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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of 1,4,5,6-Tetrachloro-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-dienylmethyl Esters of *p*-Substituted Benzoic Acids

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Abstract—The possibility of preparing 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-dienyl-methyl esters of *p*-substituted benzoic acids by [4+2]cycloaddition of tetrachlorodimethoxycyclo-pentadine to propargyl esters of the corresponding acids was examined. The optimal synthesis conditions were found. The structure of the compounds synthesized was confirmed by independent synthesis and by IR and ¹H NMR spectroscopy.

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[4+2]-Cycloaddition involving polychlorocyclopentadienes is a convenient and promising route to chlorine-substituted norbornene derivatives [3]. Functionally substituted polychlorinated norbornenes, in turn, are of interest as starting compounds for preparing new substances.

Proceeding with studies in the field of synthesis of polyhalogenated bicyclic esters [4–10], we prepared in this work 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2. 1]hepta-2,5-dienylmethyl esters of *p*-substituted benzoic acids. By esterification of propargyl aclohol I with benzoic acids **IIa–IIg**, we synthesized the corresponding starting dienophiles **IIIa–IIIg**:



The physicochemical data for propargyl esters of *p*-substituted benzoic acids **IIIa–IIIg** are given in Table 1.

The final products **Va–Vg** were prepared by [4+2]cycloaddition of dimethoxytetrachlorocyclopentadiene **IV** to **IIIa–IIIg**. The reaction follows the scheme



where R = H (Va), Me (Vb), OH (Vc), MeO (Vd), Cl (Ve), Br (Vf), NO₂ (Vg).

The physicochemical parameters of the compounds synthesized are given in Table 2.

where R = H (IIa, IIIa), Me (IIb, IIIb), OH (IIc, IIIc), MeO (IId, IIId), Cl (IIe, IIIe), Br (IIf, IIIf), NO₂ (IIg, IIIg).

The reaction was performed in the temperature range 80–160°C for 2–12 h at the diene : dienophile molar ratio of 1 : 1–4 : 1. We examined the influence of these parameters on the yield of **Va–Vg**. The influence of temperature was studied with adduct **Va**, prepared by condensation of **IV** with propargyl benzoate **IIIa**, chosen as example. The yield of **Va** strongly depends on temperature. At temperatures below 80°C, the reaction is very slow. With an increase in the temperature from 80 to 140°C, the yield of **Va** increases from 7 to 63%. Further increase in the temperature to 160°C led to adecrease in the yield to 54% and to partial tarring of the reaction mixture.

With an increase in the diene : dienophile molar ratio from 1 : 1 to 3 : 1, the yield of adduct **Va** increases from 50 to 63%. Further increase in the diene : dienophile molar ratio to 4 : 1 does not noticeably affect the yield.

Under similar optimal conditions, we performed [4+2]cycloaddition of **IV** to the other propargyl esters of *p*substituted benzoic acids, **IIIb–IIIg**. The yields of the adducts vary within 65–72%, with the lowest yield observed with propargyl *p*-hydroxybenzoate (65%). On introducing methoxy, chloro, bromo, and nitro substituents into the *p*-position of the benzene ring, the yield increases (to 72%).

The compositions and structures of Va-Vg were confirmed by independent synthesis. First, by the reaction of tetrachlorodimethoxycyclopentadiene with propargyl alcohol, following the procedure described in [11], we prepared 2-hydroxymethyl-1,4,5,6-tetrachloro-7,7-dimethylbicyclo[2.2.1]hepta-2,5-diene VI. By its esterification with *p*-substituted benzoic acids VIIa– VIIg, we prepared the corresponding bicyclic esters Va–Vg (see the scheme).

 Table 1. Constants of esters IIIa–IIIg

Compound	$T_{\rm b}$, °C (P , mm Hg)	n_{D}^{20}	d_4^{20}	Yield, %
Propargyl benzoate IIIa	85-87 (2)	1.5317	1.0208	55
Propargyl <i>p</i> -methylbenzoate IIIb	88-89 (3)	1.4970	0.9518	62
Propargyl <i>p</i> -hydroxybenzoate IIIc	92–94 (4)	1.5045	1.0357	58
Propargyl <i>p</i> -methoxybenzoate IIId	90–91 (3)	1.5030	1.0168	60
Propargyl <i>p</i> -chlorobenzoate IIIe	95–96 (1)	1.5440	1.1482	48
Propargyl <i>p</i> -bromobenzoate IIIf	$T_{\rm m}$ 35 (from heptane)	-	—	60
Propargyl <i>p</i> -nitrobenzoate IIIg	$T_{\rm m}$ 33 (from octane)	—	—	55

Table 2. Constants and analytical data for tetrachlorinated bicyclic esters of p-substituted benzoic acids Va-Vg

Compound <i>T</i>	$T_{\rm b}$, °C (P . mm Hg)	n_{D}^{20}	d_4^{20}	Found, %/Calculated, %			Formula
				С	Н	Hlg	roimula
Va	172–173 (1)	1.5480	1.3287	<u>47.2</u> 48.1	$\frac{3.0}{3.3}$	<u>34.18</u> 33.49	C ₁₇ H ₁₄ Cl ₄ O ₄
Vb	180–181 (1)	1.5580	1.3490	<u>48.3</u> 49.3	<u>3.08</u> 3.65	$\frac{33.70}{32.40}$	$\mathrm{C}_{18}\mathrm{H}_{16}\mathrm{Cl}_4\mathrm{O}_4$
Ve	185–187 (1)	1.5530	1.3710	<u>42.4</u> 41.8	<u>2.60</u> 3.18	<u>31.64</u> 32.27	$\mathrm{C}_{17}\mathrm{H}_{14}\mathrm{Cl}_{4}\mathrm{O}_{5}$
Vd	188–190 (1)	1.5600	1.3830	<u>48.4</u> 47.5	$\frac{4.10}{3.52}$	<u>30.08</u> 31.27	$\mathrm{C}_{18}\mathrm{H}_{16}\mathrm{Cl}_{4}\mathrm{O}_{5}$
Ve	205–207 (1)	1.5585	1.3915	<u>43.11</u> 44.49	<u>2.76</u> 2.83	<u>37.03</u> 38.71	$C_{17}H_{13}Cl_5O_4$
Vf	215–216 (1)	1.5760	1.5260	<u>39.40</u> 40.56	<u>2.04</u> 2.58	<u>43.21</u> 44.14	$C_{17}H_{13}Cl_4BrO_4$
Vg	<i>T</i> _m 96	_	_	<u>44.2</u> 43.5	<u>2.15</u> 2.77	$\frac{31.40}{30.28}$	$C_{17}H_{13}Cl_4O_6N$

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 $R = H (Va, VIIa), CH_3 (Vb, VIIb), OH (Vc, VIIc), CH_3O (Vd, VIId), Cl (Ve, VIIe), Br (Vf, VIIf), NO_2 (Vg, VIIg).$

All the physicochemical constants of compounds **Va–Vg** prepared by the two procedures are identical.

The structure and purity of the synthesized compounds were confirmed by IR and ¹H NMR spectra. The purity of the initial and synthesized compounds was checked by GLC and TLC.

In the IR spectra of compounds Va–Vg, there are characteristics bands of the C=O group at 1725–1740 cm⁻¹ and ester C–O group at 1200–1050 cm⁻¹. The C–Cl vibrations are manifested at low frequencies, 840–750 cm⁻¹. The C=C (C⁵, C⁶) vibration frequency is somewhat decreased, 1600–1685 cm⁻¹, because of chlorine substitution. The stretching vibrations of the nitro group in **IIg** and **IIIg** are manifested at 1390–1400 cm⁻¹. In the ¹H NMR spectra of the adducts, the C=C–H proton in the norbornene ring (C³) gives a singlet at δ 6.10–6.45 ppm. Two –CH₂O protons (C⁸) give a triplet at δ 4.10–4.20 ppm. The protons of the methoxy groups (OCH₃ at C⁷) give singlets at 3.50–3.60 ppm.

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 CCl₄ relative to internal reference HMDS. Chromatographic analysis of the reaction mixture and determination of the purity of **IIIa–IIIg** were performed with an LKhM-8MD chromatograph under the following conditions: 300 × 3-mm steel column with 5% polyethylene glycol succinate on Dinokhrom P, carrier gas He (40 cm³ min⁻¹), thermal conductivity detector, column temperature 140°C, vaporizer temperature 220°C. TLC analysis was performed by the procedure described in [12]. As sorbent we used Al_2O_3 (Brockmann grade II), eluent heptane–acetone, visualization by irradiation with a mercury lamp equipped with a color filter.

5,5-Dimethoxytetrachlorocyclopenta-1,3-diene IV was prepared by the procedure described in [13] from hexachlorocyclopentadiene, bp 108–110°C (11 mm Hg), n_D^{20} 1.5287, d_4^{20} 1.5010.

Propargyl esters of *p*-substituted benzoic acids **IIIa–IIIg** were prepared according to [14]. To 0.5 mol of *p*-substituted benzoic acids **IIIa–IIIg**, with protection from atmospheric moisture, we added dropwise with vigorous stirring 0.5 mol of POCl₃ and then 0.8 mol of propargyl alcohol. The mixture was stirred for 30 min, after which it was extracted with ether. The ether solution was washed with a 5% NaHCO₃ solution to neutral reaction and then with water, dried over MgSO₄, and distilled. The physicochemical characteristics of the esters prepared are given in Table 1.

1,4,5,6-Tetrachloro-7,7-dimethylbicyclo[2.2.1]hepta-2,5-dienylmethylbenzoateVa. Amixtureof7.92 g (0.03 mol) of tetrachlorodimethoxycyclopentadiene **IV** and 1.6 g (0.01 mol) of propargyl benzoate **IIIa** was heated at 140°C for 10 h. After vacuum distillation, we obtained 2.67 g (63%) of **Va**, bp 172–173°C (1 mm Hg), n_D^{20} 1.5480, d_4^{20} 1.3287. IR spectrum, v, cm⁻¹: 1730 (C=O), 1115 (C–O), 750 (C–Cl), 1655 (C=C). ¹H NMR spectrum, δ , ppm: 3.5 d (6H, OCH₃), 4.2 t (2H, OCH₂), 6.45 s (1H, C=C–H).

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The other adducts **Vb–Vg** were prepared similarly. The physicochemical data for the compounds prepared are given in Table 2.

2-Hydroxymethyl-1,4,5,6-tetrachloro-7,7-dimeth oxybicyclo[2.2.1]hepta-2,5-diene VI was prepared by the procedure described in [11]. Independent synthesis of Va–Vg was performed by esterification of VI with the corresponding *p*-substituted benzoic acids IIa–IIg according to [14]. All the physicochemical characteristics of compounds Va–Vg prepared by independent synthesis are identical to those of the corresponding compounds prepared by condensation of IV with propargyl esters IIIa–IIIg.

CONCLUSIONS

(1) Polychlorinated bicyclic esters of p-substituted benzoic acids were prepared by [4+2]cycloaddition of tetrachlorodimethoxycyclopentadiene to propargyl esters of p-substituted benzoic acids.

(2) Optimal synthesis conditions were found: 140°C, 10 h, diene : dienophile ratio 3 : 1; the maximal yield of the adducts was from 63 to 72%.

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