Electroreduction of Organic Compounds, 23 [1]
Preparation of the Highly Strained 1',3'-Dichlorodispiro[cyclopropane-1,2'-bicyclo][1.1.0]butane-4',1''-cyclopropane [2]

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The preparation of the title compound 4 by electrochemical reduction of 4,4,8,8-tetrachloro-dispiro[2.1.2.1]octane 3 is described. The geometry of the compounds is discussed in terms of quantum chemical calculations and spectroscopic results.

Recently we have shown that highly strained bicyclobutanes can be synthesized by electrochemical reduction of the corresponding halides [3]. The successful application of this method to the synthesis of 1 encouraged us to attempt the synthesis of the more highly strained compound 4. Due to its high strain energy this fragile structure is calling for delicate isolation techniques.

Preparation of the tetrachloro precursor to 4 was accomplished by chlorination of the dione 2. The dione 2 was prepared by the method given by Hoffmann [4], which proved to be superior to the earlier method [5]. The polarographic analysis of the tetrachloro compound 3 showed a halfwave potential of $-3.3$ V vs. Ag/Ag$^+$ (AgNO$_3$, sat. in CH$_3$CN). In contrast to the corresponding precursor of 1, which exhibited two waves at $-3.0$ and $-3.55$ V respectively, only one wave could be detected. Preparative electrolysis of 3 commenced at a working potential of $-2.8$ V and an initial substrate concentration of 23 mmole$^{-1}$l$^{-1}$. Progress of the reaction was monitored by g.l.c. None of the reaction no side products (as found for 1) could be detected. Though, if moisture was not excluded thoroughly, the hydrolysis product 5 was isolated.

The thermal [6] or photochemical [7] conversion of bicyclobutanes to butadienes or cyclobutenes has been subject to discussions. According to these, bicyclobutanes are likely to undergo thermal rearrangement to 1,3-butadienes. The activation energy typically lies between 30 and 40 kcal/mole. This barrier was high enough to allow for isolation of the title compound 4 by preparative g.l.c. None of the corresponding 1,3-butadiene could be detected.

The $^1$H NMR spectrum of 4 is very complex showing four groups of two equivalent protons each. The three observed coupling constants are typical for cis-vicinal, trans-vicinal, and geminal couplings. Obviously the molecule does not exhibit the expected symmetry with two mirror planes but, possibly due to steric repulsion between the bridgehead chloro substituents and the cyclopropane protons, is twisted to a certain extent at the spiro centers.

The effect of additional strain caused by the two spirocyclopropane rings of 4 was investigated using semiempirical quantum mechanical calculations and was found to complement results found for the 2,4-dimethylene derivative 6, which has been synthesized recently and had been subject of some ab initio calculations [8, 9]. Results have been controversial, but it seems that the corresponding triplet diradical is thermodynamically more stable than the covalent isomer. Experimentally these could be even observed as separate species [10]. In the covalent isomer the bicyclobutane ring is calculated to be considerably flattened (ref. [8]: 135°;
Table I. Characteristic data of 4 as calculated by various quantum chemical methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>d [Å]</th>
<th>angle α [°]</th>
<th>ΔH [kcal/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF</td>
<td>1.5446</td>
<td>122.0</td>
<td>111.0</td>
</tr>
<tr>
<td>RHF/Triplet/CI</td>
<td>2.0707</td>
<td>166.7</td>
<td>105.4</td>
</tr>
<tr>
<td>RHF/Singlet/CI</td>
<td>1.5446</td>
<td>153.7</td>
<td>111.0</td>
</tr>
<tr>
<td>UHF/Singlet</td>
<td>1.5534</td>
<td>122.0</td>
<td>111.0</td>
</tr>
<tr>
<td>UHF/Triplet</td>
<td>2.0660</td>
<td>179.6</td>
<td>94.2</td>
</tr>
<tr>
<td>AM1/CI</td>
<td>1.5109</td>
<td>123.3</td>
<td>146.2</td>
</tr>
<tr>
<td>AM1/Triplet/CI</td>
<td>2.0729</td>
<td>179.6</td>
<td>141.5</td>
</tr>
<tr>
<td>AM1/UHF/Triplet</td>
<td>2.0793</td>
<td>177.7</td>
<td>133.8</td>
</tr>
<tr>
<td>AM1/UHF/Singlet</td>
<td>1.5110</td>
<td>123.3</td>
<td>146.2</td>
</tr>
<tr>
<td>AM1/RHF/Saddle</td>
<td>1.8956</td>
<td>157.5</td>
<td>175.9</td>
</tr>
</tbody>
</table>

Fig. 1. Calculated geometry of the triplet state of 4.

etherless experimentally observable [10] as is the triplet diradical [13]. The compounds under investigation are certainly a different system lacking some resonance stabilization, but nevertheless our results point in the same direction. CI calculations have been performed on the diradical systems, which are included in Table I. However, to get a better picture of the situation, one has to refer to ab initio multiconfiguration methods (MCSCF) with large basis sets.

Once the existence of two minima is established the question of the energy of the saddle point arises. Therefore, saddle point calculations were performed in order to locate the transition state. A saddle point location calculation was run with the AM1 method. The results indicated a saddle point with the data given in the Table (“saddle”).

Small ring bicyclobutanes can be conveniently prepared by electrochemical reduction. The structure of the title compound has been established by its spectroscopical properties. In addition to that, semiempirical calculations have been performed, which gave a good estimate of the nature of the central bond. The dispirobicyclobutanes have two

ref. [9]: 125°, 144°) [11], and the central bond lengthened (ref. [9]: 1.64/1.88 Å; ref. [8]: 1.78 Å). The triplet state of 6 is assumed to be planar. The small ring dispiro-bicyclobutanes can be regarded as bis-homo derivatives of 6. They are obviously less strained but also less stabilized by resonance effects.

Having synthesized the derivative 4, we performed semiempirical calculations using the AM-PAC [12] package. The structure of 1',3'-Dichlorodispiro[cyclopropane-1,2'-bicyclo[1.1.0]butane-4',1''-cyclopropane] 4 was calculated by semiempirical MNDO calculations in its covalent, singlet and triplet diradical states. The characteristic values are the length d of the central C–C bond of the cyclobutane ring, the angle α between the bicyclobutane planes and the enthalpy of formation ΔH. The more significant results of the MNDO calculations are given in Table I.

Obviously the triplet diradical is more stable than the singlet diradical and the latter is isoequidistant to the covalent form. In the triplet form the central bond is cleaved and the ring flattened as illustrated in Fig. 1. Calculations on dimethylenebicyclobutane on STO-3G and 3–21 G level of theory [8,13] have also shown the diradical to have a triplet ground state. The covalent species are nev-
closely related states like dimethylenebicyclobutane 3: the covalent form 2 and the triplet diradical 4. The central bond in the bicyclobutane ring of 2 has considerable diradical character too, resulting in a stretched and flattened ring.

**Experimental**

*General and routine instrumentation.*

NMR spectra were recorded on a Bruker WH 270 spectrometer using CDCl₃ as solvent and TMS as internal standard unless otherwise stated. IR spectra on a Perkin Elmer 399 instrument and Mass spectra on a Finnigan CH 7 or 311A or a VG-analytical 70–250S. Electrochemical measurements were performed with a Bruker 310 polarograph and a Metrohm polarography stand.

4,4,8,8-Tetrachloro-dispiro[2.1.2.1]octane (3)

3 g (22 mmol) Dispiro[2.1.2.1]octane-4,8-dione (2) [4,14] and 15 g (72 mmol) phosphorus pentachloride in 100 ml dry tetrachloromethane were heated to reflux for 4 h. The reaction mixture was poured on ice and neutralized with NaHCO₃. The organic layer was separated, the aqueous phase extracted twice with CHCl₃, and the combined extracts filtrated and shaken with water. After drying (MgSO₄) the solvents were evaporated. The residue was recrystallized from ethanol to give 3.1 g (57%) colourless crystals, m.p. 142–143 °C.

- **IR (KBr):** ν = 1420, 1315, 1245, 1025, 955, 920, 815, 775, 555 cm⁻¹. – **1H NMR (270 MHz):** δ = 1.63 (s, 8 H). – **13C NMR (67.93 MHz):** δ = 20.19 (CH₃), 54.0 (Cquart), 92.23 (CCl₂), 207.01 (C = O). – **MS (70 eV):** m/z = 244/246/248/250/252 (M⁺), 209/211/213/215 (M⁺-Cl).

C₈H₈Cl₄ (245.96)

Found C 39.07 H 3.30 Cl 57.66%

Calcd C 39.30 H 3.30 Cl 57.27%

80 mg (0.32 mmol) of 3 were reduced in a small electrochemical cell [15] with CH₃CN/0.2 M TPAP as solvent/supporting electrolyte system at a working potential of -2.4 V vs. Ag/AgNO₃ 0.1 M in CH₃CN. Progress of the reduction was monitored by g.l.c. The volatile compounds of the reaction mixture were evaporated at 10⁻⁴ Torr and condensed in a trap cooled with liquid nitrogen. The resulting liquid was subjected to preparative g.l.c. (140 °C isothermal 5 m 10% SE30 on Chromosorb W/AW DMCS 100–120 mesh) to yield 35 mg (63%) of 4, m.p. 54 °C. – **1H NMR (270 MHz):** δ = 1.21 (ddd, 3 J₁ = 10.2; 3 Jtrans = 8.0; 3 Jgem = 3.6 Hz, 1H), 1.35 (ddd, 3 J₁ = 10.2; 3 Jtrans = 8.0; 3 Jgem = 3.6 Hz, 1H), 1.43 (ddd, 3 J₁ = 10.2; 3 Jtrans = 8.0; 3 Jgem = 3.6 Hz, 1H), 1.49 (ddd, 3 J₁ = 10.2; 3 Jtrans = 8.0; 3 Jgem = 3.6 Hz, 1H). – **13C NMR (67.93 MHz):** δ = 15.45 (CH₃), 17.11 (CH₂), 44.29 (Cquart), 64.48 (CCl₂).

An identical reduction in THF/TBBF as solvent/supporting electrolyte system did not yield the target molecule but 31.5 mg (52%) of 7,7-Dichlorodispiro[2.1.2.1]octane-4-one (5), m.p. 102–104 °C. – **IR (KBr):** ν = 1760 cm⁻¹ (C=O). – **1H NMR (80 MHz):** δ = 1.8 (s, 8 H). – **13C NMR (67.93 MHz, C₆D₆):** δ = 20.58 (CH₃), 56.92 (Cquart), 90.29 (CCl₃), 207.01 (C=O). – **MS (70 eV):** m/z = 190 (M⁺), 155 (M⁺-Cl), 127, 91 (100%).

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