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SHORT
COMMUNICATIONS

Synthesis of Dispiro[2.1.3.1]nonane and Trispiro[2.1.1.3^7.1^5.1^3]-dodecane

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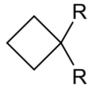
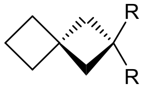
Synthesis of regular systems containing similar structural units, in particular small rings, e.g., triangulanes [1–3], ladderanes [4–7], staffanes [8], etc., has been extensively developed in recent time. Such structures attract interest as models for the design of molecular devices (rods, rotors, switches, etc.).

Spirocyclic hydrocarbons consisting of several three- and/or four-membered rings are characterized by high strain energy, enhanced reactivity, and unique physical properties [9]. Many spiro-fused cyclopropane systems have been reported [1–3]; however, compounds containing four-membered rings or three- and four-membered rings have been studied to a much lesser extent [10–14].

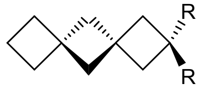
In the present communication we describe the synthesis of dispiro[2.1.3.1]nonane (**I**) and trispiro[2.1.1.3^7.1^5.1^3]dodecane (**II**) starting from diethyl cyclobutane-1,1-dicarboxylate (**III**) [15]. Compound **III** was reduced with lithium tetrahydridoaluminate to diol **IV** which was converted into bis-*p*-toluenesulfonate **V**, and condensation of the latter with diethyl malonate sodium salt gave diester **VI**. Analogous reaction sequence performed with diester **VI** afforded diester **X** through intermediate diol **VII** and bis-sulfonate **VIII**. Alternatively, by treatment of compound **VIII** with lithium bromide in acetone we obtained the corresponding dibromide **IX** which was subjected to debromination by the action of zinc in the presence of Trilon B to obtain target spiro hydrocarbon **I**. Compounds **VI** and **IX** were reported previously [16]. Successive transformations of diester **X** into diol **XI**, bis-*p*-toluenesulfonate **XII**, and dibromide **XIII**, followed by debromination, afforded compound **II**.



III–V

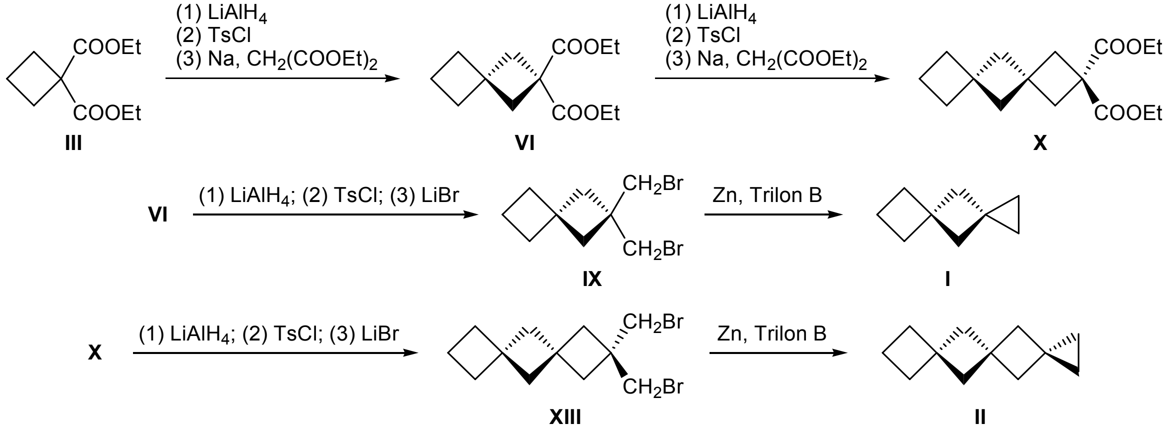


VI–IX



X–XIII

III, **VI**, **X**, R = CO_2Et; **IV**, **VII**, **XI**, R = CH_2OH; **V**, **VIII**, **XII**, R = CH_2OTs; **IX**, **XIII**, R = CH_2Br.



The structure of hydrocarbons **I** and **II** was determined by spectral methods. The ^{1}H NMR spectra of **I** and **II** contained singlets at δ 0.44 and 0.46 ppm, respectively, which belong to four methylene protons in the cyclopropane ring. Compound **I** displayed in the ^{13}C NMR spectrum a triplet at δ_C 12.3 ppm ($^1J_{CH}$ = 162 Hz) from methylene carbon atoms in the cyclopropane ring and a singlet at δ_C 15.0 ppm from the spiro carbon atom. The corresponding signals of trispiro derivative **II** were observed at δ_C 11.3 (t, $^1J_{CH}$ = 162 Hz) and 15.2 ppm (s), and signals from the other spiro atoms were located at δ_C 34.6 and 39.3 ppm.

Intermediate alcohols, *p*-toluenesulfonates, and bromides were not subjected to special purification, and they were characterized only by ^{1}H NMR spectra, which were consistent with the assumed structures.

Diethyl dispiro[3.1.3.1]decane-2,2-dicarboxylate (X). A solution of 36 g (0.15 mol) of diester **VI** in 100 ml of diethyl ether was added to a mixture of 8 g of $LiAlH_4$ and 200 ml of anhydrous diethyl ether on cooling with ice. The mixture was stirred for 6 h at room temperature and treated with 15 ml of water on cooling with ice, and the precipitate was filtered off and extracted with ethyl acetate in a Soxhlet apparatus over a period of 6 h. The organic phases were combined and dried over $MgSO_4$, and the solvent was distilled off. The residue, 28 g of spiro[3.3]heptane-2,2-diyldimethanol (**VII**), was dissolved in 100 ml of pyridine, the solution was cooled with ice, 67 g of *p*-toluenesulfonyl chloride was added under stirring, and the mixture was stirred for 2 h and left overnight. The mixture was then poured into a mixture of ice with hydrochloric acid, and the precipitate was filtered off and washed with methanol. Yield of bis-sulfonate **VIII** 51 g. The product was added under stirring to diethyl malonate sodium salt prepared from 6 g of sodium and 57 g of diethyl malonate in 150 ml of xylene. The mixture was stirred for 16 h on heating, cooled, and treated with 150 ml of water, the organic phase was separated and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was distilled in vacuo. Yield of diester **X** 16.5 g (39% calculated on the initial diester **VI**), bp 112–117°C (0.2 mm).

Dispiro[2.1.3.1]nonane (I). A mixture of 63 g of bis-sulfonate **VIII** prepared as described above in the synthesis of **X**, 55 g of anhydrous lithium bromide, and 300 ml of anhydrous acetone was heated for 7 h. The precipitate was filtered off, and the filtrate was diluted with 300 ml of water and extracted with diethyl ether. The extract was dried over $CaCl_2$ and evaporated to obtain 36 g of dibromide **IX** which was not subjected to further purification. A solution of 36 g of dibromide **IX** in 100 ml of ethanol was added under vigorous stirring to a mixture of 36 g of zinc dust, 42 g of sodium hydroxide in 150 ml of water, 300 ml of ethanol, and 120 g of Trilon B. The mixture was stirred for 4 h on heating, diluted with 300 ml of water, and filtered. The filtrate was extracted with pentane, the precipitate was washed with pentane–diethyl ether, the washings were combined with the organic extract, dried over $MgSO_4$, and evaporated, and the residue was distilled under reduced pressure. Yield 9 g (54%), bp 77–78°C (130 mm), n_D^{20} = 1.4535. IR spectrum (CCl_4), ν, cm^{-1}: 3080, 2950, 2850, 1435, 1285, 1140, 1120, 1035, 1015, 980. ^{1}H NMR spectrum, δ, ppm: 0.44 s (4H), 1.84–2.28 (6H), 2.16 s (4H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.3 t (CH_2, J_{CH} = 162 Hz), 15.0 s (C_{spiro}), 16.6 t (CH_2, J_{CH} = 135 Hz), 36.0 t (CH_2, J_{CH} = 135 Hz), 39.8 s (C_{spiro}), 44.1 t (CH_2, J_{CH} = 135 Hz). Mass spectrum: *m*/*z* 122 $[M]^+$. Found, %: C 88.07; H 11.91. C_9H_{14}. Calculated, %: C 88.45; H 11.55.

Trispiro[2.1.1.3^7.1^5.1^3]dodecane (II) was synthesized in a similar way. The reduction of 33 g of diester **X** with 9 g of $LiAlH_4$ gave 20 g of diol **XI** which was dissolved in 100 ml of pyridine, the solution was cooled with ice, 55 g of *p*-toluenesulfonyl chloride was added, and the mixture was treated as described above to isolate 25 g of bis-sulfonate **XII**. By reacting the latter with 17 g of lithium bromide in 200 ml of anhydrous acetone we obtained dibromide **XIII** which was dissolved (without purification) in 50 ml of ethanol, and the solution was added under vigorous stirring to a mixture of 18 g of zinc dust, 60 g of Trilon B, 21 g of NaOH in 75 ml of water, and 200 ml of ethanol. The mixture was stirred for 5 h on heating and treated as described above. Yield of **II** 1.5 g (13% calculated on the initial diester **X**), bp 67–69°C (15 mm), n_D^{20} = 1.4680. IR spectrum (CCl_4), ν, cm^{-1}: 3080, 2850, 1435, 1280, 1130, 1080, 1015, 980. ^{1}H NMR spectrum, δ, ppm: 0.45 s (4H), 1.90–2.10 (10H), 2.17 s (4H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.3 t (CH_2, J_{CH} = 162 Hz), 15.2 s (C_{spiro}), 16.8 t (CH_2, J_{CH} = 135 Hz), 34.6 s (C_{spiro}), 35.4 t (CH_2, J_{CH} = 135 Hz), 39.3 s (C_{spiro}), 44.4 t (CH_2, J_{CH} = 135 Hz), 48.5 t (CH_2, J_{CH} = 135 Hz). Mass spectrum: *m*/*z*: 162 $[M]^+$. Found, %: C 88.44; H 11.45. $C_{12}H_{18}$. Calculated, %: C 88.82; H 11.18.

The IR spectra were recorded on a UR-20 spectrometer from 3% solutions in CCl_4. The ^{1}H NMR spectra were measured on a Varian-HA-100D/15 instrument (100 MHz) from 15% solutions in CCl_4 using HMDS as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Hewlett Packard 5985 GC–MS system. The ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer (20 MHz) from 30% solutions in $CDCl_3$. The reaction mixtures were analyzed, and the purity of products was checked, by GLC on a Carlo Erba chromatograph equipped with a flame ionization detector; carrier gas nitrogen; glass columns: (a) 1000 × 2 mm, stationary phase 5% of SE-30 on Chromaton N-AW, (b) 2000 × 2 mm, stationary phase 10% of LAC-2R-446 on Chromaton N-AW.

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