Preparation and Properties of Stelladiones

Rolf Gleiter*, Bettina Gaa, Christoph Sigwart, Holger Lange, Oliver Borzyk, Frank Rominger, Hermann Irngartinger, and Thomas Oeser

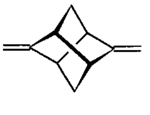
Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

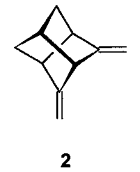
Received August 29, 1997

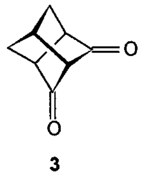
Keywords: Stelladiones / Photoelectron spectroscopy / Calculations

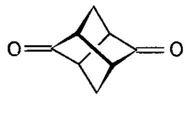
Tricyclo[3.3.0.0^{3,7}]octane-2,4-dione (2,4-stelladione, **3**), tricyclo[3.3.0.0^{3,7}]octane-2,6-dione (2,6-stelladione, **4**), and 2-oxotricyclo[3.3.0.0^{3,7}]octane-6-thione (**5**) were synthesized. Key steps in the procedures were a Paterno-Büchi reaction followed by an oxetane splitting with a strong base. Structure analysis on single crystals of **4** and **5** revealed long central C−C bonds (1.59 Å) of the stellane skeleton. The He(I) photoelectron spectra of **3**, **5**, and 4-methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (**9**) were recorded and interpreted on the basis of quantum-mechanical calculations (HF-SCF, 6-31G* basis). The large energy difference between the first PE bands of **3** (0.8 eV) is due to a strong interaction between the lone pairs on the oxygen atoms and the σ frame.

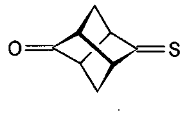
We have synthesized and investigated a number of hydrocarbons containing the tricyclo[3.3.0.0^{3,7}]octane (stellane) skeleton[1] in the past years. These investigations were undertaken for several reasons: Calculations suggested a strong interaction between two *exo* double bonds in 2,6- and 2,4-stelladienes (**1**, **2**) which could be verified by means of PE spectroscopy[2]. A second point of interest was that two stellanes could be coupled together to build a rigid molecular scaffold to study long range interactions[3]. Furthermore **1**, **2**, and its congeners proved to be interesting models for studying a stepwise Cope rearrangement[4]. Key compounds in the syntheses of the model systems were the corresponding diketones tricyclo[3.3.0.0^{3,7}]octane-2,4-dione (2,4-stelladione, **3**) and tricyclo[3.3.0.0^{3,7}]octane-2,6-dione (2,6-stelladione, **4**). In this paper we report on the syntheses of **3**, **4**, and the thioketone **5**.


1


2


3


4

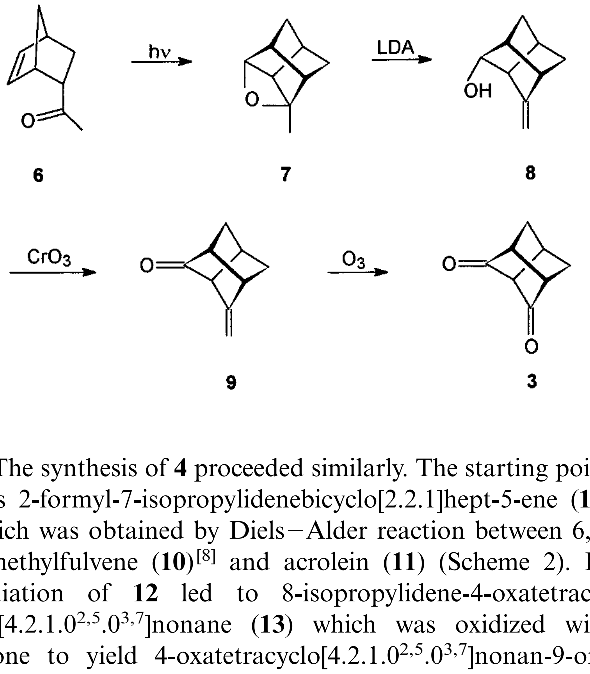

5

Results

Synthesis

The syntheses of **3** and **4** were based on work reported by Sauers et al.[5], Nakazaki and Naemura et al.[6][7]. The synthesis of **3** was accomplished from 4-methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (**9**) which had been synthesized by Nakazaki et al.[7]. The starting point in this protocol was *endo*-2-acetylbicyclo[2.2.1]hept-5-ene (**6**)[7] which was transformed to 2-methyl-3-oxatetracyclo[4.2.1.0^{2,5}.0^{4,8}]nonane (**7**) by an intramolecular Paterno-Büchi reaction (Scheme 1). Treatment of **7** with a strong base allowed the abstraction of a proton from the CH_3 group and opened the oxetane ring. The resulting 4-methylenetricyclo[3.3.0.0^{3,7}]octan-2-ol (**8**) was readily oxidized to **9**. Further oxidation with ozone yielded tricyclo[3.3.0.0^{3,7}]octane-2,4-dione (**3**).

Scheme 1

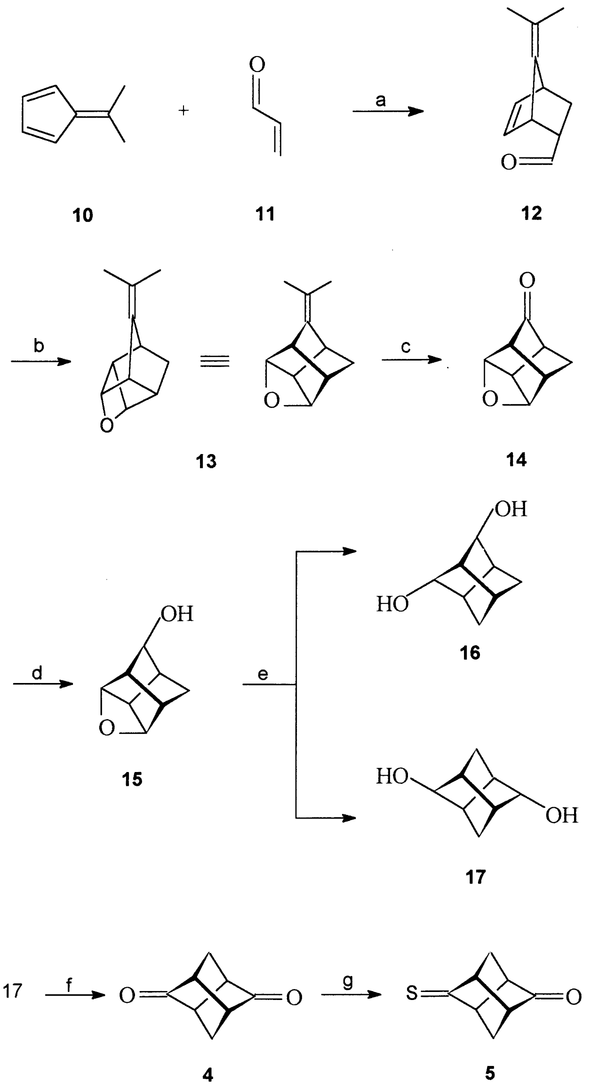


The synthesis of **4** proceeded similarly. The starting point was 2-formyl-7-isopropylidenebicyclo[2.2.1]hept-5-ene (**12**) which was obtained by Diels−Alder reaction between 6,6-dimethylfulvene (**10**)[8] and acrolein (**11**) (Scheme 2). Irradiation of **12** led to 8-isopropylidene-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (**13**) which was oxidized with ozone to yield 4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonan-9-one (**14**).

The alcohol 4-oxatetracyclo[4.2.1.0^{2,5}0^{3,7}]nonan-9-ol (**15**) was obtained by reduction of **14** with $LiEt_3BH$ in THF. The oxetane ring in **15** was cleaved with Li in EDA[9], resulting

1434−193X/98/0101−0171 $ 17.50+.50/0

Scheme 2



a: Roomtemp. – b: hν. – c: O_3. – d: $LiEt_3BH$. – e: Li/EDA. – f: $(COCl)_2$/DMSO/NEt_3. – g: P_2S_5.

in a mixture of the diastereomeric alcohols tricyclo[3.3.0.0^{3,7}]octane-2,4-diol (**16**) (26%) and tricyclo[3.3.0.0^{3,7}]octane-2,6-diol (**17**) (37%). The two isomers could be separated by column chromatography. Oxidation of **17** with the Swern reagent[10] yielded **4**. This route is a new and efficient synthesis of **4**[11]. Compound **16** was converted similarly to **3**. The thioketone **5** was obtained in 34% yield by treatment of **4** with P_2S_5 in pyridine[12].

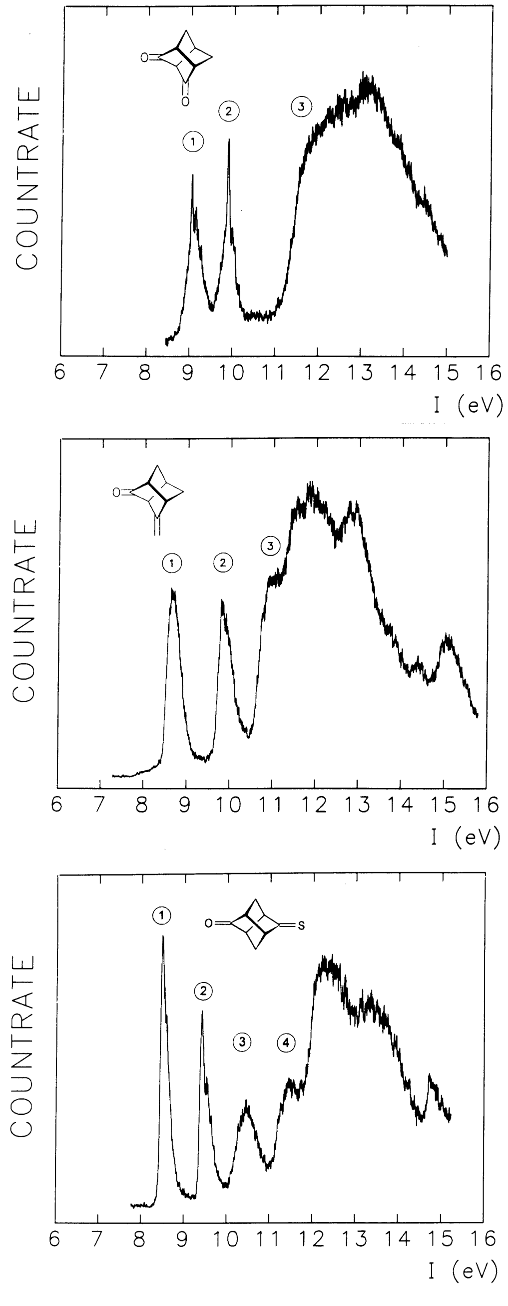
The main difference between our and Nakazaki et al.'s[11] approach to the synthesis of **4** is that we reduced the ketone **14** to **15**. In the latter compound the cleavage of the oxetane was possible while in **14** all such efforts were in vain[11]. This difference in reactivity of **14** and **15** finally allowed us to produce **3** and **4** in larger amounts. Previous routes[11] were not so efficient.

Photoelectron Spectra

Figure 1 contains the He(I) photoelectron spectra of **3**, **5**, and **9**, and the first ionization energies of all three compounds as well as the previously reported **4**[3a] are collected in Table 1. All three compounds show two to three bands between 8 and 11 eV, well separated from strongly overlapping bands at higher energy.

We assigned the first few bands of the PE spectra of **3**, **5**, and **9** by comparing them with related species and by considering quantum chemical calculations. In the latter case we made use of Koopmans' theorem[13] which allows the direct comparison of measured vertical ionization energies, $I_{v,j}$, with the negative value of calculated orbital energies, ε_j.

Figure 1. He(I) PE spectra of **3** (top), **9** (center), and **5** (bottom)



For a qualitative treatment we compared the first PE bands of **3** with those of **4**. This led us to assign the first

Table 1. Comparison between vertical ionization energies $I_{v,j}$ of **3**, **5**, **9**, and **4** with the calculated ($-\varepsilon_j$, ΔSCF, ΔMP2) energies; all values are given in eV

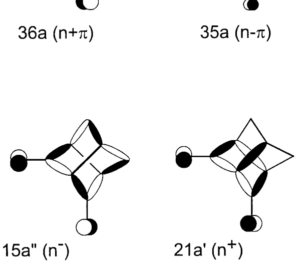
	band	$I_{v,j}$	assignment		$-\varepsilon_j$[a]	ΔSCF[a]	ΔMP2[b]	state
3	1	9.04	15a''	n^-	10.32	8.87	9.01	$1\ ^2A''$
	2	9.88	21a'	n^+	11.29	9.91	9.66	$1\ ^2A'$
	3	11.4	14a''	σ	13.19			
5	1	8.49	18b	n_S	9.04	7.43	8.25	$1\ ^2B$
	2	9.45	16b	n_O	10.85	8.29	9.31	$2\ ^2B$
	3	10.50	17b	$\pi_{C=S}$	10.65	9.22	10.37	$3\ ^2B$
	4	11.40	22a	σ	13.03	11.66	11.20	$1\ ^2A$
9	1	8.65	36a	π	9.41	8.03	9.06	$1\ ^2A$
	2	9.77	35a	n_O	10.79	9.50	10.04	$2\ ^2A$
	3	10.90	34a	σ	12.08			
4	1	8.84	$8b_1$	n_O	10.11	9.08	8.19	$1\ ^2B_1$
	2	9.90	$8b_2$	n_O	11.43	10.28	9.45	$1\ ^2B_2$
	3	11.6	11a	σ	12.98	11.74	11.31	$1\ ^2A$

[a] RHF/6-31G*//RHF/6-31G*. – [b] MP2/6-31G*//RHF/6-31G*.

band in the PE spectrum of **3** at 9.04 eV to ionization from n_-, and the second band (9.88 eV) to the n_+ linear combination of the 2p lone pairs of the oxygen atoms. Both ionization energies are close to those found for **4** (8.84 eV and 9.90 eV[3a]). The splitting between the first two bands in the PE spectrum of **3** (0.84 eV) is noteworthy. We ascribe it to a strong interaction between the 2p lone pairs and the σ frame as shown in Figure 2. For the assignment of the PE spectrum of **9** we compared it with that of 6-methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (**18**). In the latter the first two bands at 8.85 eV and 9.40 eV were assigned to ionizations from the 2p lone pair at the oxygen atom and the π MO centered at the C–C double bond, respectively[3a].

In the case of the PE spectrum of **5** it seemed appropriate to compare the ionization of the thiocarbonyl fragment with the first ionic states of the thioacetone. For this molecule two bands (n_s = 8.6 eV, π = 10.46 eV) were reported[14]. These values are close to the first and third band of the PE spectrum of **5**. This left only the 2p lone pair at oxygen atom for the assignment of the second band at 9.45 eV. The high ionization energy of the second band compared to that of the first band of stellanone (8.76 eV[3a]) indicates that the thiocarbonyl fragment exerts a strong inductive effect.

Figure 2. Schematic drawing of the wave functions of HOMO and HOMO – 1 of **3** (bottom) and **9** (top)

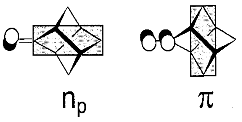


Our qualitative assignment of the first PE bands of **3**, **5**, and **9** agree with the results of quantum-chemical calculations. For our calculations we optimized the geometries of **3** (C_s), **5** (C_2), **9** (C_1), and **4** (D_2) at the Hartree–Fock level of theory using the 6-31G* basis set[15]. Since Koopmans' defects may lead to an alternation of the orbital sequence, we have also carried out ΔSCF and ΔMP2 calculations. The results are collected in Table 1. For **3** we noticed a considerable interaction between the 2p lone pairs at the oxygen atom and high-lying σ orbitals of the stellane skeleton. A schematic drawing of the highest two molecular orbitals is given in Figure 2. The wave functions of the enone **9** indicate considerable mixing between the oxygen lone pair and the olefinic π system, much stronger than that found in its p isomer **18**[3a].

The recorded energy differences $\Delta I_{v,j}$ between the functional groups in the aforementioned compounds can easily be understood in terms of the through-space/through-bond concept. The stellane system consists of two superimposed twist cyclohexane rings. The inherent strain gives rise to energetically high-lying σ orbitals. These are responsible for the strong through-bond interactions encountered in these molecules.

There are two different coupling pathways, depending on the orientation of the functional groups' p orbitals with respect to the stellane frame. Lone pairs like the n_O or n_S orbitals interact mainly via the twist cyclohexane ring they are directly connected to whereas π-type orbitals that are rotated by 90° relative to the n_p orbitals interact via the other twist cyclohexane ring. A through-bond interaction can only be effective if two functional groups interact via the same ring. Both coupling mechanisms are schematically shown in Figure 3.

Figure 3. Cyclohexane fragments which interact with the 2p lone pair at the oxygen atom n_p (left) and the π orbital of a exomethylene group π (right)

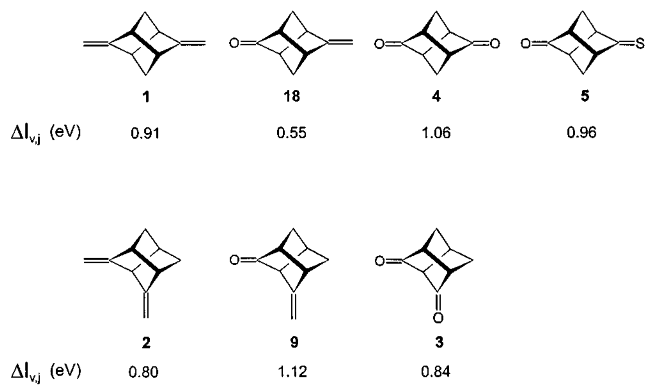


This simple concept allows us a qualitative explanation of the energetical splitting between the highest occupied orbitals in the molecules shown in Figure 4. Because the interaction is more effective if it occurs via the same twisted ring, one would expect a higher $\Delta I_{v,j}$ in **1**, **4**, and **9** than in their isomers **2**, **3**, and **18**. Indeed, in the first set the energy difference amounts to as much as 1.12 eV, while in the second set the splitting is diminished by at least 0.1 eV compared to their counterparts. This is due to the fact that in the latter molecules the interaction can only be mediated by the two central bonds that both rings have in common.

Comparing **5** to **4** one finds that the coupling between the sulfur and the oxygen lone pair is less effective than that between two oxygen lone pairs. This is explained by the larger C=S bond length (1.614 Å) compared to the C=O distance (1.201 Å). Therefore the n_s orbital is less influenced by the stellane frame. One can conclude that the through-bond coupling in the dithia analogue of **4** is probably even smaller.

Through-space interactions do not play a significant role in the seven molecules, except for **2**, where the two π bonds are close enough and have the correct orientation to interact with each other. As a result the $\Delta\Delta I_{v,j}$ (**1** − **2**) is only 0.11 eV compared to 0.22 eV (**4** − **3**) or 0.57 eV (**9** − **18**).

Figure 4. Comparison between the splitting of the first two PE bands of **1**−**5**, **9**, and **18**



X-ray Investigations

The molecular structure of 2,6-stelladione (**4**) is shown in Figure 5. In Table 2 selected bond lengths and angles of **4** are compared with those of **5**. In accordance with former studies[16] we found long central bonds *a* and *a'* in both molecules **4** [1.586(1) Å] and **5** [1.588(2) Å]. The peripheral bonds (*b* and *d*) are also longer[17] in **4** [1.558(1) and 1.560(2) Å] and in **5** [1.559(2) and 1.556(2) Å]. The bonds (*c* and *e*) between the C(sp^2) centers and the neighboring sp^3 centers were found to be 1.523(1) and 1.519(1) Å in **4** and 1.521(2) and 1.512(2) Å in **5**. The elongation of the central and peripheral bonds were anticipated from our earlier studies on four different stellane derivatives[16]. We ascribe the lengthening of the bonds due to strain caused by two effects: the considerable reduction of the angles at the sp^2 and sp^3 centers and the eclipsed conformation along the central bonds. Especially large is the angle deformation at the sp^2 centers of **4** and **5** [*cc'* = 97.8(1)° in **4** and 97.5(1)° in **5**, *ee'* = 97.7(1)° in **4** and 97.4(1)° in **5**].

Figure 5. Molecular structure of **4**[18]

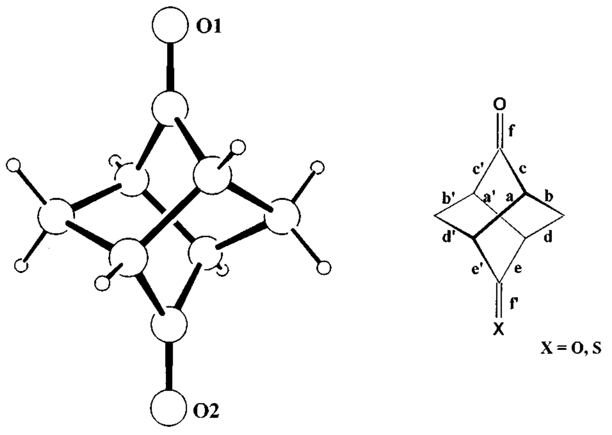


Table 2. Selected bond lengths [Å] and bond angles [°] of **4** and **5**; for the definition of the letters *a*−*f* see Figure 5; in **5** the values for a,a'−e,e' are averaged

	4	**5**
a	1.586(1)	1.588(2)
b	1.558(1)	1.559(2)
c	1.523(1)	1.521(2)
d	1.560(2)	1.556(2)
e	1.519(1)	1.512(2)
f	1.201(2)	1.204(2)
f'	1.201(2)	1.614(2)
cc'	97.8(1)	97.5(1)
ee'	97.7(1)	97.4(1)
bd	94.4(1)	94.2(1)

Support of this work by the *BASF Aktiengesellschaft*, the *Volkswagenstiftung*, and the *Fonds der Chemischen Industrie* is gratefully acknowledged. H. L. thanks the *Studienstiftung des Deutschen Volkes* for a stipend. We are greateful to *A. Flatow* for recording the PE spectra.

Experimental Section

General Procedures: Reactions were carried out in oven-dried (120°C) glassware under argon and with magnetic stirring. Solvents were dried and distilled under argon before use. − The ^{1}H- and ^{13}C-NMR spectra were recorded with Bruker AS 200 and Bruker WH 300 instruments, respectively. − Low-resolution mass spectra were recorded with a Hewlett-Packard HP 59970 CD GC/MS-MSD. High-resolution (HR) mass spectra were obtained with a ZAB high-resolution mass spectrometer (Vacuum Generators). − Microanalyses were carried out at the analytical laboratory of the "Chemische Institute der Universität Heidelberg".

Tricyclo[3.3.0.0^{3,7}]octane-2,4-dione (**3**): Through a solution of 1.5 g (11.2 mmol) of 4-methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (**9**)[7] in 400 ml of dry CH_2Cl_2 was passed a stream of oxygen containing about 3% of ozone at −60°C until a blue color persisted. Excess ozone was removed by passing argon through the solution. Subsequently, a solution of 3 ml (25 mmol) of dimethyl sulfide in 50 ml of dry CH_2Cl_2 was added at −50°C and the solution was stirred for 16 h at room temp. The solvents were removed in vacuo and the residue purified by silica gel chromatography (pentane), yielding **3** as a colorless oil which was further purified by distillation, b.p. 30°C/$6 \cdot 10^{-6}$ mbar to give 650 mg (43%) of a colorless hygroscopic solid. − IR (CD_2Cl_2): $\tilde{\nu}$ = 2998 (w) cm^{-1}, 2954 (m), 2884 (m), 1802 (m), 1739 (vs), 1281 (s). − ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 3.07−2.99 (1 H, m), 2.88−2.82 (2 H, m), 2.51−2.46 (1 H, m), 2.13 (1 H, m, J = 11 Hz), 200 (1 H, dd, J_1 = 10.8 Hz). − ^{13}C NMR (CD_2Cl_2, 50.32 MHz): δ = 204.05 (double intensity), 57.40, 50.51 (double intensity), 38.26 (double intensity), 37.37.

2-Formyl-7-isopropylidenebicyclo[2.2.1]hept-5-ene (**12**): To 23.7 g (0.22 mol) of 6,6-dimethylfulvene (**10**) was added slowly under stirring at 0°C 30 ml (0.42 mol) of freshly distilled acrolein (**11**). After standing at room temp. for 12 h, the mixture was used for further reaction without purification.

8-Isopropylidene-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (**13**): A solution of 18 ml (6.7 mmol) of **12** in 2.5 l of dry ether was irradiated with a 450-W medium-pressure mercury lamp for 18 h. After removal of the solvent, the raw material was purified by silica gel chromatography (pentane/ether, 9:1) yielding 11.0 g (31%) of **13** as colorless crystals, m.p. 28°C. − R_f (SiO_2, pentane/ether, 9:1) = 0.17. − IR ($CDCl_3$): $\tilde{\nu}$ = 2998 cm^{-1} (s), 2926 (s), 2860 (s), 1443 (m), 1370 (w), 1303 (s), 1279 (m), 1268 (w), 1260 (w), 1119 (m), 1111 (w), 1077 (m), 1035 (s), 954 (m), 854 (m), 832 (m). − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.72−4.68 (1 H, m), 4.53−4.48 (1 H, m), 3.28−3.23 (1 H, m), 3.10−3.06 (1 H, m), 2.71−2.67 (1 H, m), 2.44−2.41 (1 H, m), 1.63 (3 H, s), 1.59 (3 H, s), 1.65−1.56 (2 H, m). − ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ = 143.39, 115.32, 90.17, 88.16, 56.56, 44.37, 43.93, 40.64, 37.67, 19.74, 19.66. − $C_{11}H_{14}O$ (162.23): calcd. C 81.44, H 8.70; found C 81.50, H 8.76.

4-Oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonan-9-one (**14**): A stream of oxygen containing about 3% of ozone was passed into a cold solution (−78°C) of 11 g (68 mmol) of **13** in 500 ml of dry CH_2Cl_2 until an intensive blue color persisted. Excess ozone was removed by passing a stream of O_2 through the solution. Subsequently, 9 ml (75 mmol) of dimethyl sulfide was added and the solution was allowed to warm to room temp. After removal of the solvent, purification was accomplished by silica gel chromatography (pentane/ether, 1:2) to yield 1.4 g (85%) of **14**[2] as a colorless solid.

4-Oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonan-9-ol (**15**): To a magnetically stirred solution of 1.65 g (12 mmol) of **14** in 10 ml of dry THF 1 ml of a 1 M solution of $LiEt_3BH$ in THF was added at 0°C. After the mixture was stirred at 0°C for 30 min, 6 ml of a 30% aqueous H_2O_2 solution was added carefully and the mixture was stirred at 40°C for 1 h. The aqueous solution was percolated with ethyl acetate for 2 d. The organic layer was dried ($MgSO_4$) and concentrated. Purification of the residue by silica gel chromatography (ether) gave 1.4 g (85%) of **15** as a colorless solid, m.p. 175°C. − IR ($CDCl_3$): $\tilde{\nu}$ = 3610 cm^{-1} (vs), 3430 (m), 3002 (vs), 2940 (s), 2878 (s), 1318 (s), 1285 (s), 1282 (s), 1243 (s), 1180 (vs), 1116 (s), 1061 (vs), 1041 (vs), 1020 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70−4.67 (m, 1 H), 4.64−4.60 (m, 1 H), 3.88 (d, 1 H, J = 2.3 Hz), 3.21−3.17 (m, 1 H), 3.62−3.60 (m, 1 H), 2.36 (dd, 1 H, J_1 = 10.8 Hz, J_2 = 2.5 Hz), 2.01 (s, 1 H), 1.95 (m, 1H), 1.55 (dd, 1 H, J_1 = 11.0 Hz, J_2 = 2.1 Hz). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 90.27, 86.03, 78.30, 55.56, 48.78, 41.49, 40.92, 35.25. − GC/MS; *m/z* (%): 120 (1) [M^+ − CO], 91 (21), 82 (10), 81 (20), 79 (42), 77 (23), 67 (10), 66 (100), 65 (23), 53 (20), 50 (17). − UV/Vis (CH_3CN): λ_{max} (ε) = 234 nm (309). − $C_8H_{10}O_2$ (138.15): calcd. C 69.55, H 7.29; found C 69.20, H 7.59.

Tricyclo[3.3.0.0^{3,7}]octane-2,4-diol (**16**), *Tricyclo[3.3.0.0^{3,7}]octane-2,6-diol* (**17**): To a magnetically stirred solution of 1.5 g (10.9 mmol) of **15** in 11 ml of anhydrous ethylenediamine 200 mg (28.8 mmol) of lithium powder was added under Ar. The reaction mixture turned blue and the reaction was vigorous and exothermic, and as the blue color dissipated 912 mg (131.4 mmol) of lithium powder was added again. After the mixture was stirred at room temp. for 30 min, first ether then water was added carefully. The solution was percolated with ether for 2 d. The organic layer was separated, dried with $MgSO_4$, and concentrated. Purification of the residue by silica gel chromatography (elution with ether) gave 397 mg (26%) of **16** and 562 mg (37%) of **17**, both as colorless crystals.

16 m.p. 185°C. − IR (KBr): $\tilde{\nu}$ = 3286 cm^{-1} (vs), 2988 (vs), 2974 (vs), 1153 (s), 1099 (s), 1032 (s), 960 (vs), 953 (s). − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.65 (d, 2 H, J = 3.5 Hz), 3.82 (s, 2 H), 2.34 (dd, 2 H, J_1 = 8.0 Hz, J_2 = 2.6 Hz), 2.05 (d, 1 H, J = 2.5 Hz), 1.96 (s, 2H), 1.72 (d, 1 H, J = 2.5 Hz), 1.12 (d, 2 H, J = 8.4 Hz). − ^{13}C NMR (75.47 MHz, [D$_6$]DMSO): δ = 75.51, 49.19, 41.49, 38.00, 33.91. − UV/Vis (CH_3CN): λ_{max} (ε) = 230 nm (173). − $C_8H_{12}O_2$ (140.18): calcd. C 68.53, H 8.63; found C 68.71, H 8.60.

17: m. p. 154°C. − IR (KBr): $\tilde{\nu}$ = 3276 cm^{-1} (vs), 2964 (vs), 2961 (s), 1278 (s), 1261 (s), 1157 (s), 1095 (s), 1061 (vs), 1022 (s). − ^{1}H NMR (300 MHz, [D$_6$]DMSO): = 4.11 (s, 2 H), 2.26 (dd, 2 H, J_1 = 10.8 Hz, J_2 = 1.9 Hz), 2.41 (m, 4 H), 1.67 (s, 2H), 1.40 (d, 2 H, J = 11.2 Hz). − ^{13}C NMR (75.47 MHz, [D$_6$]DMSO): δ = 80.78, 41.41, 39.10, 32.03. − UV/Vis (CH_3CN): λ_{max} (ε) = 220 nm (120.2). − $C_8H_{12}O_2$ (140.18): calcd. C 68.53, H 8.63; found C 68.85, H 8.82.

Tricyclo[3.3.0.0^{3,7}]octane-2,6-dione (**4**): A magnetically stirred solution of 1.0 ml (11 mmol) of oxalyl chloride in 100 ml of dry CH_2Cl_2 was treated with 1.9 ml (25 mmol) of dry DMSO at −50 to −60°C. After the mixture was stirred for 2 min, a solution of 460 mg (3.3 mmol) of the diol **17** in 250 ml of dry CH_2Cl_2 was added dropwise at −50 to −60°C. The reaction mixture was stirred for 15 min, treated with 7 ml (50 mmol) of triethylamine and allowed to warm to room temp. before being poured into cold aqueous HCl (2%). Extraction was effected with CH_2Cl_2 (2 ×). The combined solvents were washed with aqueous $NaHCO_3$ (5%) and brine, dried with $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (elution with pentane/ether, 1:1) to give 340 mg (80%) of **4**[2] as colorless crystals.

2-Oxotricyclo[3.3.0.0^{3,7}]octane-6-thione (**5**): To a magnetically stirred solution of 300 mg (2.20 mmol) of dione **4** in 6 ml of anhydrous pyridine 245 mg (1.103 mmol) P_2S_5 was added in portions under Ar at 90°C. The mixture was stirred at this temperature for 4.5 h and after cooling to room temp., 100 ml of hexane was added. The organic phase was washed with water (3 ×), 2 N HCl (2 ×), and again with water (2 ×). After drying with $MgSO_4$, the solvent was evaporated and the residue purified by silica gel chromatography (pentane/ether, 2:1) to give 115 mg (34.3%) of **5** as orange crystals, m.p. 122°C. − IR (KBr): $\tilde{\nu}$ = 1773 cm^{-1} (vs), 1454 (m), 1340 (s), 1177 (s), 1140 (m), 958 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05 (s, 2 H), 2.56 (s, 2 H), 1.81 (s, 4 H). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 259.29, 209.34, 53.53, 43.06, 33.01. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 224 nm (9455), 234 (7662). − HRMS;

Table 3. Crystallographic data of **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_8H_8O_2$	C_8H_8OS
Molecular mass [g/mol]	136.15	152.20
Solvent	CH_2Cl_2	THF
Crystal size [mm]	0.5 × 0.5 × 0.45	0.54 × 0.32 × 0.23
Crystal color	colorless	orange
Crystal shape	bipyramid	irregular
Space group	*C*2/*c*	*P*2$_1$/*c*
a [Å]	8.555(2)	6.577(1)
b [Å]	9.794(1)	12.413(1)
c [Å]	7.736(1)	8.687(1)
β [°]	98.88(1)	95.881(2)
V [Å^3]	640.4(2)	705.4(1)
$D_{calcd.}$ [Mg/m^3]	1.41	1.43
Z	4	4
F(000)	288	320
T [K]	223	200
h_{min}/h_{max}	0/11	−7/7
k_{min}/k_{max}	0/12	−14/14
l_{min}/l_{max}	−10/10	−10/6
(sin Θ/λ)$_{max}$ [Å^{-1}]	0.66	0.60
μ [mm^{-1}]	0.10	0.38
Refl. collected	863	3135
Refl. unique	766	1187
Refl. observed [$I > 2\sigma(I)$]	668	1089
R_{int}	0.016	0.026
Variables	64	123
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01
R	0.037	0.033
R_w	0.056	0.087
S (Gof)	2.87	1.08
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.25	0.23
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.21	−0.22

C_8H_8OS: calcd. 152.0296; found 152.0258. − C_8H_8OS (152.0): calcd C 63.13, H 5.30; found C 62.99, H 5.38.

Photoelectron Spectra: The photoelectron spectra of **3**, **5**, and **9** were recorded with a Perkin Elmer PS 18 spectrometer. The recording temperatures were as follows **3**: 25°C; **5**: 55°C; **9**: 28°C. The calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^2P_{3/2}$ Ar line was obtained.

X-ray Diffraction Analyses of **4** *and* **5**: The X-ray data were collected with an Enraf Nonius-CAD4-diffractometer (**4**) and a Siemens CCD-diffractometer (**5**) (Mo-K_a radiation, graphite monochromator). The structures were solved with direct methods [MULTAN[19] (**4**), SHELXTL[20] (**5**)]. Refinement of the non-hydrogen atoms was carried out anisotropically according to a full-matrix least-squares technique (F^2). All hydrogen atoms were refined isotropically. The crystallographic data are listed in Table 3.

Calculations were done with the MoIEN[21] (**4**) and SHELXTL[20] (**5**) program systems. Crystallographic data (excluding structure factors) for structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100662. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [fax: int. code +44(0)1223/336-033, e-mail: deposit@ccdc.ac.uk].

---

[1] O. Borzyk, T. Herb, C. Sigwart, R. Gleiter, *Pure Appl. Chem.* **1996**, *68,* 233 and refs. cited therein.

[2] R. Gleiter, B. Kissler, C. Ganter, *Angew.Chem.* **1987**, *99*, 1292; *Angew. Chem. Int. Ed. Engl.* **1987**, *26,* 1252; R. Gleiter, B. Kissler, *Tetrahedron Lett.* **1987**, *28*, 6151.

[3] [3a] R. Gleiter, H. Lange, O. Borzyk, *J. Am. Chem. Soc.* **1996**, *118*, 4889. − [3b] R. Gleiter, O. Borzyk, *Angew. Chem.* **1995**, *107*, 1094; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1001.

[4] R. Gleiter, C. Sigwart, *J. Org. Chem.* **1994**, *59*, 1027; W. R. Roth, R. Gleiter, V. Paschmann, U. E. Hackler, G. Fritzsche, H. Lange, to be published; T. Herb, H. Lange, R. Gleiter, to be published.

[5] R. R. Sauers, W. Schinski, M. M. Mason, *Tetrahedron Lett.* **1969**, 79; R. R. Sauers, J. A. Whittle, *J. Org. Chem.* **1969**, *34*, 3579; R. R. Sauers, D. C. Lynch, *J. Org. Chem.* **1980**, *45*, 1286 and refs.cited therein.

[6] K. Naemura in *Carbocyclic Cage Compounds* (Eds.: E. Osawa, O. Yonemitzu), VCH Verlagsgesellschaft, Weinheim, **1992**.

[7] M. Nakazaki, K. Naemura, Y. Kondo, *J. Org. Chem.* **1976**, *41*, 1229.

[8] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849.

[9] R. R. Sauers, W. Schinski, M. M. Mason, E. O'Hara, B. Byrne, *J. Org. Chem.* **1973**, *38*, 642.

[10] K. Omura, D. Swern, *Tetrahedron,* **1978**, *34*, 1651; A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165.

[11] M. Nakazaki, K. Naemura, H. Harada, H. Narutaki, *J. Org. Chem.* **1982**, *47*, 3470.

[12] J. W. Greidanus, *Canad. J. Chem.* **1970**, *48*, 3530.

[13] T. Koopmans, *Physica* **1934**, *1*, 104.

[14] H. W. Kroto, B. M. Landsburg, J. R. Suffolk, R. J. Vodden, *Chem. Phys. Lett.* **1974**, *29*, 265; see also: R. Gleiter, J. Spanget-Larsen, *Top. Curr. Chem.* **1974**, *86*, 139.

[15] We used the *Gaussian 94* program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov. A. Nanyakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen. M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, **1995**.

[16] V. Siemund, H. Irngartinger, C. Sigwart, B. Kissler, R. Gleiter, *Acta Crystallogr., Sect C* **1993**, *49*, 57.

[17] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *Int. Tables for Crystallogr.*, **1995**, *vol. C*, 685.

[18] E. Keller *SCHAKAL92*, Universität Freiburg, Germany, **1992**.

[19] P. Main. S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. Woolfson, *MULTAN 11/82*, Department of Physics, University of York, York, England, **1982**.

[20] *Siemens SHELXTL 5.03*, Siemens Analytical X-ray **1994**.

[21] C. K. Fair, *MoIEN: Structure Determination System*, Enraf-Nonius, Delft Instruments X-RAY Diffraction B. V., Delft, Netherlands, **1990.**

[97258]