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Synthesis of *para*-Substituted 1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl Benzoates

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Abstract—[4+2]-Cycloaddition of hexachlorocyclopentadiene to *para*-substituted prop-2-yn-1-yl benzoates gave the corresponding 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl benzoates. The structure of the adducts was confirmed by independent synthesis, esterification of *para*-substituted benzoic acids with 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethanol.

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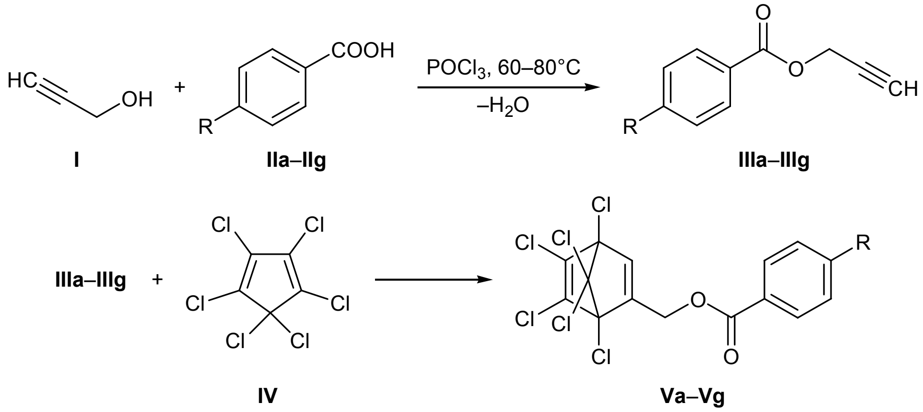
Halogenated norbornenes possess various useful properties and are promising as starting materials in the synthesis of practically important compounds [1–3]. Diels–Alder reactions of polyhalocyclopentadienes underlie most convenient methods for the preparation of polyhalogenated norbornenes [4, 5]. In continuation of our studies on the synthesis of polyhalogenated bicyclic esters [6–8], the present article reports on the synthesis of *para*-substituted 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl benzoates. Initial dienophiles **IIIa–IIIg** were not described previously; they were prepared by esterification of the corresponding benzoic acids **IIa–IIg** with prop-2-yn-1-ol (**I**). The Diels–Alder reaction of esters **IIIa–IIIg** with hexachlorocyclopentadiene **IV** gave bicyclic adducts **Va–Vg** (Scheme 1).

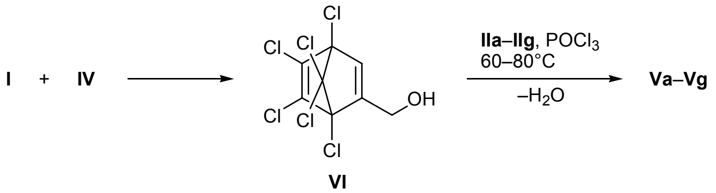
The reactions were carried out by heating the reactants at a diene-to-dienophile ratio of 1 : 1 to 4 : 1 over a period of 6–13 h. The reaction temperature was varied from 100 to 180°C. The temperature effect on the product yield was examined in the reaction of hexachlorocyclopentadiene **IV** with prop-2-yn-1-yl benzoate (**IIIa**) as an example. No reaction occurred below 100°C. Raising the temperature from 100 to

Scheme 1.



R = H (**a**), Me (**b**), HO (**c**), MeO (**d**), Cl (**e**), Br (**f**), O_2N (**g**).

Scheme 2.



160°C resulted in increase in the yield of adduct **Va** from 8 to 82%. Further raising the temperature to 180°C reduced the yield of adduct **Va** to 70%, and the reaction was accompanied by tarring. The yield of **Va** also increased (from 51 to 82%) when the diene-to-dienophile ratio was changed from 1:1 to 3:1. The yield of **Va** remained almost the same (83%) at a diene-to-dienophile ratio of 4:1.

Thus the optimal conditions for the Diels–Alder reaction of hexachlorocyclopentadiene (**IV**) with acetylenic esters **IIa**–**IIg** were: temperature 160°C, reaction time 13 h, diene-to-dienophile molar ratio 3:1. Under these conditions, the yields of adducts **Va**–**Vg** were 65–90%. The structure of compounds **Va**–**Vg** was proved by independent synthesis, by esterification of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethanol (**VI**) (prepared by cycloaddition of hexachlorocyclopentadiene to prop-2-yn-1-ol [9]) with *para*-substituted benzoic acids **IIa**–**IIg** according to the procedure described in [10] (Scheme 2). Samples of **Va**–**Vg** obtained by the two methods were identical.

The IR spectra of compounds **Va**–**Vg** contained strong absorption bands in the region 1750–1730 cm^{-1} due to stretching vibrations of the ester carbonyl group; also, absorption bands in the regions 1200–1050 (C–O), 840–600 (C–Cl), 1600–1450 (C=C), and 3100–3050 cm^{-1} (C–H) were present. In the ^{1}H NMR spectra of adducts **Va**–**Vg**, proton on C^3 in the norbornene fragment resonated as a singlet at δ 6.15–6.45 ppm, and protons in the CH_2OCOAr methylene group gave multiplets in the region δ 3.20–4.30 ppm.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on a Tesla BS-487 spectrometer (80 MHz) from solutions in carbon tetrachloride using tetramethylsilane as internal reference. Thin-layer chromatography was performed according to the procedure described in [11] using aluminum oxide of activity grade II according to Brockmann; eluent heptane–acetone; spots were visualized by irradiation with UV light using a mercury lamp equipped with a light filter.

Hexachlorocyclopentadiene (**IV**) was synthesized according to the procedure described in [12]; bp 109–111°C (11 mm), n_D^{20} = 1.5654, d_4^{20} = 1.7210; published data [12]: n_D^{20} = 1.5652, d_4^{20} = 1.7213.

***para*-Substituted prop-2-yn-1-yl benzoates IIIa–IIIg** were prepared as reported in [10]. Phosphoryl chloride, 0.7 mol, was added dropwise under vigorous stirring to 0.1 mol of *para*-substituted benzoic acid **IIa**–**IIg** in a flask protected from atmospheric moisture. Prop-2-yn-1-ol, 6.72 g (0.12 mol), was then added, and the mixture was stirred for 30 min and extracted with diethyl ether. The extract was washed with a 5% solution of $NaHCO_3$ and with water until neutral reaction, dried over $MgSO_4$, and evaporated. The residue was distilled under reduced pressure or recrystallized from appropriate solvent.

Prop-2-yn-1-yl benzoate (IIIa) was obtained from 12.2 g of benzoic acid (**IIa**). Yield 8.8 g (55%), bp 85–87°C (2 mm), n_D^{20} = 1.5317, d_4^{20} = 1.0208. IR spectrum, ν, cm^{-1}: 3050 (≡C–H), 2200 (C≡C), 1730 (C=O), 1430 (C–C$_{arom}$), 1150 (C–O). Found, %: C 75.11; H 4.91. $C_{10}H_8O_2$. Calculated, %: C 74.67; H 4.98.

Prop-2-yn-1-yl 4-methylbenzoate (IIIb) was prepared from 13.6 g of 4-methylbenzoic acid (**IIb**). Yield 10.8 g (62%), bp 88–89°C (3 mm), n_D^{20} = 1.4970, d_4^{20} = 0.9518. IR spectrum, ν, cm^{-1}: 3050 (≡C–H), 2250 (C≡C), 1740 (C=O), 1430 (C–C$_{arom}$), 1100 (C–O). Found, %: C 75.12; H 5.82. $C_{11}H_{10}O_2$. Calculated, %: C 75.86; H 5.75.

Prop-2-yn-1-yl 4-hydroxybenzoat (IIIc) was prepared from 13.8 g of 4-hydroxybenzoic acid (**IIc**). Yield 9.97 g (58%), bp 92–94°C (4 mm), n_D^{20} = 1.5045, d_4^{20} = 1.0357. IR spectrum, ν, cm^{-1}: 3100 (≡C–H), 2100 (C≡C), 1740 (C=O), 1450 (C–C$_{arom}$), 1050 (C–O). Found, %: C 69.07; H 4.45. $C_{10}H_8O_3$. Calculated, %: C 68.18; H 4.55.

Prop-2-yn-1-yl 4-methoxybenzoate (IIId) was prepared from 15.2 g of 4-methoxybenzoic acid (**IId**). Yield 11.4 g (60%), bp 90–91°C (3 mm), n_D^{20} = 1.5030, d_4^{20} = 1.0168. IR spectrum, ν, cm^{-1}: 3050 (≡C–H), 2100 (C≡C), 1730 (C=O), 1450 (C–C$_{arom}$), 1100 (C–O). Found, %: C 68.93; H 5.39. $C_{11}H_{10}O_3$. Calculated, %: C 69.47; H 5.26.

Prop-2-yn-1-yl 4-chlorobenzoate (IIIe) was prepared from 15.6 g of 4-chlorobenzoate (**IIe**). Yield 9.31 g (48%), bp 95–96°C (1 mm), n_D^{20} = 1.5444, d_4^{20} = 1.1482. IR spectrum, ν, cm^{-1}: 3100 (≡C–H), 2200 (C≡C), 1740 (C=O), 1450 (C–C_{arom}), 1150 (C–O). Found, %: C 62.15; H 3.79; Cl 19.01. $C_{10}H_7ClO_2$. Calculated, %: C 61.86; H 3.61; Cl 18.30.

Prop-2-yn-1-yl 4-bromobenzoate (IIIf) was prepared from 20.1 g of 4-bromobenzoic acid (**IIf**). Yield 15.42 g (60%), mp 35°C (from heptane). IR spectrum, ν, cm^{-1}: 3100 (≡C–H), 2250 (C≡C), 1730 (C=O), 1450 (C–C_{arom}), 1050 (C–O), 500 (C–Br). Found, %: C 50.35; H 2.75; Br 33.01. $C_{10}H_7BrO_2$. Calculated, %: C 50.21; H 2.93; Br 33.47.

Prop-2-yn-1-yl 4-nitrobenzoate (IIIg) was prepared from 16.7 g of 4-nitrobenzoate (**IIg**). Yield 12.26 g (55%), mp 33°C (from octane). IR spectrum, ν, cm^{-1}: 3020 (≡C–H), 2200 (C≡C), 1740 (C=O), 1450 (C–C_{arom}). 1050 (C–O). Found, %: C 57.91; H 3.39; N 7.11. $C_{10}H_7NO_4$. Calculated, %: C 58.54; H 3.41; N 6.83.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl benzoates Va–Vg (*general procedure*). A mixture of 8.19 g (0.03 mol) of hexachlorocyclopentadiene (**IV**) and 0.01 mol of ester **IIIa–IIIg** was heated for 13 h at 160°C in a sealed ampule. The ampule was cooled and opened, and the mixture was distilled under reduced pressure.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl benzoate (Va) was synthesized from 1.6 g of ester **IIIa**. Yield 3.54 g (82%), bp 195–196°C (2 mm), n_D^{20} = 1.5820, d_4^{20} = 1.5760. IR spectrum, ν, cm^{-1}: 3050 (=C–H), 1730 (C=O), 1450 (C=C), 1100 (C–O), 600 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.94 m and 4.20 m (1H each, 2-CH_2), 6.45 s (1H, 3-H), 7.1–8.0 d.d (5H, H_{arom}). Found, %: C 40.7; H 2.28; Cl 50.8. $C_{15}H_8Cl_6O_2$. Calculated, %: C 41.6; H 1.85; Cl 49.2.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-methylbenzoate (Vb) was synthesized from 1.74 g of ester **IIIc**. Yield 3.91 g (83%), bp 205–206°C (2 mm), n_D^{20} = 1.6050, d_4^{20} = 1.5010. IR spectrum, ν, cm^{-1}: 3100 (=C–H), 1740 (C=O), 1460 (C=C), 1150 (C=O), 700 (C–O). ^{1}H NMR spectrum, δ, ppm: 2.2 s (3H, CH_3), 3.93 m and 4.25 m (1H each, 2-CH_2), 6.40 s (1H, 3-H), 7.0–8.0 d.d (4H, H_{arom}). Found, %: C 42.1; H 1.8; Cl 48.3. $C_{16}H_{10}Cl_6O_2$. Calculated, %: C 42.9; H 2.24; Cl 47.6.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-hydroxybenzoate (Vc) was synthesized from 1.9 g of ester **IIIc**. Yield 3.76 g (90%), bp 198–200°C (1 mm), n_D^{20} = 1.5880, d_4^{20} = 1.5658. IR spectrum, ν, cm^{-1}: 3600 (=C–H), 3050 (OH), 1740 (C=O), 1500, 1280 (C–O), 700 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.92 m and 4.30 m (1H each, 2-CH_2), 5.4 s (1H, OH), 6.40 s (1H, 3-H), 7.5–8.0 d.d (4H, H_{arom}). Found, %: C 41.4; H 2.4; Cl 48.9. $C_{15}H_8Cl_6O_3$. Calculated, %: C 40.09; H 1.178; Cl 47.04.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-methoxybenzoate (Vd) was synthesized from 1.9 g of ester **IIId**. Yield 4.15 g (89%), bp 201–203°C (2 mm), n_D^{20} = 1.6030, d_4^{20} = 1.5670. IR spectrum, ν, cm^{-1}: 3050 (=C–H), 1740 (C=O), 1500 (C–O), 650 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.3 s (3H, OCH_3), 3.92 m and 4.30 m (1H each, 2-CH_2), 6.40 s (1H, 3-H), 7.0–8.0 d.d (4H, H_{arom}). Found, %: C 42.5; H 1.6; Cl 45.2. $C_{16}H_{10}Cl_6O_3$. Calculated, %: C 41.46; H 1.16; Cl 46.0.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-chlorobenzoate (Ve) was synthesized from 1.94 g of ester **IIIe**. Yield 3.69 g (89%), mp 98°C (from isooctane). IR spectrum, ν, cm^{-1}: 3100 (=C–H), 1730 (C=O), 1500 (C–O), 700 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.1–7.9 d.d (4H, H_{arom}), 6.40 s (1H, 3-H), 4.29 m and 3.90 m (1H each, 2-CH_2). Found, %: C 37.3; H 2.1; Cl 52.2. $C_{15}H_7Cl_7O_2$. Calculated, %: C 38.5; H 1.9; Cl 53.1.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-bromobenzoate (Vf) was synthesized from 3.39 g of ester **IIIf**. Yield 2.33 g (65%), mp 115°C (from isooctane). IR spectrum, ν, cm^{-1}: 3050 (=C–H), 1740 (C=O), 1550 (C–O), 700 (C–Cl), 600 (C–Br). ^{1}H NMR spectrum, δ, ppm: 3.90 m and 4.30 m (1H each, 2-CH_2), 6.40 s (1H, 3-H), 7.1–8.0 d.d (4H, H_{arom}). Found, %: C 34.4; H 2.0; Hlg 58.2. $C_{15}H_7BrCl_6O_2$. Calculated, %: C 35.15; N 1.38; Hlg 57.3.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl 4-nitrobenzoate (Vg) was synthesized from 2.05 g (0.01 mol) of ester **IIIg**. Yield 3.95 g (83%), mp 137°C (from isooctane). IR spectrum, ν, cm^{-1}: 3100 (=C–H), 1740 (C=O), 1550 (C–O), 1230 (C–N), 700 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 3.91 m and 4.30 m (1H each, 2-CH_2), 6.4 s (1H, 3-H), 7.1–8.0 d.d (4H, H_{arom}). Found, %: C 37.1; H 1.9; Cl 43.6. $C_{15}H_7Cl_6NO_4$. Calculated, %: C 37.6; H 1.46; Cl 44.5.

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-dien-2-ylmethanol (VI) was synthesized as described in [9] by condensation of hexachlorocyclopentadiene (**IV**) with prop-2-yn-1-ol (**I**). Compounds **Va–Vg** were also obtained by esterification of bicyclic alcohol **VI** with the corresponding *para*-substituted benzoic acids

IIa–**IIg** according to the procedure described above for the synthesis of esters **IIIa**–**IIIg**. Samples of **Va**–**Vg** prepared by esterification of alcohol **VI** with acids **IIa**–**IIg** were identical to those obtained by Diels–Alder reaction of hexachlorocyclopentadiene (**IV**) with esters **IIIa**–**IIIg**.

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