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Synthesis of *para*-Substituted Bicyclo[2.2.1]hept-5-en-2-ylmethyl Benzoates

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Abstract—*para*-Substituted bicyclo[2.2.1]hept-5-en-2-ylmethyl benzoates were synthesized by the Diels–Alder reaction of cyclopentadiene with the corresponding *para*-substituted allyl benzoates, and optimal reaction conditions were found. The product structure was confirmed by independent synthesis and IR and ^{1}H NMR spectroscopy.

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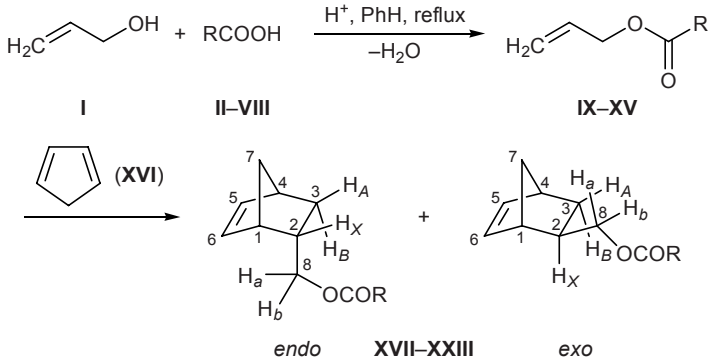
Compounds of the norbornene series possess various useful properties. Molecules of these compounds have a rigid cage-like structure with fixed orientations of substituents and are promising models for studying structure–property relations [1]. Some norbornene derivatives were found to exhibit analgesic and antiseptic effects [2, 3]. Accessibility of norbornene derivatives strongly increased due to improvement of procedures for Diels–Alder reactions involving cyclopentadiene which is a large-scale chemical product. On the one hand, esters derived from norbornene attract interest from the viewpoint of their practical importance; on the other hand, their molecules contain reactive fragments capable of undergoing various chemical transformations [4–7].

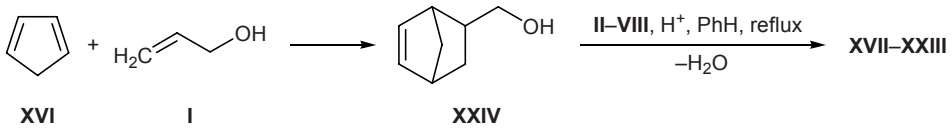
In the present article we report on the synthesis of *para*-substituted bicyclo[2.2.1]hept-5-en-2-ylmethyl benzoates. Previously unknown initial dienophiles **IX**–**XV** were obtained by esterification of the corresponding *para*-substituted benzoic acids **II**–**VIII** with allyl alcohol (**I**), and Diels–Alder reaction of cyclopentadiene with esters **IX**–**XV** gave compounds **XVII**–**XXIII** (Scheme 1). The Diels–Alder reactions were carried out at 120–180°C (reaction time 6–12 h), the diene–

Scheme 1.



II, **IX**, **XVII**, R = Ph; **III**, **X**, **XVIII**, R = *p*-MeC_6H_4; **IV**, **XI**, **XIX**, R = *p*-HOC_6H_4; **V**, **XII**, **XX**, R = *p*-$MeOC_6H_4$; **VI**, **XIII**, **XXI**, R = *p*-ClC_6H_4; **VII**, **XIV**, **XXII**, R = *p*-BrC_6H_4; **VIII**, **XV**, **XXIII**, R = *p*-$O_2NC_6H_4$.

Scheme 2.



dienophile molar ratio being 1:1 to 1:4. We examined the effect of the reaction temperature on the yield and isomeric composition of adduct **XVII**. The yield of **XVII** increased from 33 to 45% as the temperature rose from 120 to 160°C. Further raising the temperature to 180°C resulted in reduced yield and *endo*-selectivity; the latter decreased from 94 to 83%. The optimal conditions were temperature 140°C, reaction time 8 h, diene–dienophile ratio 1:1.5.

Under the optimal conditions, the Diels–Alder reactions of cyclopentadiene with allyl esters **IX**–**XV** gave 48–65% of the corresponding adducts **XVII**–**XXIII**. The maximal yield (65%) was obtained in the reaction with allyl *p*-nitrobenzoate (**XV**), and the minimal (48%), in the reaction with allyl *p*-methylbenzoate (**X**). The reaction of cyclopentadiene with allyl *p*-bromobenzoate (**XIV**) was characterized by the highest *endo*-selectivity (92%).

The structure of compounds **XVII**–**XXIII** was proved by independent syntheses. For this purpose, by Diels–Alder reaction of cyclopentadiene with allyl alcohol according to the procedure described in [8] we obtained bicyclo[2.2.1]hept-5-en-2-ylmethanol (**XXIV**) which was then used to esterify *p*-substituted benzoic acids **II**–**VIII** (Scheme 2). Bicyclo[2.2.1]hept-5-en-2-ylmethyl esters **XVII**–**XXIII** thus obtained were identical to the products synthesized according to Scheme 1.

The IR spectra of compounds **XVII**–**XXIII** contained a strong carbonyl absorption band at 1655–1650 cm^{-1}; absorption bands in the regions 3070–3040 [ν(=C–H)] and 725–700 cm^{-1} [δ(=C–H)] indicated the presence of a strained double C=C bond in their molecules. In the ^1H NMR spectra of **XVII**–**XXIII**, nonequivalent protons at the double bond in the norbornene skeleton resonated as multiplets at δ 5.85–5.70 (5-H) and 6.15–5.90 ppm (6-H), respectively ($J_{5,6}$ = 7.0 Hz). Signals from protons in the bridgehead positions were located at δ 2.74–2.40 (m, 1-H) and 3.00–2.84 ppm (m, 4-H). Methylene protons in the CH_2O group (8-H_a and 8-H_b) gave rise to a multiplet in the region δ 4.25–3.31 ppm ($J_{a,b}$ = 9.0 Hz).

The isomeric composition of esters **XVII**–**XXIII** was determined by GLC analysis. Alkaline hydrolysis of **XVII**–**XXIII** gave bicyclo[2.2.1]hept-5-en-2-ylmethanol (**XXIV**) whose isomeric composition was the same as that of the initial esters. It is known that alcohol **XXIV** prepared as described in [8, 9] consists mainly of the *endo* isomer. By comparing isomeric compositions of alcohol **XXIV** obtained by different methods we determined the isomeric composition of adducts **XVII**–**XXIII**.

EXPERIMENTAL

The IR spectra were recorded in the range from 4000 to 400 cm^{-1} on a UR-20 spectrometer; samples were examined as thin films or KBr pellets. The ^1H NMR spectra were measured on a Tesla BS-487 spectrometer (80 MHz) from solutions in carbon tetrachloride using tetramethylsilane as internal reference. Gas–liquid chromatography was performed on an LKhM-8 MD instrument equipped with a thermal conductivity detector and a 300×0.3 cm column; stationary phase 5% of poly(ethylene glycol succinate), carrier gas helium, flow rate 40 ml/min; oven temperature 150°C, injector temperature 250°C.

***p*-Substituted allyl benzoates IX–XV** were prepared by esterification of the corresponding benzoic acids with allyl alcohol (**I**) in benzene in the presence of sulfuric acid (5 wt % with respect to the entire reaction mixture). The mixture was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated. When the reaction was complete, the mixture was washed first with a solution of sodium hydrogen carbonate and then with distilled water until neutral washings and dried over $MgSO_4$, the solvent was distilled off, and the residue was distilled under reduced pressure.

Allyl benzoate (IX) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 12.2 g (0.1 mol) of benzoic acid. Yield 13.8 g (80%), bp 74–75°C (1 mm), n_D^{20} = 1.5156, d_4^{20} = 0.8861. IR spectrum, ν, cm^{-1}: 3040, 1740, 1600, 1390.

Allyl *p*-methylbenzoate (X) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 13.6 g (0.1 mol) of *p*-methylbenzoic acid. Yield 10.2 g (58%), bp 90–92°C (1 mm), n_D^{20} = 1.4950, d_4^{20} = 0.08861. IR spectrum, ν, cm^{-1}: 3040, 1740, 1600, 1410.

Allyl *p*-hydroxybenzoate (XI) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 13.8 g (0.1 mol) of *p*-hydroxybenzoic acid. Yield 11.6 g (60%), bp 85–87°C (1 mm), n_D^{20} = 1.5040, d_4^{20} = 1.0348. IR spectrum, ν, cm^{-1}: 3060, 1750, 1600, 1440.

Allyl *p*-methoxybenzoate (XII) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 15.2 g (0.1 mol) of *p*-methoxybenzoate. Yield 11.5 g (60%), bp 90–91°C (1 mm), n_D^{20} = 1.5010, d_4^{20} = 1.0115. IR spectrum, ν, cm^{-1}: 3070, 1745, 1620, 1400.

Allyl *p*-chlorobenzoate (XIII) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 15.6 g (0.1 mol) of *p*-chlorobenzoate. Yield 15.3 g (78%), bp 85–89°C (1 mm), n_D^{20} = 1.6343, d_4^{20} = 1.2055. IR spectrum, ν, cm^{-1}: 3070, 1730, 1620, 1400, 820.

Allyl *p*-bromobenzoate (XIV) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 20.1 g (0.1 mol) of *p*-bromobenzoic acid. Yield 19.68 g (82%), bp 95°C (1 mm), n_D^{20} = 1.5546, d_4^{20} = 1.3305. IR spectrum, ν, cm^{-1}: 3060, 1740, 1620, 1400, 600.

Allyl *p*-nitrobenzoate (XV) was obtained from 5.8 g (0.1 mol) of allyl alcohol and 16.7 g (0.1 mol) of *p*-nitrobenzoate. Yield 12 g (58%), bp 128–132°C (1 mm), n_D^{20} = 1.5420, d_4^{20} = 1.1278. IR spectrum, ν, cm^{-1}: 3040, 1740, 1620, 1500, 550.

Diels–Alder reaction of cyclopentadiene with allyl benzoates IX–XV (*general procedure*). A mixture of 0.1 mol of freshly distilled cyclopentadiene and 0.15 mol of ester **IX**–**XV** was heated for 8 h at 140°C in a sealed ampule. The ampule was cooled and opened, and esters **XVII**–**XXIII** were isolated by vacuum distillation.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl benzoate (XVII) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 24.3 g (0.15 mol) of allyl benzoate (**IX**). Yield 10.26 g (45%), bp 125–126°C (1 mm), n_D^{20} = 1.5265, d_4^{20} = 1.0058. IR spectrum, ν, cm^{-1}: 3070, 1745, 1655, 1390. ^{1}H NMR spectrum, δ, ppm: 0.45 m (1H, H_A), 1.15 q (1H, *anti*-7-H), 1.6 m (1H, *syn*-7-H), 1.7 m (1H, H_B), 2.1 m (1H, H_X), 2.5 m (1H, 1-H), 2.9 m (1H, 4-H), 3.91 m (1H, H_a), 4.25 m (1H, H_b), 5.7 m (1H, 5-H), 5.95 m (1H, 6-H); J_{AB} = –11.4, J_{AX} = 3.9, J_{BX} = 9.2 Hz. Found, %: C 78.9; H 5.86. $C_{15}H_{16}O_2$. Calculated, %: C 79.5; H 6.07.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-methylbenzoate (XVIII) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 26.4 g (0.15 mol) of ester **X**. Yield 11.65 g (48%), bp 125–127°C (1 mm), n_D^{20} = 1.5010, d_4^{20} = 1.035. IR spectrum, ν, cm^{-1}: 3070, 1740, 1600, 1400. ^{1}H NMR spectrum, δ, ppm: 0.40 m (1H, H_A), 1.15 q (1H, *anti*-7-H), 1.65 m (1H, *syn*-7-H), 1.75 m (1H, H_B), 2.1 q (1H, H_X), 2.45 m (1H, 1-H), 3.0 m (1H, 4-H), 3.31 m (1H, H_a), 4.25 m (1H, H_b), 5.7 m (1H, 5-H), 5.9 m (1H, 6-H), J_{AB} = –11.4, J_{AX} = 3.9, J_{BX} = 8.9 Hz. Found, %: C 79.3; H 7.48. $C_{16}H_{18}O_2$. Calculated, %: C 79.04; H 7.13.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-hydroxybenzoate (XIX) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 27.7 g (0.15 mol) of ester **XI**. Yield 8.15 g (53%), bp 132–135°C (1 mm), n_D^{20} = 1.5340, d_4^{20} = 1.0660. IR spectrum, ν, cm^{-1}: 3070, 1735, 1620, 1495. ^{1}H NMR spectrum, δ, ppm: 0.45 m (1H, H_A), 1.10 q (1H, *anti*-7-H), 1.60 m (1H, *syn*-7-H), 1.75 q (1H, H_B), 2.1 q (1H, H_X), 2.40 m (1H, 1-H), 2.80 m (1H, 4-H), 3.92 m (1H, H_a), 4.21 m (1H, H_b), 5.75 m (1H, 5-H), 5.90 m (1H, 6-H); J_{AB} = –11.3, J_{AX} = 3.9, J_{BX} = 8.9 Hz. Found, %: C 74.6; H 6.1. $C_{15}H_{16}O_3$. Calculated, %: C 73.8; H 6.6.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-methoxybenzoate (XX) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 28.8 g (0.15 mol) of allyl *p*-methoxybenzoate (**XII**). Yield 14.96 g (58%), bp 138–141°C (1 mm), n_D^{20} = 1.5410, d_4^{20} = 0.9429. IR spectrum, ν, cm^{-1}: 3040, 1735, 1650, 1495. ^{1}H NMR spectrum, δ, ppm: 0.55 m (1H, H_A), 1.10 q (1H, *anti*-7-H), 1.50 m (1H, *syn*-7-H), 1.70 q (1H, H_B), 2.1 q (1H, H_X), 2.65 m (1H, 1-H), 2.85 m (1H, 4-H), 3.95 m (1H, H_a), 4.25 m (1H, H_b), 5.85 m (1H, 5-H), 6.15 m (1H, 6-H); J_{AB} = –11.8, J_{AX} = 3.9, J_{BX} = 9.0 Hz. Found, %: C 75.2; H 6.3. $C_{16}H_{18}O_3$. Calculated, %: C 74.4; H 6.9.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-chlorobenzoate (XXI) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 29.5 g (0.15 mol) of ester **XIII**. Yield 13.79 g (60%), bp 149–151°C (1 mm), n_D^{20} = 1.5435, d_4^{20} = 1.2814. IR spectrum, ν, cm^{-1}: 3070, 1735, 1660, 1390, 795. ^{1}H NMR spectrum, δ, ppm: 0.45 m (1H, H_A), 1.10 q (1H, *anti*-7-H), 1.50 m (1H, *syn*-7-H), 1.70 q (1H, H_B), 2.1 q (1H, H_X), 2.40 m (1H, 1-H), 2.90 m (1H, 4-H), 3.97 m (1H, H_a), 4.45 m (1H, H_b), 5.75 m (1H, 5-H), 6.00 q (1H, 6-H); J_{AB} = –11.9, J_{AX} = 3.9, J_{BX} = 9.0 Hz. Found, %: C 68.45; H 5.25; Cl 13.20. $C_{15}H_{15}ClO_2$. Calculated, %: C 69.57; H 5.72; Cl 13.22.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-bromobenzoate (XXII) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 36 g (0.15 mol) of allyl *p*-bromobenzoate (**XIV**). Yield 17.74 g (58%), bp 178–180°C (1 mm), n_D^{20} = 1.5632, d_4^{20} = 1.5150. IR spectrum, ν, cm^{-1}: 3070, 1730, 1660, 1395, 650. ^{1}H NMR spectrum, δ, ppm: 0.50 m (1H, H_A), 1.15 q (1H, *anti*-7-H),

1.55 m (1H, *syn*-7-H), 1.70 q (1H, H_B), 2.1 q (1H, H_X), 2.74 m (1H, 1-H), 2.84 m (1H, 4-H), 3.98 m (1H, H_a), 4.45 m (1H, H_b), 5.70 m (1H, 5-H), 6.10 m (1H, 6-H); J_{AB} = –11.9, J_{AX} = 4.7, J_{BX} = 8.1 Hz. Found, %: C 58.24; H 4.36; Br 27.4. $C_{15}H_{15}BrO_2$. Calculated, %: C 58.63; H 4.89; Br 26.67.

Bicyclo[2.2.1]hept-5-en-2-ylmethyl *p*-nitrobenzoate (XXIII) was synthesized from 6.6 g (0.1 mol) of cyclopentadiene and 31 g (0.15 mol) of compound **XV**. Yield 17.74 g (65%), mp 135°C. IR spectrum, ν, cm^{-1}: 3040, 1735, 1660, 1450. ^{1}H NMR spectrum, δ, ppm: 0.55 m (1H, H_A), 1.1 q (1H, *anti*-7-H), 1.50 m (1H, *syn*-7-H), 1.75 q (1H, H_B), 2.1 q (1H, H_X), 2.73 m (1H, 1-H), 2.90 m (1H, 4-H), 3.31 m (1H, H_a), 4.20 m (1H, H_b), 5.85 m (1H, 5-H), 6.15 m (1H, 6-H); J_{AB} = –11.4, J_{AX} = 4.5, J_{BX} = 9 Hz. Found, %: C 65.62; H 5.36. $C_{15}H_{15}NO_4$. Calculated, %: C 65.93; H 5.50.

Compounds **XVII**–**XXIII** were also synthesized by esterification of the corresponding *p*-substituted benzoic acids **II**–**VIII** with bicyclic alcohol **XXIV** according to the procedure described above for the preparation of esters **IX**–**XV**. The products obtained by the two methods were identical in physical constants and spectral parameters. Bicyclo[2.2.1]hept-5-en-2-ylmethanol (**XXIV**) was prepared by the Diels–Alder reaction of cyclopentadiene with allyl alcohol [8].

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