

# 9-Oxabicyclo[3.3.1]nona-2, 6-diene. Short Access and Allylic Bromination

Ghada Bassioni<sup>a</sup>, Fernando S. Delgado<sup>b</sup>, Matthieu Jaeggy<sup>a</sup>, Frank H. Köhler<sup>a</sup>, Stefan Nogai<sup>a</sup>, and Catalina Ruiz-Pérez<sup>b</sup>

<sup>a</sup> Department Chemie, Technische Universität München, D-85747 Garching, Germany

<sup>b</sup> Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental II, Universidad de La Laguna, Avda Astrofísico Francisco Sanchez, E-38204 La Laguna, Spain

Reprint requests to Prof. Dr. F. H. Köhler. E-mail: f.h.koehler@lrz.tu-muenchen.de

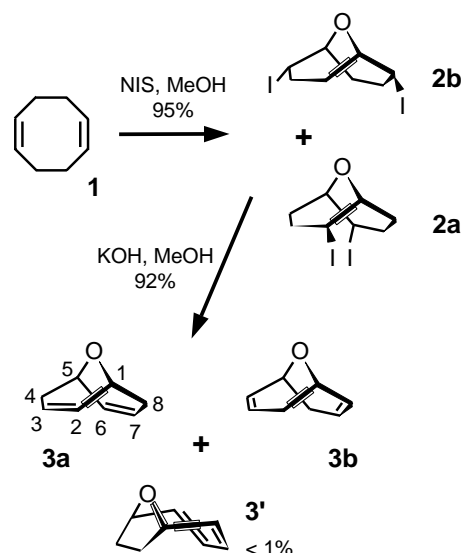
Z. Naturforsch. **60b**, 1143 – 1148 (2005); received June 26, 2005

9-Oxabicyclo[3.3.1]nona-2, 6-diene (**3**) has been synthesized from cycloocta-1, 5-diene in two steps in an overall yield of 88%. The dihedral-angle dependence of its <sup>1</sup>H solution NMR data and the double signal set of its <sup>13</sup>C CP MAS NMR spectrum correspond to the results of the single crystal structure analysis. Reaction of **3** with N-bromosuccinimide in the presence of sodium peroxodisulfate or benzoylperoxide has led in good yield to a dibromo derivative **4**, and a tribromo derivative **5**, respectively. Compounds **4** and **5** feature two allylic bromine substituents, while an additional vinylic bromine atom is present in **5**. According to a single crystal structure study the lattice of **4** consists of pairs of enantiomers similar to those found in the case of **3**.

**Key words:** Bicyclic Ether, Allylic Bromination, Vinylic Bromination, Crystal Structure

## Introduction

The parent bicyclic ether 9-oxabicyclo[3.3.1]nona-2, 6-diene (*cf.* **3** in Scheme 1; for simplicity, the same atom numbering is used for both enantiomers) has been known for almost four decades [1], and yet it attracts current interest, because it is a potential ligand of catalytically active metal complexes [2, 3]. Thus, a zirconium complex derived from **3** has been claimed to catalyze the polymerization of ethylene and the copolymerization of ethylene and 1-butene [3]. For this sort of studies and for the preparation of substituted derivatives an efficient synthesis of **3** was necessary. An effort has been made by Eaton and Millikan [4] who have reviewed early work and designed an improved synthesis, which led to a 7/1 mixture of **3** and the isomer 9-oxabicyclo[4.2.1]nona-2, 4-diene, **3'**. Checking their procedure [5] showed that the overall yield of 29% starting from cycloocta-1,5-diene could not be improved. Also, attempts to replace the toxic solvent HMPT by quinoline gave **3** and **3'** in a ratio of only 2/1, while N-methylpyrrolidone failed to give any bicyclic ether. Therefore, we have worked out a new procedure and thoroughly characterized the title compound. Parallel to this work [5, 6] the group of Haufe has obtained similar results [7]. As a basis for further studies, first steps towards functionalizing the allylic position of **3** gave two new bromo derivatives.



Scheme 1.

## Results and Discussion

When using cycloocta-1, 5-diene (**1**), as starting compound for the synthesis of **3** the key problem is to avoid the formation of any 9-oxabicyclo[4.2.1]nonane derivatives as a byproduct of the desired 9-oxabicyclo[3.3.1]nonane isomers. The best procedure is the reaction of **1** with N-iodosuccinimide with a 85% yield

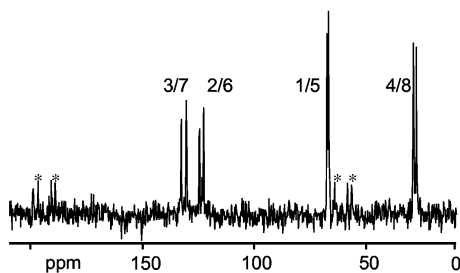


Fig. 1.  $^{13}\text{C}$  CP MAS NMR spectrum of **3** at  $-15\text{ }^{\circ}\text{C}$  and  $\nu_{\text{rot}} = 5\text{ kHz}$ . Spinning sidebands are labeled by asterisks.

of the diiodo derivatives **2** and with only 1% contamination of the [4.2.1]-bicyclic analogue [8] (Scheme 1). It turned out that the yield of **2** can be increased to 95%. Two single crystal X-ray studies [7, 9] have shown that the synthesis yields the enantiomers **2a** and **2b**. As has been demonstrated previously, dehydrohalogenation of **2a** and **2b** gives **3** in 18% and 90% yield when using KOH [10] and dicyclohexylmethylamine [11], respectively. We have optimized the first procedure (92%), while Haufe's group [7] has applied the second one with virtually the same result (88%). It is worth noting that because of the high volatility of **3** careful control is advisable for any solvent removal.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal shifts of **3** in solution mostly confirmed previous reports [2, 12, 13] within the experimental error limits. This work adds proton coupling constants (Table 1, Experimental Section), which reflect the geometry of **3** as far as three-bond couplings and their dihedral angle dependence are concerned (for details see below). The  $^1\text{H}$  NMR signals showed symmetric many-line patterns originating from couplings as small as 0.4 Hz. Small couplings are not given in Table 1, because the assignment was ambiguous. The two multiplet components of the signal of H4/8<sub>exo</sub> (separation 17.2 Hz) are somewhat asymmetric so that the coupling constants are less precise.

In the solid-state  $^{13}\text{C}$  NMR spectrum of **3** (Fig. 1) signals were found at positions very close to those of the solution spectrum, which means that intermolecular  $\pi$  interactions must be small. The olefinic signals showed a pronounced shift anisotropy as expected [14]. Surprisingly, however, two sets of signals were found rather than one in solution. This could be due to two different molecules in the asymmetric unit or to a change from  $C_2$  symmetry in solution to  $C_1$  in the solid state. A single crystal X-ray study established symmetry lowering to be responsible. Two pairs

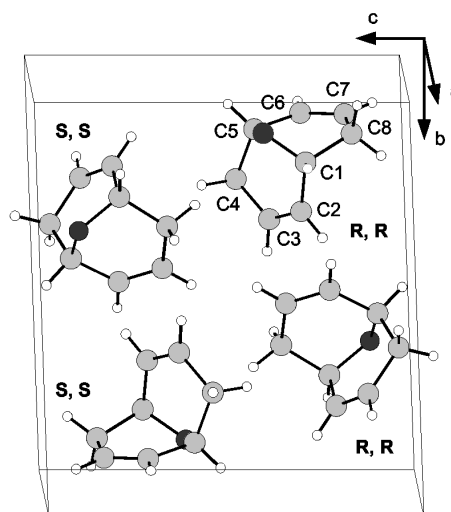
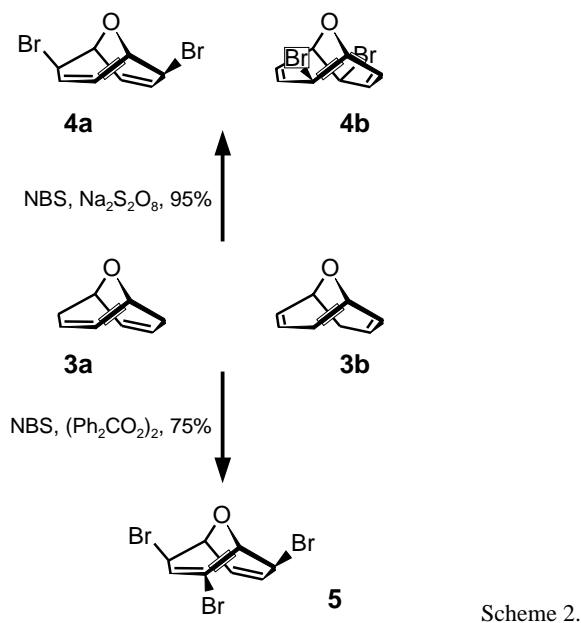


Fig. 2. Organization of 9-oxa bicyclo[3.3.1]nona-2, 6-diene molecules (**3**) in the unit cell. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^{\circ}$ ]: C1–C2 1.5059(18), C5–C6 1.5061(17), C2–C3 1.3241(19), C6–C7 1.3257(17), C3–C4 1.5017(17), C7–C8 1.5006(18), C4–C5 1.5311(17), C1–C8 1.5291(17), O–C1 1.4406(14), O–C5 1.4404(14), O–C1–C2 110.60(9), O–C5–C6 110.57(9), O–C1–C8 108.54(10), O–C5–C4 109.15(10), C2–C1–C8 112.40(12), C4–C5–C6 111.65(10), C1–O–C5 109.96(9).

of enantiomers **3a** and **3b** are present in the unit cell (Fig. 2) in accordance with the centrosymmetric space group  $P2_1/c$ . The molecules are arranged such that irregular stacks of only R, R or S, S enantiomers are formed in a and b direction of the unit cell, while along the c direction the stacks are made up from alternating enantiomers. Enantiopure samples of **3a** and **3b** have been prepared recently [2], but no solid-state studies have been performed. The intermolecular olefinic  $\text{C} \cdots \text{C}$  distances of **3a** and **3b** exceed  $5.4\text{ \AA}$ , which confirms the absence of  $\pi$  interactions as indicated by the  $^{13}\text{C}$  MAS NMR data. The molecules adopt a distorted double-chair conformation of two six-membered rings that are fused at C1, C5, and O9. This entails dihedral angles of  $\phi(\text{H3}, \text{C3}, \text{C4}, \text{H4}_{\text{exo}}) = 73.8^{\circ}$ ,  $\phi(\text{H7}, \text{C7}, \text{C8}, \text{H8}_{\text{exo}}) = 74.6^{\circ}$ ,  $\phi(\text{H3}, \text{C3}, \text{C4}, \text{H4}_{\text{endo}}) = 45.2^{\circ}$ , and  $\phi(\text{H7}, \text{C7}, \text{C8}, \text{H8}_{\text{endo}}) = 44.3^{\circ}$ . The dihedral angle dependence of vicinal coupling constants is well known [15, 16] and can be expressed as  $^3J(\text{H}, \text{H}) = 7 - \cos\phi + 5\cos 2\phi$ . Inserting mean angles into the equation yields  $^3J(\text{H}, \text{H})$  values (Table 1) which are in agreement with the experimental data. The fragment H7, C7, C8, H8 yields very similar values. It follows that in solution and in the crystal the structure of **1** is very similar, and if rapid conformational changes like



chair-boat flips occur, the distorted double-chair must be more stable.

The entry to 9-oxabicyclo[3.3.1]nona-2, 6-dienes which are substituted in the allylic position was achieved by Wohl-Ziegler bromination [17,18]. As illustrated in Scheme 2, the reaction of **3** with *N*-bromosuccinimide (NBS) did not only lead to substitution in the allylic but also the vinylic positions. The reaction turned out to depend strongly on the radical starter. Thus, when dibenzoylperoxide was used the tribromo derivative **5** was obtained in 85% yield, while in the case of 2, 2'-azoisobutyronitrile only a tetrabromo derivative lacking double bonds was detected by GC/MS and NMR analysis. In contrast, sodium peroxodisulfate gave a 95% yield of the enantiomeric dibromo derivatives **4a** and **4b**. Quite notably, the reaction is stereoselective with bromine only in the *exo* position of **4** and **5** as established by the coupling constants  $^3J(\text{H}3/7, \text{H}4/8)$  (5.2 to 5.6 Hz in Table 1) and confirmed by X-ray analysis of **4**.

In the crystal *exo, exo*-4, 8-dibromo-9-oxabicyclo[3.3.1]nona-2,6-diene features two pairs of enantiomers **4a** and **4b** in line with the space group *Cc* (Fig. 3). The alignment of **4** in the crystal resembles that of **3** after rearranging the crystal axes, and the geometric data do not depend strongly on the substitution. Likewise, the conformation of **4** is similar to that of **3**. There is a distortion of the double chair due to the olefinic carbon atoms which entail small dihedral an-

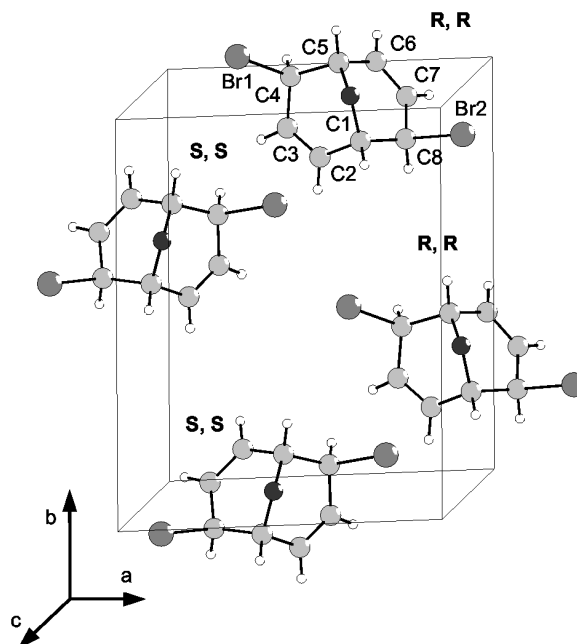
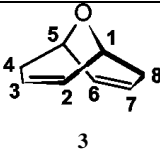
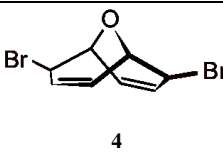
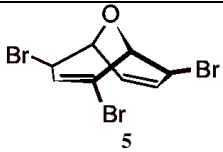


Fig. 3. Organization of the *exo, exo*-4, 8-dibromo-9-oxabicyclo[3.3.1]nona-2, 6-diene molecules (**4**) in the unit cell. Selected bond lengths [Å] and angles [°]: C1-C2 1.485(27), C5-C6 1.496(35), C2-C3 1.47(2), C6-C7 1.482(18), C3-C4 1.462(21), C7-C8 1.493(19), C4-C5 1.519(20), C1-C8 1.504(34), O-C1 1.421(16), O-C5 1.420(15), C4-Br1 1.984(43), C8-Br2 1.981(12), O-C1-C2 110.2(9), O-C5-C6 112.1(9), O-C1-C8 109.9(9), O-C5-C4 108.8(9), C2-C1-C8 110.2(11), C4-C5-C6 109.6(9), C1-O-C5 109.8(8).

gles for C1, C2, C3, C4 (**4**: 0.85°, **3**: 2.0°) and C5, C6, C7, C8 (**4**: -3.3°, **3**: 1.9°), while those of O, C5, C4, C3 (**4**: 49.2°, **3**: 47.3°) and O, C1, C8, C7 (**4**: 50.2°, **3**: 45.6°) are only 10–15° smaller than expected for undistorted rings. The calculation of the  $^3J(\text{H}, \text{H})$  coupling constants from the dihedral angle pairs  $\phi(\text{H}3, \text{C}3, \text{C}4, \text{H}4_{\text{endo}}) = 45.2^\circ$ , and  $\phi(\text{H}7, \text{C}7, \text{C}8, \text{H}8_{\text{endo}}) = 44.3^\circ$  as well as  $\phi(\text{H}1, \text{C}1, \text{C}8, \text{H}8_{\text{endo}}) = 76.7^\circ$  and  $\phi(\text{H}5, \text{C}5, \text{C}4, \text{H}4_{\text{endo}}) = 73.3^\circ$  gave values which are in good agreement with the experiment (Table 1).

The tribromo derivative **5** has been established by elemental analysis as well as by mass spectrometry and NMR spectroscopy. In particular, the three-bond proton coupling constants of H4 and H8 leave no doubt that the allylic bromo substituents are in *exo* position. All coupling patterns of the  $^1\text{H}$  NMR spectrum are comparatively simple and prove to be helpful for the assignment of the corresponding spectra of compounds **3** and **4**. Work aiming at metal-halogen exchange is now in progress.

Table 1. NMR data<sup>a</sup> of compounds **3**, **4**, and **5**.

			
$\delta$ (C1/5) solid	67.2, 66.6		
$\delta$ (C1/5)	66.3	72.7	
$\delta$ (H1/5)	4.31	4.79	4.77 (H1), 4.76 (H5)
$^3J$ (H1/5, H2/6)	$\sim 3.8$	4.1	4.1 (H5, H6)
$^3J$ (H1/5, H8/4exo)	$\sim 7.0$ (6.0)		
$^3J$ (H1/5, H8/4endo)	<sup>b</sup>	1.8 (2.4)	<sup>b</sup>
$^4J$ (H1/5, H3/7)	<sup>b</sup>	1.5	1.4 (H5, H7)
$\delta$ (C2/6) solid	124.3, 122.5		
$\delta$ (C2/6)	122.6	125.8	
$\delta$ (H2/6)	5.50	5.88	5.82 (H6)
$^3J$ (H2/6, H3/7)	10.2	10.0	10.1 (H6, H7)
$^3J$ (H2/6, H1/5)	3.8	4.1	4.1 (H6, H5)
$^4J$ (H2/6, H4/8exo)	2.6		
$\delta$ (C3/7) solid	132.5, 130.0		
$\delta$ (C3/7)	130.0	128.1	
$\delta$ (H3/7)	5.62	5.98	6.24 (H3), 6.02 (H7)
$^3J$ (H3/7, H2/6)	10.2	10.0	10.1 (H7, H6)
$^3J$ (H3/7, H4/8endo)	5.5 (6.3)	5.2 (5.9)	5.6 (H3, H4), 5.2 (H7, H8)
$^3J$ (H3/7, H4/8exo)	2.0 (2.5)		
$^4J$ (H3/7, H1/5)	<sup>b</sup>	1.5	1.4 (H7, H5)
$\delta$ (C4/8) solid	28.6, 27.2		
$\delta$ (C4/8)	28.3	41.6	
$\delta$ (H4/8exo)	2.33		
$^3J$ (H4/8exo, H4/8endo)	17.2		
$^3J$ (H4/8exo, H5/1)	$\sim 7.0$ (6.0)		
$^3J$ (H4/8exo, H3/7)	$\sim 2.0$ (2.5)		
$^4J$ (H4/8exo, H2/6)	$\sim 2.6$		
$\delta$ (H4/8endo)	1.39	4.25	4.54 (H4endo), 4.30 (H8endo)
$^2J$ (H4/8endo, H4/8exo)	17.1		
$^3J$ (H4/8endo, H3/7)	5.6 (6.3)	5.2 (5.9)	5.6 (H4, H3), 5.2 (H8, H7)
$^4J$ (H4/8endo, H5/1)	<sup>b</sup>	1.8 (2.4)	<sup>b</sup>

<sup>a</sup>  $\delta$ -Values (ppm) in solution unless stated otherwise; coupling constants in Hz,  $^3J$  couplings calculated from X-ray results in italics (see text); <sup>b</sup> assignment of coupling ambiguous.

## Experimental Section

All starting chemicals were commercially available except for *endo*, *endo*-2, 6-diiodo-9-oxabicyclo[3.3.1]nonane (**2**) which was synthesized from *cis*, *cis*-cycloocta-1, 5-diene [8]. The NMR spectra were recorded with Jeol Delta 400 (for solutions) and Bruker Avance 300 (for solid **3**) spectrometers. The mass spectra were obtained through GC/MS coupling by using a Hewlett Packard 5890 Series II gas chromatograph equipped with a HP-1 capillary (crosslinked silicone gum, 12 m  $\times$  0.2 mm  $\times$  0.33  $\mu$ m film) and a HP 5971 mass detector, temperature program SPLTL500.M; masses are given for  $^{79}\text{Br}$ . Elemental analyses were carried out by the microanalytical laboratory of the Department Chemie at Garching.

**9-Oxabicyclo[3.3.1]nona-2, 6-diene (3a/b):** A solution of **2** (40.5 g, 107 mmol) and KOH (43.6 g, 0.78 mol) in 270 ml of dry methanol was heated at 150 °C in a stainless steel autoclave. The HI elimination was monitored by integrating the  $^1\text{H}$  NMR spectra. Thus, after 24 h the reaction mixture contained **2**, the monoiodo derivative, and **3** in the ratio 21/27/52. The ratio shifted to 49/20/31 and 26/31/43 after two and three days, respectively, until the reaction was complete after four days. The autoclave was allowed to reach ambient temperature. To its content was added diethylether until a homogeneous phase was obtained, and the reaction mixture was worked up with water, a saturated solution of  $\text{NH}_4\text{Cl}$  in water and brine. The organic layer was dried with  $\text{MgSO}_4$  and the solvent was distilled off slowly by using a Vigreux column leaving behind brown crystals. Recrystallization from hexane

	<b>3a/b</b>	<b>4a/b</b>
Empirical formula	C <sub>8</sub> H <sub>10</sub> O	C <sub>8</sub> H <sub>8</sub> OBr <sub>2</sub>
Chemical formula weight	122.16 g/mol	279.96 g/mol
Unit cell dimensions	$a = 5.4167$ (1) Å $b = 11.5589$ (3) Å $c = 10.2632$ (2) Å $\alpha = 90.00^\circ$ $\beta = 100.66$ (10) $^\circ$ $\gamma = 90.00^\circ$ $V = 631.50$ (2) Å <sup>3</sup>	$a = 9.242$ (2) Å $b = 11.6221$ (2) Å $c = 8.959$ (2) Å $\alpha = 90.00^\circ$ $\beta = 111.04$ (3) $^\circ$ $\gamma = 90.00^\circ$ $V = 898.1$ (3) Å <sup>3</sup>
Cell formula units	4	4
Density	1.285 g cm <sup>-3</sup>	2.071 g cm <sup>-3</sup>
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $Cc$
Rad. wavelength $\lambda$ (MO-K $\alpha$ )	0.71073 Å	0.71073 Å
Temperature	143(2) K	293(2) K
Exptl. Absorption coefficient	0.083 mm <sup>-1</sup>	8.966 mm <sup>-1</sup>
F(000)	264	536
Index region	$0 \leq h \leq 6$ , $0 \leq k \leq 13$ , $-12 \leq l \leq 12$	$-12 \leq h \leq 11$ , $-13 \leq k \leq 15$ , $-11 \leq l \leq 9$
Diffraction reflections $\theta$	$2.68^\circ < \theta < 25.11^\circ$	$6.5^\circ < \theta < 27.5^\circ$
Completeness to $\theta = 25.11$	93.5%	97.9%
Absorption correction	None	None
Reflections collected / unique	13829 / 1058 [ $R(\text{int}) = 0.030$ ]	2835 / 1581 [ $R(\text{int}) = 0.1092$ ]
Reflection number $> 2\sigma(I)$	1348	1348
Data / restraints / parameters	1058 / 0 / 83	1581 / 2 / 107
Extinction coefficient	0.108 (18)	none
Goodness-of-fit	1.064	1.110
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0392$ , $wR2 = 0.1057$	$R1 = 0.0622$ , $wR2 = 0.1497$
$R$ Indices (all data)	$R1 = 0.0394$ , $wR2 = 0.1060$	$R1 = 0.0763$ , $wR2 = 0.1616$
Largest diffract. peak and hole	0.167 and $-0.185$ eÅ <sup>-3</sup>	1.345 and $-0.664$ eÅ <sup>-3</sup>
Weighing scheme <sup>a</sup>	$a = 0.0628/b = 0.1817$	$a = 0.0759/b = 6.2911$

Table 2. Crystallographic data and details of the data collection and structure refinement for compounds **3a/b** and **4a/b**.

$$^a w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp];$$

$$p = (F_o^2 + 2F_c^2)/3.$$

gave **3a/b** as a white microcrystalline powder. Yield 12.1 g (92%). – MS (EI, 70 eV):  $m/z$  (%) = 122 (90) [ $M^+$ ], 104 (20) [ $C_8H_8^+$ ], 91 (65) [ $C_7H_7^+$ ], 77 (85) [ $C_6H_5^+$ ], 68 (100) [ $C_4H_4O^+$ ]. – C<sub>8</sub>H<sub>10</sub>O (122.16): calcd. C 78.65, H 8.25; found C 78.63, H 8.32. Experimental and calculated NMR data are collected in Table 1.

*exo, exo-4, 8-Dibromo-9-oxabicyclo[3.3.1]nona-2, 6-diene (4a/b)*: *N*-Bromosuccinimide (2.9 g, 16.3 mmol) was suspended in a solution of **3** (1.0 g, 8.2 mmol) in 85 ml of dry CCl<sub>4</sub>. After addition of 0.15 g Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> the suspension was heated to reflux for 40 h. The hot reaction mixture was filtered, water (100 ml) was added, the phases were separated, and the organic layer was dried with MgSO<sub>4</sub>. After removal of CCl<sub>4</sub> by using a rotary evaporator brown crystals were obtained which after washing with clean CCl<sub>4</sub> became colorless. Yield 1.5 g (95%). – MS (EI, 70 eV):  $m/z$  (%) = 282 (15) [ $MH^+$ ], 278 (6) [ $M^+$ ], 199 (100) [ $M^+ - Br$ ], 119 (38) [ $M^+ - 2Br$ ]. – C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>O (279.96): calcd. C 34.32, H 2.88; found C 34.35, H 2.96. Experimental and calculated NMR data are collected in Table 1.

*Bromination of 3 with N-bromosuccinimide/dibenzoylperoxide*: The same quantities and the same procedure as described in the previous paragraph were used except for re-

placing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> by 10 mg of dibenzoylperoxide. After workup a white microcrystalline powder was obtained which according to GC/MS consisted of 2, *exo, exo*-4, 8-tribromo-9-oxabicyclo[3.3.1]nona-2, 6-diene (**5**) and **4** in the ratio 85/15. Yield 2.5 g (**5**: 75%, **4**: 13%). – MS (EI, 70 eV):  $m/z$  (%) = 359 (2) [ $M^+$ ], 281 (14) [ $MH^+ - Br$ ], 277 (13) [ $M^+ - Br$ ], 199 (14) [ $M^+ - 2Br$ ], 172 (14) [ $M^+ - 2Br$ ], 169 (100) [ $M^+ - 2Br$ ], 119 (27) [ $M^+ - 3Br$ ].

#### Single crystal X-ray structure determination of compounds **3a/b** and **4a/b**

Suitable crystals of **3a/b** and **4a/b** were grown by recrystallization from hexane and by slow evaporation of a saturated solution in CH<sub>2</sub>Cl<sub>2</sub>, respectively. Crystal data and details of the structure determination are summarized in Table 2.

**3a/b**: A crystal of suitable quality and size was mounted on the end of a quartz fiber in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction was done using the DENZO\SCALEPACK [19] suite of programs. The structure was solved by direct methods and refined with full-

matrix least-squares calculations on  $F^2$  using the SHELXS-97 [20] and SHELXL-97 [20] programs. Thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated in ideal positions and refined after a riding model. A summary of the crystallographic data and structure refinement is given in Table 2.

**4a/b:** A single crystal of the compound was mounted on a Bruker-Nonius KappaCCD diffractometer. Orientation matrix and lattice parameters were obtained by least-squares refinement of the reflections obtained by a  $\theta$ - $\chi$  scan (Dirax/lsc method). Diffraction data were collected employing graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). All calculations for data reduction, structure solution, and refinement were done by standard procedures

(WINGX) [21]. The structure was solved by direct methods and refined with full-matrix least-squares technique on  $F^2$  using the SHELXS-97 [20] and SHELXL-97 [20] programs. The hydrogen atoms were positioned from and refined with isotropic temperature factors. The final geometrical calculations were carried out with PARST97 [22] program. A summary of the crystallographic data and structure refinement is given in Table 2. – CCDC reference numbers 279270 (**3a/b**), 286021 (**4a/b**).

#### Acknowledgements

Helpful discussion with Dr. E. Herdtweck and financial support by the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

- 
- |   |  |
|---|--|
| <p>[1] H. Stetter, H.-J. Meissner, <i>Tetrahedron Lett.</i> <b>4599</b> (1966).</p> <p>[2] A. Takahashi, M. Aso, M. Tanaka, H. Suemune, <i>Tetrahedron</i> <b>56</b>, 1999 (2000).</p> <p>[3] S. Nagy, K. L. Neal-Hawkins, J. L. Schuchardt (Equestar Chemical) WO 2003008464.</p> <p>[4] P. E. Eaton, R. Millikan, <i>Synthesis</i> <b>483</b> (1990).</p> <p>[5] G. Bassioni, Master thesis, Ain Shams University, Cairo (Egypt) (2000).</p> <p>[6] G. Bassioni, PhD thesis, Technische Universität München (Germany) (2004).</p> <p>[7] K. Hegemann, R. Fröhlich, G. Haufe, <i>Eur. J. Org. Chem.</i> <b>2181</b> (2004).</p> <p>[8] G. Haufe, <i>Tetrahedron Lett.</i> <b>25</b>, 4599 (1984).</p> <p>[9] R. Wartchow, U. Albrecht, H. M. R. Hoffmann, <i>Z. Kristallogr.</i> <b>211</b>, 328 (1996).</p> <p>[10] C. Ganter, W. Wicker, W. Zwahlen, K. Schaffner-Sabba, <i>Helv. Chim. Acta</i> <b>53</b>,</p> <p>[11] H. Stetter, K. Heckel, <i>Tetrahedron Lett.</i> <b>801</b> (1972).</p> <p>[12] N. S. Zefirow, S. V. Rogozina, <i>Tetrahedron</i> <b>30</b>, 2352 (1973).</p> | <p>[13] E. Cuthbertson, D. D. McNicol, <i>J. Chem. Soc., Perkin Trans.</i> <b>1893</b> (1974).</p> <p>[14] T. M. Duncan, <i>A Compilation of Chemical Shift Anisotropies</i>, Farragut Press, Chicago (1990).</p> <p>[15] A. P. Marchand, <i>Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems</i>, Verlag Chemie International, Deerfield Beach, Florida, USA (1982).</p> <p>[16] H. Günther, <i>NMR Spectroscopy</i>, Wiley, Chichester (1995).</p> <p>[17] C. Djerassi, <i>Chem. Rev.</i> <b>43</b>, 271 (1948).</p> <p>[18] L. Horner, E. H. Winkelmann, <i>Angew. Chem.</i> <b>71</b>, 349 (1959).</p> <p>[19] Z. Otwinowski, W. Minor, <i>Methods Enzymol.</i> <b>276</b>, 307 (1997).</p> <p>[20] G. M. Sheldrick, SHELXS-97 &amp; SHELXL-97, Programs for Crystal Structure Analysis (Release 97-2). Institut für Anorganische Chemie der Universität, Tammanstraße 4, D-3400 Göttingen, Germany (1998).</p> <p>[21] L. J. Farrugia, <i>J. Appl. Crystallogr.</i> <b>32</b>, 837 (1999).</p> <p>[22] M. Nardelli, <i>J. Appl. Crystallogr.</i> <b>28</b>, 659 (1995).</p> |
|---|--|