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Synthesis of 3,6,10,13-Tetrathia[6.6.2]-propellanes from 1,1,2,2-*Tetrakis*-(bromomethyl)cyclobutane

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Summary. A synthesis of two new tetrathia[6.6.2]propellane systems, each containing one cyclobutane ring, is described. On the basis of ^{1}HNMR, UV/Vis and mass spectra, the possibility of the formation of an isomeric bispirane is discussed.

Keywords. Propellanes; Spiranes; Polycyclic compound.

Synthese von 3,6,10,13-Tetrathia[6.6.2]propellanen aus 1,1,2,2-*Tetrakis*(brommethyl)cyclobutan

Zusammenfassung. Es werden die Synthesen zweier neuer Tetrathia[6.6.2]propellansysteme beschrieben, die jeweils einen Cyclobutanring enthalten. Auf der Grundlage von NMR-, UV/Vis- und Massenspektroskopie wird die Möglichkeit der Bildung isomerer Bispirane diskutiert.

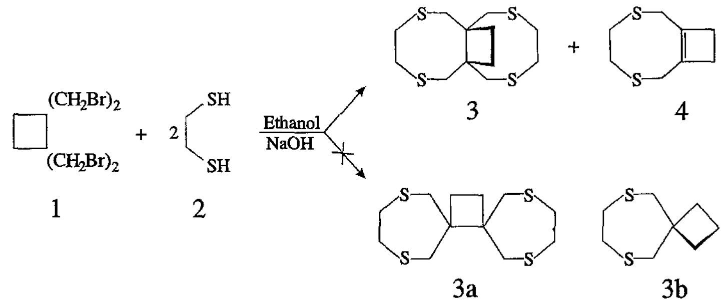
Introduction

Earlier studies carried out in our laboratory were connected with constitutionally symmetrical [*n.n.*1]propellanes [1, 2]. Recently, we have extended our investigations towards [*n.n.*2]propellane systems. Interest in [*n.n.*2]propellane systems($n = 3$, 4) has grown during the recent years because of their potential use for stereochemical studies and theoretical calculations [3, 4]. Furthermore, some of these systems were detected as parts of natural products [5]. Our interest in this field includes propellane compounds containing a cyclobutane ring. Such propellanes can be synthesized either by ethylene cycloaddition to an appropriate double bond of bicyclic systems [6] or by double ring closure of an appropriate cyclobutane derivative [7].

Results and Discussion

We have prepared new [6.6.2]propellane systems containing two eight membered rings from 1,1,2,2-*tetrakis*(bromomethyl)cyclobutane (**1**) by a condensation reaction with the sodium salt of 1,2-ethanedithiol (**2**) or 1,2-benzenedithiol (**5**), respectively. Thus, the disodium salt of 1,2-ethanedithiol (**2**) afforded 3,6,10,13-

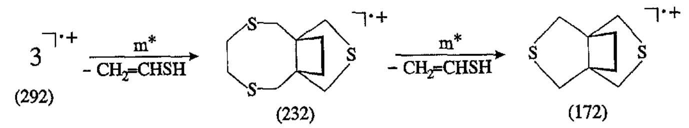
tetrathia[6.6.2]propellane (**3**), and 3,6-dithiabicyclo[6.2.0]deca-1(8)-en (**4**) upon treatment with **1** in alcoholic medium.



Scheme 1

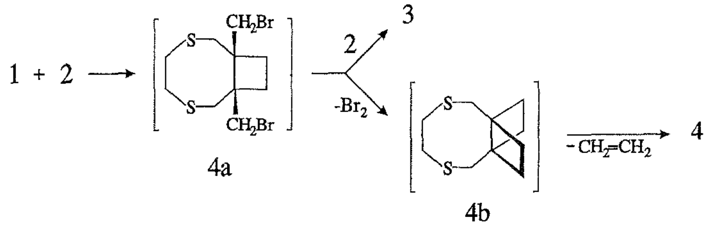
The propellane structure **3** rather than that of bispirane **3a** is supported by chemical and spectroscopic methods. The obtained propellane **3** is a stable compound, melting at 117–118°C. The ^{1}H NMR spectrum reveals two singlets (methylene protons, $\delta = 2.73$ and 2.84 ppm) and multiplet (cyclobutane protons, $\delta = 1.52 - 1.81$ ppm). The methylene protons of **3b** [8] ($\delta = 2.88$ and 3.12 ppm) are shifted to lower field in compared to the corresponding signals of **3**, thus supporting its propellane structure.

The electron impact mass spectra also indicate a propellane structure for compound **3**. The fragmentation of the well marked molecular ion of **3** starts with a destruction of the heterocyclic rings, whereas a cleavage of the cyclobutane ring characteristic for spirane systems does not occur. The fragmentation of the heterocyclic rings combined with the liberation of $CH_2 = CHSH$ afford a stable radical ion producing a peak at $m/z = 232$. The second heterocyclic ring decomposes *via* the same pathway to form radical ions with $m/z = 172$. The structure of these radical ions seems to be identical with those of the molecular ion of 3,7-dithia[3.3.2]propellane [9].



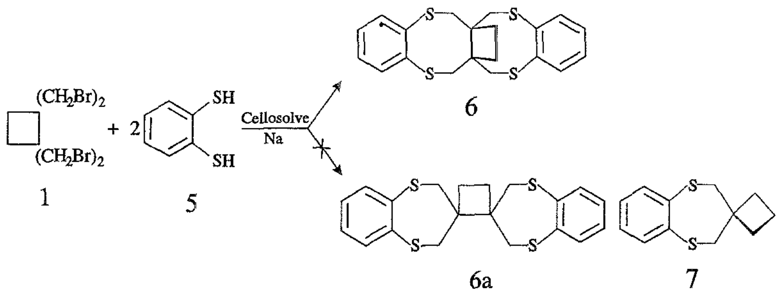
Scheme 2

Reaction of 1,1,2,2-*tetrakis*(bromomethyl)cyclobutane (**1**) with ethanedithiol (**2**) provides a convenient synthesis of [6.6.2]propellane **3**. From the formation of the by-product **4** it could be deduced that *cis*-1,2-*bis*(bromomethyl)-3,6-dithiabicyclo[6.2.0]decane (**4a**) was indeed formed during the reaction. Elimination of the bromine probably leads to propellane **4b** which in the next step eliminates ethylene to give compound **4**.



Scheme 3

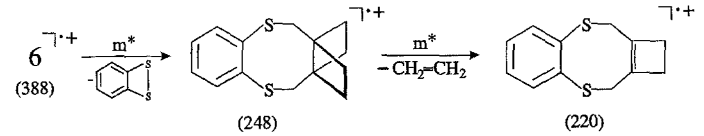
The aromatic analogue **6** of propellane **3** was obtained from tetrabromide **1** and 1,2-benzenedithiol (**5**). Again, no bispirane **6a** could be detected.



Scheme 4

The structure assigned to compound **6** is supported by elemental analysis as well as by UV/Vis, IR, ^{1}H, and ^{13}C NMR spectroscopy. The UV/Vis spectrum of **6** exhibits two characteristic absorption bands at $\lambda_{max} = 260\,nm\,(\lg\varepsilon = 4.12)$ and $\lambda = 271\,nm\,(\lg\varepsilon = 4.10)$. In contrast, the model monospirane **7** shows only one band at $\lambda_{max} = 269\,nm\,(\lg\varepsilon = 3.84)$. It has been found earlier that the UV/Vis spectra of bispiranes and their corresponding monospiranes are rather similar [9]. The ^{1}H NMR spectrum of compound **6** shows broad singlets at $\delta = 1.98$ and 3.29 ppm for the cyclobutane and methylene protons, respectively, and a multiplet for the aromatic protons ($\delta = 7.09$–7.41 ppm).

Strong arguments for the propellane structure of **6** are provided by the electron impact fragmentation of both compounds **6** and **7**. Thus, the mass spectrum of the monospirane **7** contains peaks corresponding to the ions formed due to the cleavage of the cyclobutane ring. This process, accompanied by hydrogen migrations, is responsible for peaks at $m/z = 197$, 196, and 195. They are produced by stepwise decomposition of the molecular ion with loss of an ethylene radical, an ethylene molecule, and an ethyl radical. On the contrary, fragmentation of the molecular ion of propellane **6** starts with cleavages of the heterocyclic moiety. The first step of the fragmentation of **6** affords the radical ion at $m/z = 248$ ([6.2.2]propellane). This ion loses an ethylene fragment, thus forming an ion at $m/z = 220$.



Scheme 5

From the above evidence it may be concluded that 1,1,2,2-*tetrakis*(bromomethyl)cyclobutane reacts with dithiols to new tetrathia[6.6.2]propellane systems.

Experimental

Melting points were determined on a Boetius apparatus and are uncorrected. IR: Bruker IFS 48; UV/Vis: Unicam SP-1800; ^{1}H and ^{13}C NMR: Bruker WM 500 (500 MHz), *TMS* as internal standard; MS: Finnigan MAT 44S (70 eV). Elemental analyses: Heraeus automatic C,H,N analyzer; the obtained values correspond with the calculated ones within experimental error.

3,6,10,13-Tetrathia[6.6.2]propellane (**3**; $C_{12}H_{20}S_4$) and *3,6-dithiabicyclo[6.2.0]deca-1(8)-en* (**4**; $C_8H_{12}S_2$)

A solution of 1,1,2,2-*tetrakis*(bromomethyl)cyclobutane (**1**, 1.30 g, 3 mmol) and 1,2-ethanedithiol (**2**, 0.58 g, 6 mmol) in benzene (60 ml) was added dropwise to a boiling solution of sodium hydroxide (0.50 g) in ethanol (300 ml). The solution was refluxed for 12 h. After evaporation of the solvent, the residue was dissolved in benzene and the precipitate was filtered off. The resulting solution was purified by column chromatography over silica gel (Aldrich, 70–230 mesh, elution with CH_2Cl_2/hexane (4:1)) to give **4** and **3**, respectively.

3: Colourless crystals (benzene-ethanol 1:1); 0.80 g (45%); m.p.: 117–118°C; IR (KBr): $\tilde{\nu}$ = 3040, 2950, 2920, 2840, 1420, 1260, 1190, 1140, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) : δ = 1.52–1.81 (m, 4H, CH_2-cyclobutane), 2.73 (s, 8H, CH_2S), 2.84 (s, 8H, vic. CH_2S) ppm; MS (70 eV): m/z (%) = 292 (6) [M$^+$], 232 (9), 172 (15), 139 (14) [172-SH], 125 (100) [172-CH_2SH], 111 (11) [172-CH_2SCH_3], 105 (60) [139-H_2S].

4: Colourless crystals (benzene – petroleum ether 2:1); 0.30 g (29%); m.p.: 56–57°C; IR(KBr): $\tilde{\nu}$ = 3015, 2940, 2900, 2820, 1630, 1420, 1260, 1180, 690 cm^{-1}; ^{1}H NMR $(CDCl)_3$:δ = 1.90(s, 4H, CH_2-cyclobutane), 2.68 (brs, 8H, CH_2S); MS (70 eV): m/z(%) = 172 (100)[M$^+$], 139 (32) [M-SH], 125 (36) [M-CH_2SH], 111(24) [M-CH_2SCH_3], 105(18) [139-H_2S].

3,6,10,13-Tetrathia(4,5,11,12-dibenzo)-[6.6.2]propellane (**6**; $C_{20}H_{20}S_4$)

Sodium (0.46 g, 20 mmol) was added to 25 ml of ethyl cellosolve in a thick walled tube. After the reaction was completed, 1,2-benzenedithiol (**5**, 1.42 g, 10 mmol) was added, followed by 1,1,2,2-*tetrakis*(bromomethyl)cyclobutane (**1**, 2.14 g, 5 mmol). The sealed tube was then heated at 120°C for 60 h. After evaporation of the solvent, the residue was dissolved in benzene, and the inorganic salt was filtered off. After removing the solvent, a little ethanol was added to precipitate the crude product. It was purified by high vacuum sublimation and following crystallization from benzene.

Colourless crystals; 0.71 g (36%); m.p.: 155–156°C; IR (KBr): $\tilde{\nu}$ = 3049, 2954, 2892, 1260, 1103, 1034, 871, 745 cm^{-1}; ^{1}H NMR $CDCl_3$: δ = 1.99 (br s, 4H, CH_2-cyclobutane), 3.29 (br s, 8H, CH_2S), 7.09–7.42 (m, 8H, ar) ppm; ^{13}C NMR ($CDCl_3$): δ = 2.97, 38.9, 48.0, 128.3, 129.0, 132.4 ppm; UV/Vis ($CHCl_3$): λ_{max} (lgε) = 260 (4.12), 271 (4.10) nm; MS (70 eV): m/z(%) = 388(35)[M$^+$], 248 (18), 247 (66), 220 (12), 153 (100), 105 (71), 91 (34).

Spiro(benzo-1,5-dithiepan-3,1'-cyclobutane) (**7**; $C_{12}H_{14}S_2$)

In an identical procedure, sodium (0.46 g, 20 mmol) was added to 25 ml of ethyl cellosolve. After the reaction was completed, 1,2-benzenedithiol (**5**, 0.71 g, 5 mmol) was added, followed by 1,1-*bis*(bromomethyl)cyclobutane (1.21 g, 5 mmol). The sealed tube was then heated for at 100°C 50 h.

Colourless crystals (benzene-ethanol 1:1), 0.33 g (30%); m.p.: 58–59°C; IR (KBr): $\tilde{\nu} = 3040$, 2985, 2950, 2880, 1450, 1225, 1020, 870, 760 cm^{-1}; UV/Vis ($CHCl_3$: $\lambda_{max}(\lg\varepsilon) = 269$ nm (3.84); ^1H NMR ($CDCl_3$): $\delta = 1.62$ (br s, 6H, CH_2-cyclobutane), 3.05 (br s, 4H, CH_2S), 7.15–7.52 (m, 4H, ar) ppm; MS (70 eV): $m/z(\%) = 222$ (100) [M^+], 195 (15), 196 (41), 197 (18), 141 (23), 91 (33).

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