinated norbornenylmethyl derivatives show an *ABX* pattern. The lowest-field signal was assigned to the proton adjacent to the electronegative substituent, H^X. As indicated in [11], the coupling constants of H^X with protons H^A and H^B differ by a factor of approximately 2. The *endo* orientation of the substituent at C^2 is confirmed by the ^1H NMR spectra (Table 4) whose parameters are similar to those of the spectra of the known chlorinated analogs [12], hexabromonorbornenes [13], and 1,4,5,6-tetrabromo-7,7-dimethoxynorbornenes [14]. The *endo* orientation of the CN substituent at the C^2 atom of the hexabromonorbornene core is confirmed by comparison of the experimental and calculated dipole moments [13]. In addition, it is known that, in the case of *exo* orientation of the CN substituent at the C^2 atom of pentachloronorbornene, the parameters of the ^1H NMR spectrum are essentially different [15].

The *endo* configuration of 2*S*-(–)-menthyl hexachloronorborn-5-ene-2-carboxylate was confirmed by single crystal X-ray diffraction [16].

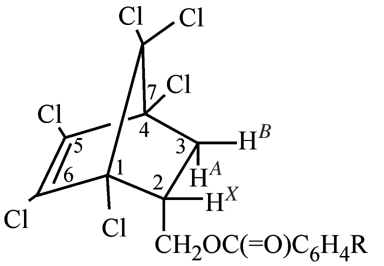
The synthesized compounds **IX**–**XV** were tested as photostabilizers for polymer formulations based on high-density polyethylene (HDPE). These compounds were added in amounts of 0.2, 0.5, and 0.8%. Compounds **IX** and **XIV** appeared to be the most active. On adding stabilizer **IX** to HDPE, the relative breaking elongation ε of the irradiated samples increased by a factor of almost 2 compared to the pure polymer, which is due to good compatibility of the stabilizer with HDPE. The results of the tests are given in Table 5.

After UV irradiation for 200 h, the stabilized formulations exhibited considerably better properties than straight high-density polyethylene. The breaking tensile stress (σ_B) of the initial polymer decreased upon irradiation by 70%, and that of the stabilized polymer, by only 10–13%. The dielectric loss tangent ($\tan\delta$) of the stabilized samples also varied significantly. The lack of degradation of the stabilized HDPE after UV irradiation is confirmed by the results of UV studies. The suggested photostabilizers are light yellow, and their performance meets the requirements of the modern standards.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer 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 hexamethyldisiloxane. The TLC analysis was performed by the

Table 4. ^{1}H NMR spectra of **IX**–**XV**



Compound	R	Chemical shift, δ, ppm				Coupling constant, Hz		
		H^A, q	H^B, q	H^X, m	OCH_2 (2H), t	J_{AX}	J_{BX}	J_{AB}
IX	H	1.73	2.60	3.17	4.20	8.3	4.80	–11.90
X	CH_3	2.00	2.73	3.25	4.20	8.5	4.25	–12.10
XI	OH	2.15	2.80	3.40	4.30	8.4	4.15	–12.31
XII	OMe	2.10	2.86	3.30	4.50	8.1	4.29	–12.27
XIII	Cl	1.90	2.70	3.30	4.14	8.4	4.15	–12.60
XIV	Br	1.93	2.70	3.25	4.30	8.2	4.10	–12.50
XV	NO_2	2.10	2.80	3.50	4.30	8.5	4.25	–12.70

Table 5. Properties of stabilized formulations based on compounds **IX** and **XIV**

Formulation	Stabilizer content, %	Parameter value after irradiation for 200 h				
		σ_B, kgf cm^{-2}	shrinkage, %	MFI, g/10 min	$\tan\delta \times 10^{-4}$	ε, %
HDPE	–	80	–	–	–	–
HDPE + stabilizer:						
IX	0.2	120	8	0.14	8.7	2.2
IX	0.5	150	8	0.05	11.8	2.0
IX	0.8	130	12	0.08	20.0	2.1
XIV	0.2	240	16	0.11	5.6	2.0
XIV	0.5	230	16	0.21	8.8	2.0
XIV	0.8	230	14	0.46	10.9	19

procedure described in [17]. Alumina (Brockmann grade II) was used as sorbent, and heptane–acetone, as eluent. The spots were visualized by irradiation with a mercury lamp equipped with a light filter.

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

Allyl esters of *p*-substituted benzoic acids **II**–**VIII** were prepared by the standard procedure, esterification in benzene in the presence of an acid catalyst (sulfuric acid, 5 wt % relative to the reaction mixture). The mixture was washed with a $NaHCO_3$ solution and water, dried over $MgSO_4$, and distilled. The physicochemical parameters of the esters are given in Table 1.

Hexachloronorbornenylmethyl esters of *p*-substituted benzoic acids **IX**–**XV** were prepared by diene synthesis from HCCPD and the corresponding dienophiles **II**–**VIII**.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hept-2-enylmethyl benzoate IX. A mixture of 1.6 g (0.01 mol) of **II** and 5.46 g (0.02 mol) of HCCPD was heated at 150°C for 12 h. Adduct **IX** was obtained; yield 3.58 g (83%). Adducts **X**–**XV** were prepared similarly. The conditions and results are given in Tables 2 and 3.

***endo*-2-Hydroxymethyl-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene XVI** was prepared according to [19]. Independent synthesis of **IX**–**XV** was performed by esterification of alcohol **XVI** with the corresponding benzoic acids **XVII**–**XXIII** in the presence of an acid catalyst (5% H_2SO_4) in refluxing benzene with azeotropic distillation of water. All the physicochemical parameters of compounds **IX**–**XV** prepared by independent synthesis are identical to those of the respective compounds prepared by the condensation of HCCPD with allyl esters **II**–**VIII**.

CONCLUSIONS

(1) The Diels–Alder reaction of allyl esters of *p*-substituted benzoic acids with hexachlorocyclopentadiene, performed at 150°C for 12 h at the diene : dienophile ratio of 2 : 1, gave in good yields (65–90%) the corresponding adducts, exclusively in the form of *endo* isomers.

(2) It was demonstrated by the example of high-density polyethylene that polychlorobicyclic esters of *p*-substituted benzoic acids are effective photostabilizers.

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