Synthesis and X-Ray Crystal Structure of 1,3,3,4,5,6-Hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-Oxide

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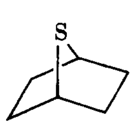
Refluxing a toluene solution containing equimolar quantities of hexamethyl-2,4-cyclohexadienone and ethylene episulfoxide under nitrogen affords hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-oxide (10) in nearly quantitative yield. The detailed molecular geometry of 10 follows from its x-ray crystal structure. Treatment of 3,4,6,6-tetramethyl-2,4-cyclohexadienone under identical conditions returns starting material.

Although 7-thiabicyclo[2.2.1]heptane (1) has been known for some time,[2] only one unsaturated derivative of 1 has been isolated.[3] Bailey and Cummins found that treatment of thiophene 1,1-dioxide (2) with diethyl acetylenedicarboxylate at 0 °C gave a crystalline compound of molecular formula $C_{12}H_{14}O_6S$ which lost sulfur dioxide upon gentle heating to give diethyl phthalate (4).[3] In view of these results, the intermediate was assigned structure **3**.[3]



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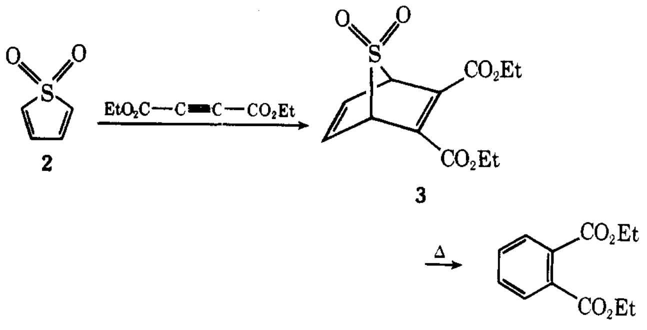

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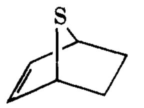
In principle, the 7-thiabicyclo[2.2.1]hept-2-ene skeleton (5) should be accessible by the Diels–Alder addition of sulfur monoxide or sulfur dioxide to 1,3-cyclohexadiene (6). However, treatment of 6 with sulfur dioxide at −50 °C in the presence or absence of oxygen only leads to copolymerization.[4] Since 1,3-cycloheptadiene (7) reacts with sulfur dioxide to give a nearly quantitative yield of 8-thiabicyclo[3.2.1]oct-6-ene 8,8-dioxide (8),[5] it has been contended that isolation of the monoadduct of 6 with sulfur dioxide has not been achieved owing to the instability of the Diels–Alder product.[6] We now wish to report the synthesis of a stable derivative of 5.



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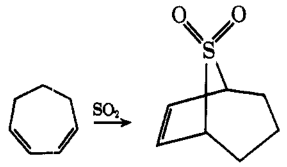

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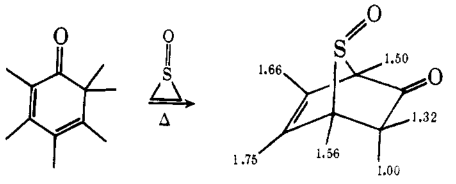
Results and Discussion

Refluxing a toluene solution containing equimolar quantities of hexamethyl-2,4-cyclohexadienone (9)[7] and ethylene episulfoxide (which is known to thermally decompose at ca. 100 °C to ethylene and sulfur monoxide[8]) under nitrogen for 5 h proceeded with a ca. 40% conversion of 9 to give a nearly quantitative yield of hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-oxide (10).[9] Changing the molar ratio of the reacting species, the time of reaction, or not employing a nitrogen atmosphere all resulted in reduced yields of **10**. However, refluxing **10** in toluene for 1.5 h did not lead to its thermal decomposition.



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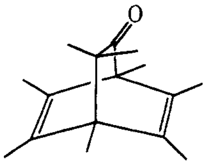
Unreacted dienone **9** was readily removed from the product by vacuum distillation. Upon extended standing, sulfoxide **10** slowly crystallized from the distillation residue. Alternatively, **9** and **10** could be separated by chromatography on silica gel with benzene–methylene chloride as eluent. Repeated recrystallization of **10** from pentane gave white crystals of mp 84.5–85 °C. The preliminary structure assignment of **10** followed from its spectroscopic characteristics. The infrared spectrum of **10** contains a strong carbonyl absorption at 1738 cm^{-1}, indicative of a five-membered ring ketone, and a strong sulfoxide absorption at 1070 cm^{-1}. The ^1H NMR spectrum of **10** consists of aliphatic methyl singlets at δ 1.56, 1.50, 1.32, and 1.00 and allylic methyl quartets (J = 1 Hz) at δ 1.75 and 1.66. The ^1H NMR spectrum of **10** derived from dienone **9** with a CD_3 group at C-3 in 9[10] lacks the quartet at δ 1.66 and the quartet at δ 1.75 has sharpened to a singlet. Similarly, the ^1H NMR spectrum of **10** prepared from dienone **9** with a CD_3 group at C-5 in 9[10] is missing the singlet at δ 1.56. Since the *gem*-dimethyls in 11[11] and 12[12] appear at δ 0.82 and 0.90, respectively, the chemical shifts of all of the methyl groups in **10** can be confidently assigned as indicated in the figure.



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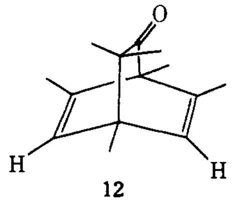

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In order to complete the structure assignment of **10**, it remained to define the stereochemistry at sulfur. Recrystallization of **10** ($C_{12}H_{18}O_2S$, mol wt 226.33) from heptane gave

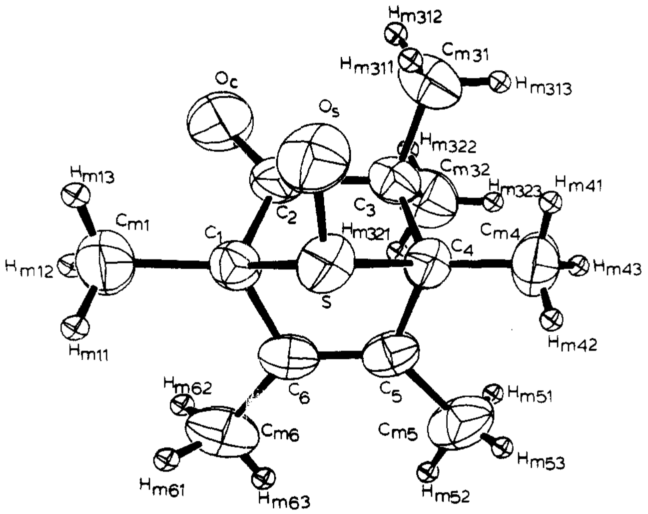

Figure 1. An ORTEP drawing showing the solid-state molecular structure of 1,3,3,4,5,6-hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-oxide (**10**). All atoms except hydrogen are represented by a (50% probability) ellipsoid having the shape, orientation, and relative size consistent with the refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

single crystals suitable for x-ray studies which were orthorhombic of space group P_{bca}-D_{2h}^{15} (no. 61)[13] with $a = 9.494 \pm 0.001$ Å, $b = 13.123 \pm 0.001$ Å, $c = 20.012 \pm 0.002$ Å, and $Z = 8$ at 20 ● 1 °C [$d_{\text{calcd}} = 1.207$ g cm^{-3}, $d_{\text{measd}} = 1.199$ g cm^{-3} μ_a(Cu K$\overline{\alpha}$)[14] = 2.074 mm^{-1}]. Intensity measurements for a spherical specimen 0.48 mm in diameter ($\mu r = 0.50$) on a Syntex P$\overline{1}$ autodiffractometer with 1° wide ω scans and graphite-monochromated Cu K$\overline{\alpha}$ radiation gave a total of 1679 independent reflections having $2\theta_{\text{CuK}\overline{\alpha}} < 115°$ (the equivalent of 0.60 limiting Cu K$\overline{\alpha}$ spheres). For those reflections having $2\theta_{\text{CuK}\overline{\alpha}} < 84°$, a scanning rate of 3°/min was employed for the scan between ω settings 0.50° respectively above and below the calculated K$\overline{\alpha}$ doublet value ($\lambda_{\text{K}\overline{\alpha}} = 1.54178$ Å). A scanning rate of 2°/min was used for the remaining reflections. Each 1° scan was divided into 19 equal (time) intervals and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan (13/19 of the total scan time), were measured at ω settings 1° above and below the calculated K$\overline{\alpha}$ doublet value for each reflection. The data were corrected for absorption as a strict function of the scattering angle.[15]

The 15 nonhydrogen atoms comprising the asymmetric unit appeared simultaneously on an E map which was calculated from a trial set of statistical direct methods (MULTAN) phases. All 18 chemically anticipated hydrogen atoms were located from a difference Fourier synthesis calculated from a full-matrix least-squares refined structural model [R (unweighted) = 0.084, r (weighted) = 0.104 for 1334 reflections having $2\theta_{\text{CuK}\overline{\alpha}} < 105°$ and $I > 3\sigma(I)$] which incorporated unit weighting and anisotropic thermal parameters for all nonhydrogen atoms. All structure factor calculations employed a least-squares refineable extinction correction[16] of the form $1/(1 + gI_c)^{1/2}$, the atomic form factors compiled by Cromer and Mann,[17] and an anomalous dispersion correction to the scattering factor of the sulfur atom.[18] The final cycles of empirically weighted full-matrix least-squares refinement which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to values of 0.034 and 0.041 for R and r, respectively, for 1603 independent reflections having $2\theta_{\text{CuK}\overline{\alpha}} < 115°$ and $I > \sigma(I)$.

Figure 1 shows a computer-generated drawing of **10**.[19] The x-ray crystal structural analysis clearly indicates that the sulfoxide oxygen atom is anti to the C_5–C_6 double bond. Examination of the bond length and bond angle data in Tables I–III reveals that significant distortions from idealized geometries for certain atoms are present in **10**. As might be anticipated, the bond angles are affected considerably more than the bond lengths. The C_1SC_4 angle of 81.4 (1)°[20] is considerably smaller than that proposed in any normal hybridization scheme for sulfur and well outside the 95.2–98.2° range found for CSC angles in several sulfoxides in which the sulfur atom is not part of a small (<six atoms) ring.[21] Five of the six CCC bond angles within the six-membered ring are also significantly smaller than their respective idealized sp^2 or sp^3 hybridized values. Unfavorable intramolecular contacts of 2.41 (3) and 3.022 (3) Å for O_s with H_{m311} and C_2, respectively (the corresponding van der Waals contact values[22] are 2.60 and 3.10 Å) are probably responsible for the 0.22 Å elongation of the C_4–S bond relative to C_1–S and the 8.4° opening of the C_2C_1S and C_3C_4S pair of bond angles relative to the C_6C_1S and C_5C_4S pair.

Whereas many of the bond angles exhibit major departures from their idealized values, bond lengths of a given type show much less deviation from their generally accepted (x-ray) values. Average values for the five sp^3–sp^3 and the six sp^2–sp^3 C–C single bonds in **10** are 1.528 (3, 16, 21)[20] and 1.515 (3, 10, 17) Å, respectively. The C–H bonds have an average length of 0.96 (3, 3, 6) Å, which is in excellent agreement with values determined by x-ray studies of compounds containing similar bonds.[23] Intermolecular contacts for only two pairs of atoms (each pair contains one oxygen and one hydrogen atom) in the crystal are less than the sum of their respective van der Waals radii (2.60 Å in this case[22]). These short contacts include a 2.46 (3) Å $O_2 \cdots H_{m11}$ and a 2.57 (4) Å $O_c \cdots H_{m62}$ separation. Each atom of the following groups is coplanar to within 0.04 Å with Å $O_2 \cdots H_{m11}$ and a 2.57 (4) Å $O_c \cdots H_{m62}$ separation. Each atom of the following groups is coplanar to within 0.04 Å with all other members of the group: C_2, C_3, C_5, and C_6, group I; C_1, C_2, C_3, C_4, and O_c, group II; C_1, C_4, C_5, C_6, C_{m5}, and C_{m6}, group III; and C_{m1}, C_1, S, C_4, and C_{m4}, group IV. Angles between the normals to the least-square mean planes for these groupings follow (in pairs): I–II, 28.7°; I–III, 31.3°; I–IV, 85.1°; II–III, 60.0°; II–IV, 56.4°; and III–IV, 63.6°.

It appears that a trace amount of the 7-*syn*-oxide of **10** is also formed in the addition of sulfur monoxide to **9**. The ^{1}H NMR spectrum of the first fraction containing **10** (ca. 30 mg) eluted during the column chromatography of the reaction mixture obtained from treatment of 1.62 g of **9** with an equimolar quantity of ethylene episulfoxide shows in addition to the signals for the 7-*anti*-oxide of **10** what are presumably aliphatic methyl singlets at δ 1.40, 1.36, 1.27, and 0.93 and allylic methyl quartets (J = 1 Hz) at δ 1.84 and 1.74. Although the syn and anti isomers of **10** appear to be present in approximately equal amounts in this fraction, the material in all of the other fractions from the column chromatographic separation was isomerically pure.

The preponderance of the 7-*anti*-oxide of **10** formed in the addition of sulfur monoxide to **9** parallels the addition of sulfur monoxide to *cis,cis*-1,3-cyclooctadiene (**13**) which is reported to give "essentially exclusive formation of stereo-

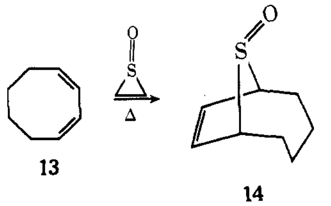

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Table I. Bond Lengths in Crystalline $C_{12}H_{18}O_2S$[a]

Type[b]	Bond length, Å	Type[b]	Bond length, Å	Type[b]	Bond length, Å
$S–C_1$	1.848 (2)	$C_1–C_{ml}$	1.507 (3)	$C_{m31}–H_{m313}$	0.95 (3)
$S–C_4$	1.870 (2)	$C_4–C_{m4}$	1.510 (3)	$C_{m32}–H_{m321}$	1.01 (3)
		$C_3–C_{m31}$	1.540 (4)	$C_{m32}–H_{m322}$	0.94 (3)
$S–O_s$	1.483 (2)	$C_3–C_{m32}$	1.536 (4)	$C_{m32}–H_{m323}$	0.95 (3)
		$C_3–C_4$	1.547 (3)	$C_{m4}–H_{m41}$	1.00 (3)
$C_2–O_c$	1.200 (3)			$C_{m4}–H_{m42}$	0.95 (4)
		$C_5–C_6$	1.329 (3)	$C_{m4}–H_{m43}$	1.02 (3)
$C_1–C_2$	1.526 (3)			$C_{m5}–H_{m51}$	0.91 (4)
$C_1–C_6$	1.523 (3)	$C_{m1}–H_{m11}$	1.01 (3)	$C_{m5}–H_{m52}$	0.98 (4)
$C_2–C_3$	1.525 (3)	$C_{m1}–H_{m12}$	0.91 (4)	$C_{m5}–H_{m53}$	0.90 (4)
$C_4–C_5$	1.515 (3)	$C_{m1}–H_{m13}$	0.99 (3)	$C_{m6}–H_{m61}$	0.95 (3)
$C_5–C_{m5}$	1.503 (4)	$C_{m31}–H_{m311}$	1.00 (3)	$C_{m6}–H_{m62}$	0.97 (4)
$C_6–C_{m6}$	1.498 (3)	$C_{m31}–H_{m312}$	0.97 (3)	$C_{m6}–H_{m63}$	0.91 (3)

[a] The number in parentheses following each entry is the least-squares estimate of the standard deviation of the last significant figure. [b] Atoms labeled to agree with Figure 1.

Table II. Bond Angles for Nonhydrogen Atoms in Crystalline $C_{12}H_{18}O_2S$[a]

Type[b]	Bond angle, deg	Type[b]	Bond angle, deg	Type[b]	Bond angle, deg
C_1SC_4	81.4 (1)	$C_1C_2C_3$	111.0 (2)	$C_{m4}C_4S$	111.2 (2)
C_1SO_s	111.2 (1)	$O_cC_2C_3$	125.6 (2)	$C_{m4}C_4C_3$	117.0 (2)
C_4SO_s	112.9 (1)	$C_2C_3C_4$	103.1 (2)	$C_{m4}C_4C_5$	117.4 (2)
C_2C_1S	101.0 (1)	$C_2C_3C_{m31}$	109.4 (2)	$C_3C_4C_5$	108.9 (2)
C_6C_1S	95.0 (1)	$C_2C_3C_{m32}$	109.6 (2)	$C_4C_5C_6$	111.2 (2)
$C_{m1}C_1S$	114.4 (2)	$C_4C_3C_{m31}$	113.8 (2)	$C_4C_5C_{m5}$	121.4 (2)
$C_{m1}C_1C_2$	115.4 (2)	$C_4C_3C_{m32}$	111.9 (2)	$C_6C_5C_{m5}$	127.4 (3)
$C_{m1}C_1C_6$	119.8 (2)	$C_{m31}C_3C_{m32}$	108.8 (2)	$C_5C_6C_1$	111.1 (2)
$C_2C_1C_6$	108.0 (2)	C_3C_4S	105.0 (1)	$C_1C_6C_{m6}$	120.2 (2)
$C_1C_2O_c$	123.4 (2)	C_5C_4S	94.3 (1)	$C_5C_6C_{m6}$	128.6 (2)

[a] The number in parentheses following each entry is the least-squares estimate of the standard deviation of the last significant figure. [b] Atoms labeled to agree with Figure 1.

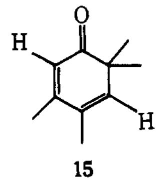
Table III. Bond Angles Involving Hydrogen Atoms in Crystalline $C_{12}H_{18}O_2S$[a]

Type[b]	Bond angle, deg	Type[b]	Bond angle, deg	Type[b]	Bond angle, deg
$C_1C_{m1}H_{m11}$	112 (2)	$C_3C_{m32}H_{m321}$	111 (2)	$C_5C_{m5}H_{m51}$	109 (2)
$C_1C_{m1}H_{m12}$	109 (2)	$C_3C_{m32}H_{m322}$	107 (2)	$C_5C_{m5}H_{m52}$	112 (2)
$C_1C_{m1}H_{m13}$	112 (2)	$C_3C_{m32}H_{m323}$	107 (2)	$C_5C_{m5}H_{m53}$	113 (2)
$H_{m11}C_{m1}H_{m12}$	105 (3)	$H_{m321}C_{m32}H_{m322}$	108 (3)	$H_{m51}C_{m5}H_{m52}$	105 (3)
$H_{m11}C_{m1}H_{m13}$	109 (2)	$H_{m321}C_{m32}H_{m323}$	116 (3)	$H_{m51}C_{m5}H_{m53}$	110 (3)
$H_{m12}C_{m1}H_{m13}$	109 (3)	$H_{m322}C_{m32}H_{m323}$	108 (3)	$H_{m52}C_{m5}H_{m53}$	108 (3)
$C_3C_{m31}H_{m311}$	112 (2)	$C_4C_{m4}H_{m41}$	110 (2)	$C_6C_{m6}H_{m61}$	112 (2)
$C_3C_{m31}H_{m312}$	108 (2)	$C_4C_{m4}H_{m42}$	111 (2)	$C_6C_{m6}H_{m62}$	111 (2)
$C_3C_{m31}H_{m313}$	109 (2)	$C_4C_{m4}H_{m43}$	110 (2)	$C_6C_{m6}H_{m63}$	111 (2)
$H_{m311}C_{m31}H_{m312}$	105 (3)	$H_{m41}C_{m4}H_{m42}$	111 (3)	$H_{m61}C_{m6}H_{m62}$	102 (3)
$H_{m311}C_{m31}H_{m313}$	113 (3)	$H_{m41}C_{m4}H_{m43}$	108 (2)	$H_{m61}C_{m6}H_{m63}$	110 (3)
$H_{m312}C_{m31}H_{m313}$	109 (3)	$H_{m42}C_{m4}H_{m43}$	108 (3)	$H_{m62}C_{m6}H_{m63}$	110 (3)

[a] The number in parentheses following each entry is the least-squares estimate of the standard deviation of the last significant figure. [b] Atoms labeled to agree with Figure 1.

isomer 14".[9c] A rationale which accounts for these observations has already been presented.[9d]

The synthesis of 7-thiabicyclo[2.2.1]hept-5-en-2-one 7-oxides by Diels–Alder addition of sulfur monoxide to 2,4-cyclohexadienones does not seem to be general. For example, treatment of 3,4,6,6-tetramethyl-2,4-cyclohexadienone (15)[24] under the identical conditions employed for 9 → 10 gives only recovered starting material. Of course, this result may be a consequence of the instability of the Diels–Alder adduct of sulfur monoxide and 15 at 110 °C.



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Experimental Section

Hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-Oxide (10). A solution of freshly distilled ethylene episulfoxide[8] (2.9 g, 37.8

mmol) and hexamethyl-2,4-cyclohexadienone[7] (6.7 g, 37.6 mmol) in 137 mL of toluene was heated at reflux under nitrogen for 5 h. After cooling, the solvent was evaporated at reduced pressure to give an oil. ^{1}H NMR analysis of the crude reaction mixture showed that the reaction had proceeded with a ca. 40% conversion of the starting dienone to give a quantitative yield of **10**. Most of the dienone was removed by distillation (55 °C, 0.03 mm). Upon extended standing, sulfoxide **10** slowly crystallized from the distillation residue. Repeated recrystallizations from pentane gave **10** as a white, crystalline solid: ν (CCl$_4$) 2970, 2935, 1738, 1475, 1455, 1435, 1385, 1375, 1290, 1190, 1110, 1100, 1070, and 1005 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02; S, 14.17. Found: C, 63.69; H, 7.85; S, 13.96.

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Registry No.—**9**, 3854-96-4; *anti*-**10**, 61966-92-5; *syn*-**10**, 61966-93-6; ethylene episulfoxide, 7117-41-1.

Supplementary Material Available. A listing of fractional coordinates for nonhydrogen atoms, anisotropic thermal parameters for nonhydrogen atoms, refined fractional coordinates and isotropic thermal parameters for hydrogen atoms, observed and calculated structure factor amplitudes, and a detailed description of the experimental conditions for the crystallographic study (15 pages). Ordering information is given on any current masthead page.

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(1) (a) University of Delaware; (b) University of Nebraska; (c) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.
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(19) Tables of fractional coordinates for nonhydrogen atoms, anisotropic thermal parameters for nonhydrogen atoms, refined fractional coordinates and isotropic thermal parameters for hydrogen atoms, and observed and calculated structure factor amplitudes will be found in the microfilm edition.
(20) The first number in parentheses following a given bond length or angle is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when included, are the average and maximum deviations from the average value, respectively.
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Synthesis of Methyl-Substituted Bisdehydro[13]annulenones. Conformational Isomerism and Ring Current Effects in Conjugated 13-Membered Cyclic Ketones[1]

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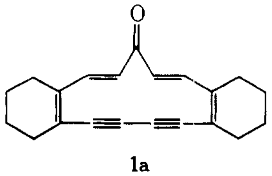
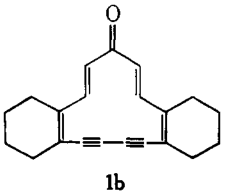
Syntheses of 5,10-dimethyl-6,8-bisdehydro[13]annulenone (**3**) and 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone (**4**) are described. It was found that the extra methyl group in **4** causes a change of conformation as compared with **3**. The ^{1}H NMR spectrum of **4** proved to be temperature dependent, due to rotation of the trans double bond. Both **3** and **4** are weakly paratropic, and the paratropicity is increased by dissolution in deuteriotrifluoroacetic acid.

The synthesis of the bis(cyclohexene)-annelated bisdehydro[13]annulenone **1** in these laboratories has been described previously.[2] Although inspection of models suggested that the conformation **1a** would be the preferred one for this compound, ^{1}H NMR spectrometry [nuclear Overhauser experiments and Eu(fod)$_3$ shifts], combined with selective deuteration, pointed to conformation **1b**.[2]

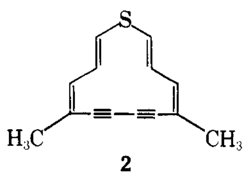


1a



1b

Since this work was carried out, it has been shown that the related dimethylbisdehydrothia[13]annulene **2** is conforma-



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