4-(Phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one: Synthesis, Alkylation, and Base-Induced Dimerisation☆

Ulrike Kunz[a], Stefan Krimm[a], Thomas Fischer[a], Thomas Kottke[b], Dietmar Stalke[b], and Manfred Christl*[a]

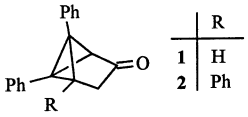
Institut für Organische Chemie[a] and Institut für Anorganische Chemie,[b] Universität Würzburg
Am Hubland, D-97074 Würzburg, Germany
Fax:[a] (internat.) + 49(0)931/888-4606
E-mail:[a] christl@chemie.uni-wuerzburg.de

Received May 4, 1998

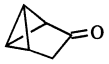
Keywords: Autoxidation / Dimerisation / Enolates / Isomerisations / Strained molecules

3-(Phenylsulfanyl)benzvalene (**6**) was prepared by dehydrochlorination from the adduct **5** of phenylsulfenyl chloride to benzvalene (**4**) with potassium *tert*-butoxide. An autoxidation transformed **6** readily to the tricyclo[3.1.0.0^{2,6}]hexanone **7**, which was converted into its 4-deuterio derivative [4-D]-**7** under mild conditions. The treatment of **7** with potassium hydride in the presence of methyl iodide and 1,3-diiodopropane afforded the alkyl derivatives **9** and **10**, respectively, of **7**. In the absence of an active alkylating agent, the reaction of **7** with potassium hydride gave rise to the bicyclohexyltricyclohexanes **11** being dimers of **7**. Presumably, this process is initiated by the rearrangement of **7** to the bicyclohexenone **13** and completed by a Michael addition of **7** to **13**.

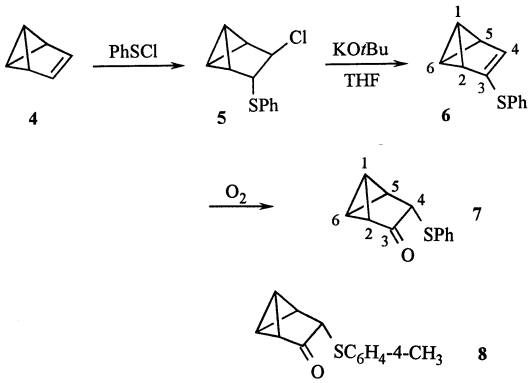
So far only a few enolisable tricyclo[3.1.0.0^{2,6}]hexan-3-ones are known. The diphenyl derivative **1**[1] and the triphenyl derivative **2**[2] have been prepared already in the initial stage of bicyclobutane chemistry, whereas the parent compound **3** was synthesised by Kraft[3] as late as 1989. Since the access to these compounds is rather laborious, only a few studies of their properties have been carried out and very little is known about their enolates.



	R
1	H
2	Ph



3



4 **5** **6** **7** **8**

Results and Discussion

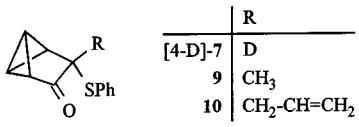
In our efforts to utilise benzvalene (**4**) and its derivatives in cycloaddition reactions,[4] we have also successfully employed 3-(phenylsulfanyl)benzvalene (**6**).[5] This compound was prepared from the adduct **5**[6] of phenylsulfenyl chloride to **4** by elimination of hydrogen chloride by using potassium *tert*-butoxide in THF, but could not be obtained pure, since it decomposed during distillation and chromatography. As expected, one impurity was diphenyl sulfide, which should be the result of the ready thermal rearrangement of **6**, whereas another one was isolated and identified to be the (phenylsulfanyl)tricyclohexanone **7** only during the use of **6** in a Pauson-Khand reaction.[5b] It turned out that **7** arose from **6** by autoxidation. Accordingly, after having stirred a solution of **6** in dichloromethane at 25°C under oxygen, we obtained **7** in 23% yield over three steps from **4**.

The formation of α-(phenylsulfanyl) ketones from 1-(phenylsulfanyl)alkenes and oxygen in the presence of two to four equivalents of benzthiol is well known.[7] Although the addition of benzthiol did not increase the yield in our case, the radical chain mechanism proposed previously[7] rationalises the result as shown by a control experiment: when **6** was oxidised in the presence of three equivalents of 4-tolylthiol a 1:4 mixture of **7** and its 4-(tolylsulfanyl) analogue **8** was produced.

The deprotonation of **7** by LDA at −78°C followed by the addition of the cold solution to an electrophile kept at 0°C did not give a compound having a tricyclo[3.1.0.0^{2,6}]hexane skeleton. The ^{1}H-NMR spectrum of the product formed contained only signals of aromatic groups. On the other hand, **7** was readily converted into [4-D]-**7** upon stirring in a mixture of CH_3OD, D_2O, and K_2CO_3 at 20°C. Two 4-alkylated derivatives of **7** were prepared by treatment of **7** with potassium hydride in the presence of electrophiles at −10 to 0°C: methyl iodide gave the methyltricyclohexanone **9** and 1,3-diiodopropane the allyl compound **10** in 58 and 62% yield, respectively. It was not examined whether the elimination of hydrogen iodide in the

  1434−193X/98/1010−2171 $ 17.50+.50/0

case of **10** occurred before or after the alkylation of the enolate **12**.



As an electrophile, 1-bromo-3-chloropropane was not reactive enough, since the 4-(3-chloropropyl) derivative of **7** could not be observed. The dimers **11a**, **b** of **7** were formed instead. When the reaction of **7** with potassium hydride was performed in the absence of an electrophile, **11a** and **11b** were isolated in yields of 30 and 25%, respectively. The identity of **11b** was determined by an X-ray structure analysis (Figure 1). That the other product is the diastereomer **11a** was deduced from the similarity of the NMR-spectral data.

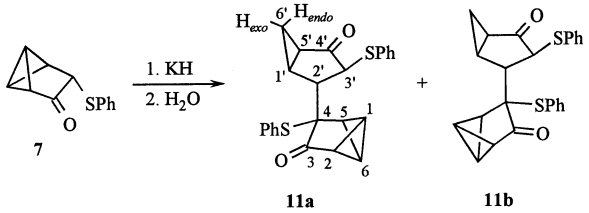
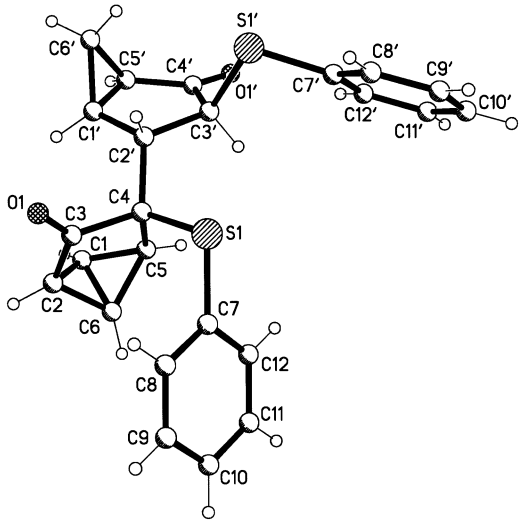
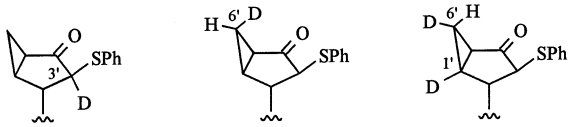


Figure 1. Molecular structure of the oxobicyclo[3.1.0]hexyltricyclo-[3.1.0.0^{2,6}]hexanone **11b** as determined by X-ray diffraction.

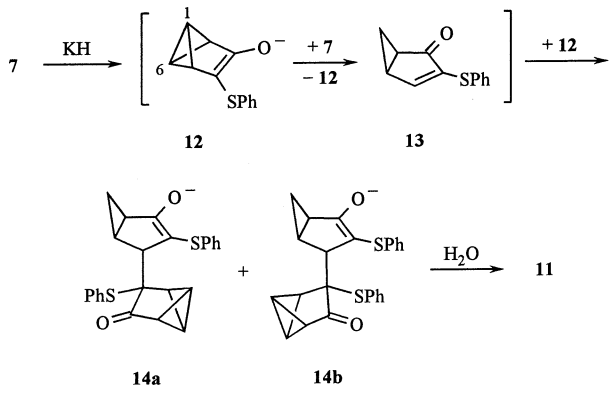


The comparison with literature data shows that bond lengths and angles of the bicyclobutane subunit of **11b** have values in the regions expected for tricyclo[3.1.0.0^{2,6}]hexanes.[4c][8] The distance C-3−C-4 appears to be unusually large (154.9 pm) for a bond between an sp^2- and an sp^3-hybridised carbon atom. However, in tetramethyltricyclo[3.1.0.0^{2,6}]hexane-3,4-dione, the corresponding bond is even longer (155.7 pm) although both carbon atoms involved are sp^2-hybridised.[9] In spite of the *endo* location of the phenylsulfanyl group, the bicyclo[3.1.0]hexane moiety prefers the boat conformation established previously for the parent hydrocarbon.[10] As a consequence, the sulfur atom approaches the methylene group rather closely. Typical of an acceptor-substituted cyclopropane,[11] the distance C-1′−C-6′ (148.0 pm) is considerably shorter than the bond lengths C-1′−C-5′ (151.3 pm) and C-5′−C-6′ (152.9 pm).



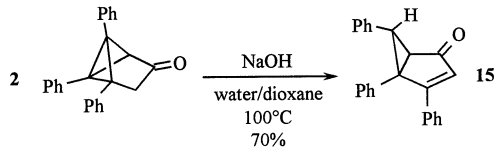
[3′-D]-**11** [*endo*-6′-D]-**11** [1′,*exo*-6′-D$_2$]-**11**

Viewed formally, the compounds **11** arise from an addition of the 4-CH group of **7** to the C-5−C-6 bond of a second molecule of **7**. Therefore, the reaction is reminiscent of electrophilic HX additions to bicyclobutanes, which frequently proceed with cleavage of a lateral C−C bond.[12] In order to gain information about the mechanism, we performed the following labelling experiments. When the reaction mixture was quenched with D_2O instead of H_2O, the deuterium atom appeared in the 3′-position of the products ([3′-D]-**11**). The treatment of [4-D]-**7** with potassium hydride in THF or [D_8]THF furnished [*endo*-6′-D]-**11** and **11** in a ratio of ca. 1:1. Since half of the product was unlabelled, we prepared [1,6-D_2]-**7** and exposed it to potassium hydride in THF. Although the substrate consisted only to ca. 50% of the doubly labelled **7**, it could be unambiguously established that [1′,*exo*-6′-D_2]-**11** was formed exclusively (see Experimental Section). Obviously, the attachment of the new hydrogen atom at the cyclopropane subunit occurs with high stereoselection at the *endo* position. This conclusion relies on the specific assignment of the signals of the methylene group in the ^{1}H-NMR spectra of **11**. As usual, it has been assumed that *endo*-6′-H, as compared to *exo*-6′-H, maintains smaller coupling constants to 1′- and 5′-H.

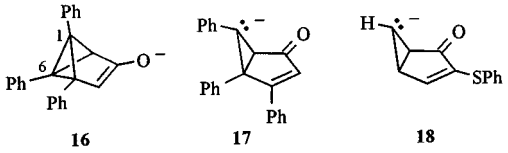


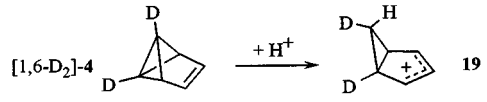
These findings support the following mechanism. Initially, the enolate **12** is generated by deprotonation of **7**. Then, C-1 or C-6 of **12** abstracts a proton from the 4-CH group of the still present **7**, giving rise to the α,β-unsaturated ketone **13**, which reacts with **12** in a Michael addition. The resulting enolates **14** are transformed to **11** and [3′-D]-**11** on addition of water and heavy water, respectively. On use of [4-D]-**7** only half of the product was deuterated, probably because the cleavage of the C−D bond suffers from a primary isotope effect. Thus, proton sources can

successfully compete. Because of their acidity the bicyclobutane bridgehead CH groups of **7** and **14** are possible candidates. In competition to the protonation leading to **13**, the benzvalene derivative **12** should undergo an electrocyclic reaction[4a] with formation of *o*-(phenylsulfanyl)phenolate rather readily.



There is a precedent for the postulated isomerisation of **7** to **13**. On exposure to hot aqueous sodium hydroxide, the tricyclohexanone **2** rearranges to the bicyclohexenone **15**.[2b] The author proposes a three-step process, according to which the initially formed enolate **16** is subject to a retrograde Michael addition generating the cyclopropyl anion **17**, and this, retaining its configuration, is finally converted into **15** by protonation. By analogy, the cyclopropyl anion **18** could be an intermediate en route to **13**.





Although no immediate evidence is available against such a pathway at present, we want to propose an alternative to the intermediacy of the cyclopropyl anions **17** and **18**, because the protonation of the benzvalene derivatives **12** and **16** to give directly the bicyclohexenones **15** and **13**, respectively, is closely related to the formation of the bicyclo[3.1.0]hexenyl cation on reaction of unsubstituted benzvalene (**4**) with acids. Recourse to 1,6-dideuteriobenzvalene ([1,6-D_2]-**4**) shows that the proton exclusively attacks the bicyclobutane subunit from the *endo* face, generating the cation **19**.[4a] Thus, the steric course resembles that of the protonations of **12** and **16** to bring about **13** and **15**, respectively. If the latter indeed occur in one step, they demonstrate a high basicity of the bicyclobutane bridgehead carbon atoms in the enolates **12** and **16**, which would be strongly increased above that of **4**. This would have to be ascribed to the delocalisation of electron density from the enolate into the bicyclobutane subunit and would not be unexpected due to the interaction between ethene and bicyclobutane moiety in **4** as being manifest in a UV band centred at 217 nm,[13] whereas 1,2-dialkylethenes and the parent bicyclobutane do not exhibit a significant absorption above 200 nm.

We are grateful to the *Deutsche Forschungsgemeinschaft* as well as to the *Fonds der Chemischen Industrie* for financial assistance and to the *CHEMETALL GmbH* for gifts of chemicals.

Experimental Section

General: NMR: Bruker AC 200, AC 250, and WM 600, internal standards TMS and $CHCl_3$ (δ = 7.26) for ^{1}H NMR and $CDCl_3$ (δ = 77.0) for ^{13}C NMR. − IR: Perkin-Elmer 1420 ratio recording infared spectrophotometer. − MS: Finnigan MAT 90. − Elemental analyses: LECO CHNS 932. − Melting points: Kofler hot stage from C. Reichert, Optische Werke A. G., Wien, Austria. − All experiments described below, except the autoxidations, were conducted in anhydrous solvents in dry glassware and under dry nitrogen.

trans-3-Chloro-4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexane (**5**): This compound was prepared according to Katz and Nicolaou,[6] who did not give much details.

To a stirred solution of benzvalene (**4**)[14] (102 mmol, 175 ml 0.583 M in ether), cooled to −78°C, a solution of phenylsulfenyl chloride[15] (14.7 g, 102 mmol) in dichloromethane (250 ml) was added dropwise over 75 min. Stirring was continued at −78°C for 3.5 h. Then the mixture was allowed to warm to 20°C within 3.5 h and concentrated in vacuo at that temperature to give a red liquid (21.7 g, 96%; ref.[6] quantitative yield), which was characterised as rather pure **5** by the NMR spectra. This material was used without purification for the preparation of **6**. − ^{1}H NMR ($CDCl_3$): δ = 2.29 (m, 5-H), 2.43 (m, 2-H), 2.34−2.54 (m, 1,6-H), 3.46 (br. s, 4-H), 4.00 (br. s, 3-H), 7.18 (*p*-H), 7.28 (*m*-H), 7.39 (*o*-H). − ^{13}C NMR ($CDCl_3$): δ = 6.8, 9.0 (C-1,6), 36.5 (C-5), 40.6 (C-2), 57.5 (C-4), 67.8 (C-3), 126.1 (*p*-C), 128.8 (*m*-C), 129.5 (*o*-C), 135.4 (*i*-C); the assignments are based on H,H- and C,H-COSY spectra of [1,6-D_2]-**5** (see below).

[1,6-D_2]-**5**: This compound is mentioned in ref.[6] as well. We prepared it from 109 mmol (371 ml 0.293 M in ether) of [1,6-D_2]-**4**[16] and phenylsulfenyl chloride (15.8 g, 109 mmol) in dichloromethane (100 ml) according to the above procedure. The crude product was purified by flash chromatography [SiO_2, petroleum ether of b.p. 30−50°C (PE)/*tert*-butyl methyl ether (MTBE), 100:1] to give 22.4 g (91%) of [1,6-D_2]-**5** as a yellowish liquid. − ^{1}H NMR ($CDCl_3$): As compared to that of **5**, the m at δ = 2.34−2.54 is missing and the multiplicities of the signals at δ = 2.29 (br. d, $J_{2,5}$ = 5.0 Hz), 2.43 (dd, $J_{2,3}$ = 1.1 Hz), 3.46 (t, $J_{3,4}$ = $J_{4,5}$ = 1.2 Hz), and 4.00 (approx. t) are changed. − ^{13}C NMR ($CDCl_3$): Unlike as in that of **5**, C-1 and C-6 absorb as 1:1:1 triplets ($J_{C,D}$ = 34 Hz) at δ = 6.4 and 8.6. − $C_{12}H_9ClD_2S$ (224.8): calcd. C 64.13, S 14.27; found C 63.83, S 14.14.

3-(Phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hex-3-ene (**6**): A mixture of freshly sublimed KO*t*Bu (47.5 g, 423 mmol) and THF (650 ml) was added dropwise to a stirred solution of **5** (40.4 g, 181 mmol) in THF (150 ml) over 30 min at room temperature. Stirring was continued until **5** was consumed completely (40 min) as determined by TLC (Al_2O_3, PE/MTBE, 50:1). The mixture was then concentrated in vacuo at 20°C, and the remaining solid was extracted with pentane (4 × 200 ml). The combined extracts were passed through Celite with suction and concentrated in vacuo at 20°C to give 31.3 g of an orange oil, which consisted mainly of **6** and diphenyl sulfide in the ratio 4.5:1.0 and contained small amounts of **7** and several unidentified compounds. The yield of **6** was estimated to be 50−70%. − ^{1}H NMR ($CDCl_3$): δ = 2.14 (ddt, $J_{2,5}$ = 6.3, $J_{4,5}$ = 1.9, $J_{1,5}$ = 1.5 Hz, 5-H), 2.18 (dq, $J_{1,2}$ = $J_{2,4}$ = 1.5 Hz, 2-H), 3.89 (t, 1,6-H), 6.03 (dd, 4-H), 7.11−7.36 (m, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 37.0, 40.5 (2 × dm, $J_{C,H}$ = 168 Hz, C-2,5), 45.4 (dd, $J_{C,H}$ = 208, 3 Hz, C-1,6), 125.9 (dt, *p*-C), 128.7 (dt, *o*-C), 128.8 (dd, *m*-C), 134.9 (dt, $J_{C,H}$ = 176, 6 Hz, C-4), 136.4, 138.3 (C-3, *i*-C).

[1,6-D_2]-**6**: According to the procedure for the preparation of **6**, [1,6-D_2]-**5** (6.13 g, 27.3 mmol) was treated with KO*t*Bu (10.1 g, 90.0

mmol). After completion of the reaction, 564 mg (28.2 mmol) of D_2O was added to the mixture, which was stirred then for 30 min at room temp. The work-up started with concentration of the mixture in vacuo and was continued as above to give 3.86 g of a brown liquid, shown to contain [1,6-D_2]-**6**, [1-D]-**6**, and **6** with the proportions decreasing in that order. As approximate measure of the ratio (11:6:1), the heights of the ^{13}C-NMR signals at δ = 36.79, 36.88, and 37.01 were taken. This result shows that the elimination step was accompanied by some deuterium-hydrogen exchange at C-1,6 as a consequence of the formation of HO*t*Bu. The addition of D_2O after the elimination step increased the deuterium content of the product significantly. − ^{1}H and ^{13}C NMR of [1,6-D_2]-**6** ($CDCl_3$): As compared to **6**, in the ^{1}H-NMR spectrum the signal at δ = 3.89 is missing and the signals of 2,5-H (2 × dd) are shifted upfield by approx. 0.02 ppm, and in the ^{13}C-NMR spectrum, the signals of C-1,6 (t, $J_{C,D}$ = 32 Hz) and C-2,5 are shifted upfield by 0.52 and 0.21 ppm, respectively. − ^{1}H and ^{13}C NMR of [1-D]-**6** ($CDCl_3$): In the ^{1}H-NMR spectrum only the signal of 6-H (m) is clearly discernible; as compared to **6**, it is shifted upfield by approx. 0.01 ppm, whereas in the ^{13}C-NMR spectrum the signals of C-1 (t, $J_{C,D}$ = 32 Hz), C-6, and C-2,5 are shifted upfield by 0.36, 0.15, and 0.11 ppm, respectively.

4-(Phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one (**7**): A solution of crude **6** (31.3 g) in 1 l of dichloromethane was stirred under oxygen with a pressure of slightly above 1 atm at room temperature for 24 h. Then the solvent was evaporated in vacuo, and the residue was purified by flash chromatography (SiO_2, PE/MTBE, 8:1 initially, then 4:1, and finally 2:1) to give 8.76 g (23% from **4**) as yellowish crystals, m.p. 46−47°C. − IR (film): $\tilde{\nu}$ = 1743 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 2.42 (dt, $J_{2,5}$ = 4.8, $J_{1,2}$ = $J_{2,6}$ = 1.8 Hz, 2-H), 2.56 (dtd, $J_{1,5}$ = $J_{5,6}$ = 1.8, $J_{4,5}$ = 1.0 Hz, 5-H), 2.92 (ddt, $J_{1,6}$ = 7.1, $J_{4,6}$ = 2.8 Hz, 6-H), 2.99 (dq, $J_{1,4}$ = 1.6 Hz, 1-H), 3.24 (approx. dt, 4-H), 7.23−7.34 (*m*,*p*-H), 7.50 (*o*-H). − ^{13}C NMR ($CDCl_3$): δ = 9.8 (dd, $J_{C,H}$ = 229, 4 Hz, C-1), 10.0 (ddd, $J_{C,H}$ = 228, approx. 12, 4 Hz, C-6), 34.2 (dd, $J_{C,H}$ = 176, 11 Hz, C-5), 41.7 (ddt, $J_{C,H}$ = 177, 8, 2 Hz, C-2), 47.8 (dt, $J_{C,H}$ = 149, 5 Hz, C-4), 127.0 (dt, *p*-C), 128.5 (dd, *m*-C), 131.7 (dt, *o*-C), 133.2 (m, *i*-C), 210.4 (dt, $J_{C,H}$ = 8, 4 Hz, C-3). − $C_{12}H_{10}OS$ (202.3): calcd. C 71.25, H 4.98, S 15.85; found C 70.95, H 5.01, S 15.62.

[1,6-D_2]-**7**: According to the procedure for the preparation of **7**, the crude mixture of [1,6-D_2]-**6**, [1-D]-**6** and **6** (3.86 g), as obtained above, was oxidised to give, after chromatography, a yellow solid (516 mg, 9% from [1,6-D_2]-**5**), which was shown to contain [1,6-D_2]-**7**, [1-D]-**7**, [6-D]-**7**, and **7** in a ratio of about 5:2:2:1 as determined by the integrals in the ^{1}H-NMR spectrum and the heights of the C-2 signals in the ^{13}C-NMR spectrum. − ^{1}H and ^{13}C NMR of [1,6-D_2]-**7** ($CDCl_3$): As compared to **7**, in the ^{1}H-NMR spectrum the signals at δ = 2.92 and 2.99 are missing, the multiplicities of the signals of 2-H (d), 4-H (d), and 5-H (dd) are reduced, and the signals of 2-H and 5-H are shifted upfield by ca. 0.03 ppm; in the ^{13}C-NMR spectrum, the signals of C-1,6 (2 × t, $J_{C,D}$ = 35 Hz), C-2, and C-5 are shifted upfield by 0.44, 0.18, and 0.24 ppm, respectively. − ^{1}H and ^{13}C NMR of [1-D]- and [6-D]-**7** ($CDCl_3$): In the ^{1}H-NMR spectrum, the signals of 1-H (m), 6-H (m), 2-H (dd), and 5-H (ddd) are not entirely superimposed by the signals of [1,6-D_2]-**7** and shifted upfield by approx. 0.02 ppm relative to the signals of **7**; as compared to **7**, in the ^{13}C-NMR spectrum, the signals of C-1 (t, $J_{C,D}$ = 35 Hz), C-6 and C-1, C-6 (t, $J_{C,D}$ = 35 Hz) are shifted upfield by 0.43, 0.16 and 0.16, 0.43 ppm, respectively, those of C-2 and C-5 by 0.09 and 0.12 ppm, respectively.

[4-D]-**7**: A mixture of **7** (400 mg, 1.98 mmol), CH_3OD (8.8 ml), D_2O (0.5 ml), and anhydrous Na_2CO_3 (400 mg) was stirred for 6.5 h at room temperature and then concentrated in vacuo. Water (20 ml) was added to the residue, the resulting mixture was extracted with MTBE (5 × 20 ml), the combined extracts were dried with $MgSO_4$ and concentrated in vacuo to give 340 mg (84%) of [4-D]-**7** as a yellow liquid. − ^{1}H NMR ($CDCl_3$): Compared to the spectrum of **7**, the signal at δ = 3.24 was missing and the signals of 1,2,5,6-H were doublets of triplets. − ^{13}C NMR ($CDCl_3$): Other than in the spectrum of **7**, the signal of C-4 (δ = 47.7) was a triplet with $J_{C,D}$ = 23 Hz.

4-(p-Tolylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one (**8**): A solution of crude **6** (2.78 g, ca. 12 mmol) and *p*-tolylthiol (3.71 g, 29.9 mmol) in 150 ml of dichloromethane was stirred under oxygen with a pressure of slightly above 1 atm at room temperature for 2 d. Then the mixture was extracted with aqueous NaOH (4 × 100 ml 2 M) and water (2 × 100 ml), dried with K_2CO_3, and concentrated in vacuo. The residue was purified by flash chromatography as in the case of **7** to give an orange liquid (1.02 g, 28% from **4**) which was shown to be a rather pure 4:1 mixture of **8** and **7**. − ^{1}H NMR of **8** ($CDCl_3$): δ = 2.33 (s, CH_3), 2.39 (2-H), 2.53 (5-H), 2.89 (6-H), 2.97 (1-H), 3.16 (4-H), 7.10, 7.40 (C_6H_4); the coupling constants are the same as in **7**. − ^{13}C NMR of **8** ($CDCl_3$): δ = 9.9 (C-1), 10.2 (C-6), 21.0 (CH_3), 34.4 (C-5), 41.9 (C-2), 48.4 (C-4), 129.2 (C-1′), 129.5, 133.0 (C-2′,3′), 137.6 (C-4′), 210.7 (C-3); the assignments are based on a C,H-COSY spectrum.

4-Methyl-4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one (**9**): To a solution of **7** (100 mg, 0.49 mmol) and methyl iodide (209 mg, 1.47 mmol) in THF (6 ml), cooled to −10°C, KH (44 mg, 1.10 mmol) was added. The mixture was stirred at −10°C for 24 h and at 0°C for 23 h and then hydrolysed with NaOH (20 ml 2 M). The resulting mixture was stirred at room temperature for 30 min, THF was evaporated in vacuo, and the residue was extracted with MTBE (5 × 50 ml). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo. By flash chromatography (SiO_2, PE/MTBE, 2:1 at the beginning, then 1:1, and finally 1:2) of the residue, 62 mg (58%) of **9** were obtained as a yellowish liquid. − IR (film): $\tilde{\nu}$ = 1739 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, CH_3), 2.30, 2.38 (2 × dt, $J_{2,5}$ = 4.9, $J_{1,2}$ ≈ $J_{1,5}$ ≈ $J_{2,6}$ ≈ $J_{5,6}$ = 1.7−1.9 Hz, 2,5-H), 2.73, 2.93 (2 × dt, $J_{1,6}$ = 7.0 Hz, 1,6-H), 7.24−7.41 (*m*,*p*-H), 7.55 (*o*-H). − ^{13}C NMR ($CDCl_3$): δ = 9.7, 10.7 (C-1,6), 20.6 (CH_3), 40.0, 41.1 (C-2,5), 51.2 (C-4), 128.4 (*m*-C), 129.0 (*p*-C), 130.2 (*i*-C), 136.9 (*o*-C), 212.4 (C-3); the assignments are based on a C,H-COSY spectrum. − MS (70 eV); *m/z* (%): 216 (76) [M$^+$], 188 (9), 173 (8), 111 (24), 110 (21), 109 (22), 107 (100), 79 (43), 78 (17), 77 (65), 65 (10), 53 (8), 51 (12), 39 (13). − HRMS: calcd. for $C_{13}H_{12}OS$ [M$^+$] 216.0609; found 216.0610. − $C_{13}H_{12}OS$ (216.3): calcd. C 72.19, H 5.59, S 14.82; found C 72.63, H 5.71, S 14.75.

4-Allyl-4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one (**10**): To a suspension of KH (43 mg, 1.08 mmol) in THF (2 ml), cooled to −10°C, 1,3-diiodopropane (580 mg, 1.96 mmol) and then **7** (100 mg, 0.49 mmol) were added at once. The mixture was stirred at 0°C for 21 h. Since TLC analysis (SiO_2, PE/MTBE, 1:2) still indicated the presence of some **7**, further KH was added until the generation of a gas (H_2) ceased. Stirring was then continued at 0°C for 2.5 h. Water (1 ml) was added and from the resulting mixture the major amount of THF was evaporated in vacuo. The residue was extracted with MTBE (4 × 20 ml), and the combined extracts were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, PE/MTBE, 1:1) to give 74 mg (62%) of **10** as an orange oil. − IR (film): $\tilde{\nu}$ = 1739 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 2.25 (ddt, ^2J = 14.4, ^3J = 7.5, ^4J = 1.2 Hz), 2.41 (ddt, ^3J = 7.0, ^4J = 1.0 Hz) (CH_2−CH=CH_2), 2.31, 2.38 (2 × dt, $J_{2,5}$ = 4.8, $J_{1,2}$ ≈ $J_{1,5}$ ≈ $J_{2,6}$ ≈ $J_{5,6}$ =

1.8−2.0 Hz, 2,5-H), 2.71, 2.94 (2 × dt, $J_{1,6}$ = 6.9 Hz, 1,6-H), 5.08 (dm, =CH_Z), 5.10 (dm, =CH_E), 5.88 (≈ ddt, J_{trans} = 16.0, J_{cis} = 10.9 Hz, C*H*=CH$_2$), 7.24−7.42 (*m*,*p*-H), 7.56 (*o*-H). − ^{13}C NMR ($CDCl_3$): δ = 9.9, 10.2 (C-1,6), 37.7, 41.5 (C-2,5), 38.4 (*C*H$_2$−CH=CH$_2$), 54.1 (C-4), 118.3 (CH=*C*H$_2$), 128.5 (*m*-C), 129.0 (*p*-C), 130.1 (*i*-C), 132.7 (*C*H=CH$_2$), 137.0 (*o*-C), 211.1 (C-3); the assignments are based on a C,H-COSY spectrum. − MS (70 eV); *m*/*z* (%): 242 (46) [M$^+$], 201 (16), 135 (19), 133 (41), 131 (17), 109 (16), 105 (100), 103 (39), 91 (16), 79 (66), 78 (15), 77 (67), 65 (20), 55 (16), 51 (26), 45 (16), 41 (18), 39 (33). − HRMS: calcd. for $C_{15}H_{14}OS$ [M$^+$] 242.0765; found 242.0773.

(4S,1′S*,2′R*,3′S*,5′R*)-* (**11a**) *and (4R*,1′S*,2′R*,3′S*,5′R*)-{4-Oxo-3-(phenylsulfanyl)bicyclo[3.1.0]hex-2-yl}-4-(phenylsulfanyl)tricyclo[3.1.0.0^{2,6}]hexan-3-one* (**11b**): To a suspension of KH (52 mg, 1.30 mmol) in THF (5 ml), cooled to −10°C, **7** (131 mg, 0.65 mmol) was added and the mixture was stirred at 0°C until **7** was consumed completely as determined by TLC (3 h). Water (2 ml) was added, from the resulting mixture the major amount of THF was evaporated in vacuo, the residue was extracted with MTBE (4 × 20 ml), and the combined extracts were dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, PE/MTBE, 1:1 at the beginning and then 1:2) to give **11a (**39 mg, 30%) as a viscous colourless oil and **11b** (33 mg, 25%) as colourless crystals, m.p. 141−142°C.

11a: IR (film): ṽ = 1730 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.20 (td, *endo*-6′-H), 1.24 (ddd, $J_{5',6'}$ = 9.1, $J_{1',6'}$ = 7.8, $J_{6',6'}$ = 5.2 Hz, *exo*-6′-H), 1.98 (dddd, $J_{1',5'}$ = 4.8, $J_{5',6'endo}$ = 3.4, $J_{3',5'}$ = 1.4 Hz, 5′-H), 2.18, 2.31 (2 × dt, $J_{2,5}$ = 4.9, $J_{1,2}$ ≈ $J_{1,5}$ ≈ $J_{2,6}$ ≈ $J_{5,6}$ = 1.8−1.9 Hz, 2,5-H), 2.52 (d, $J_{2',3'}$ = 2.3 Hz, 2′-H), 2.62, 2.83 (2 × dt, $J_{1,6}$ = 6.8 Hz, 1,6-H), 2.66 (dt, $J_{1',6'endo}$ = 4.8 Hz, 1′-H), 3.55 (dd, 3′-H), 7.28−7.33 (m, 4 *m*-H, 1 *p*-H), 7.39 (1 *p*-H), 7.47 (2 *o*-H), 7.54 (2 *o*-H). − ^{13}C NMR ($CDCl_3$): δ = 9.6, 10.7 (C-1,6), 13.4 (C-6′), 21.3 (C-1′), 28.3 (C-5′), 36.4, 42.2 (C-2,5), 48.3 (C-2′), 51.8 (C-3′), 57.5 (C-4), 128.3, 129.4 (2 × *p*-C), 128.7, 129.1 (2 × *m*-C), 128.9, 133.9 (2 × *i*-C), 133.5, 137.3 (2 × *o*-C), 208.7, 209.7 (C-3,4′); the assignments are based on a C,H-COSY spectrum. − $C_{24}H_{20}O_2S_2$ (404.6): calcd. C 71.25, H 4.98, S 15.85; found C 71.04, H 5.07, S 15.93.

11b: IR (KBr): ṽ = 1735, 1720 cm^{-1} (2 × C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.23 (ddd, $J_{5',6'}$ = 9.5, $J_{1',6'}$ = 8.0, $J_{6',6'}$ = 5.4 Hz, *exo*-6′-H), 1.39 (ddd, $J_{1',6'}$ = 4.7, $J_{5',6'}$ = 3.1 Hz, *endo*-6′-H), 1.84 (dt, $J_{1',5'}$ = 4.8 Hz, 1′-H), 2.02 (dddd, $J_{3',5'}$ = 1.3 Hz, 5′-H), 2.28, 2.43 (2 × dt, $J_{2,5}$ = 4.8, $J_{1,2}$ ≈ $J_{1,5}$ ≈ $J_{2,6}$ ≈ $J_{5,6}$ = 1.8−2.0 Hz, 2,5-H), 2.63 (d, $J_{2',3'}$ = 2.0 Hz, 2′-H), 2.86, 3.03 (2 × dt, $J_{1,6}$ = 6.8 Hz, 1,6-H), 3.92 (≈ t, 3′-H), 7.29 (2 *m*-H, 1 *p*-H), 7.33 (2 *m*-H), 7.38 (1 *p*-H), 7.54 (2 *o*-H), 7.57 (2 *o*-H). − ^{13}C NMR ($CDCl_3$): δ = 9.3, 11.9 (C-1,6), 14.4 (C-6′), 22.7 (C-1′), 27.9 (C-5′), 35.2, 42.5 (C-2,5), 47.9 (C-2′), 50.0 (C-3′), 58.1 (C-4), 128.0, 129.5 (2 × *p*-C), 128.6, 129.1 (2 × *m*-C), 128.8, 134.6 (2 × *i*-C), 132.4, 137.5 (2 × *o*-C), 209.0, 209.1 (C-3,4′); the assignments are based on a C,H-COSY spectrum. − $C_{24}H_{20}O_2S_2$ (404.6): calcd. C 71.25, H 4.98, S 15.85; found C 71.21, H 5.21, S 15.52.

X-ray Diffraction Analysis of **11b**: $C_{24}H_{20}O_2S_2$, *M* = 404.56, colourless block (0.4 × 0.2 × 0.2 mm), monoclinic space group $P2_1/c$, *a* = 1135.1(2), *b* = 1067.29(10), *c* = 1634.6(4) pm, β = 105.919(10)°, *V* = 1.9043(6) nm^3 (from 25 reflections, 10° < θ < 15°), *Z* = 4, $\rho_{calcd.}$ = 1.411 Mg m^{-3}, μ = 0.298 mm^{-1}, *F*(000) = 848, *T* = 173(2) K. 3003 reflections collected (3.18° ≤ θ ≤ 22.49°), of which 2478 were independent (R_{int} = 0.019) and used in the structure refinement. The structure was solved by direct methods (G. M. Sheldrick, *Acta Cryctallogr., Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares iteration against F^2 employing all data (G. M. Sheldrick, *Program for Crystal Structure Refinement*, Göttingen, **1996**). All non-hydrogen atoms were refined anisotropically, H(phenyl) atoms were refined applying a riding model, all other hydrogen atoms were refined isotropically and free. *R* values: *R*1 = 0.036 [$I > 2\sigma(I)$], *wR*2 = 0.078 (all data); *GOF* = 1.034 for 283 parameters; largest difference peak and hole: 0.153 and −0.196 e nm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100851. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[3′-D]-**11a** *and* -**11b**: The reaction of **7** with KH was performed as for the preparation of **11a**, **b**, but D_2O was added instead of H_2O. Thus from 100 mg of **7**, 21 mg (21%) of [3′-D]-**11a** and 12 mg (12%) of [3′-D]-**11b** were isolated by chromatography. − ^{1}H NMR ($CDCl_3$): As compared to **11a**, **b**, the signals at δ = 3.55 and 3.91, respectively, were missing and the multiplicities of the 2′- and 5′-H signals were correspondingly reduced.

[*endo*-6′-D]-**11a** *and* -**11b**: The reaction of [4-D]-**7** with KH was performed as that of **7** in the preparation of **11a,b**. By chromatography, a 1:1 mixture of **11a** and [*endo*-6′-D]-**11a** and a 1:1 mixture of **11b** and [*endo*-6′-D]-**11b** were isolated. When [D_8]THF was used as solvent instead of THF, the result was the same. − ^{1}H NMR of [*endo*-6′-D]-**11a** ($CDCl_3$): As compared to **11a**, the signal at δ = 1.20 was missing and the signals of 1′-H, 5′-H, and *exo*-6′-H showed the expected reduced multiplicities and were shifted upfield by 0.005, 0.009, and 0.015 ppm, respectively. − ^{13}C NMR of [*endo*-6′-D]-**11a** ($CDCl_3$): As compared to **11a**, the signals of C-1′, C-2′, C-5′, and C-6′ (1:1:1 t) were shifted upfield by 0.08, 0.06, 0.11, and ca. 0.3 ppm, respectively. − ^{1}H NMR of [*endo*-6′-D]-**11b** ($CDCl_3$): As compared to **11b**, the signal at δ = 1.39 was missing and the signals of 1′-H, 5′-H, and *exo*-6′-H showed the expected reduced multiplicities and were shifted upfield by ca. 0.01 ppm. − ^{13}C NMR of [*endo*-6′-D]-**11b** ($CDCl_3$): As compared to **11b**, the signals of C-1′, C-2′, C-5′, and C-6′ (1:1:1 t) were shifted upfield by 0.08, 0.05, 0.11, and ca. 0.3 ppm, respectively.

[1′,*exo*-6′-D_2]-**11a** *and* -**11b**: The reaction of a 5:2:2:1 mixture of [1,6-D_2]-**7**, [1-D]-**7**, [6-D]-**7**, and **7** with KH was performed as that of **7** in the preparation of **11a**, **b**. By chromatography, two fractions were obtained corresponding to **11a** and **11b**. If the new hydrogen atom at the bicyclohexane subunit had been incorporated with high stereoselection, both fractions should have been composed of 16 isotopomers, containing up to four deuterium atoms. Since the isotope effects of the deuterium atoms of the tricyclohexane moiety exerted on the bicyclohexane moiety and vice versa are negligible and only the sites of the deuterium atoms in the bicyclohexane subunit are of interest, those isotopomers that were equally labelled there are considered as one species. Corresponding to this definition, the presence of [1′,*exo*-6′-D_2]-**11a**, [1′-D]-**11a**, [*exo*-6′-D]-**11a**, and **11a** in the first fraction and of [1′,*exo*-6′-D_2]-**11b**, [1′-D]-**11b**, [*exo*-6′-D]-**11b**, and **11b** in the second fraction with a ratio of 5:2:2:1 in both cases was indicated by 600-MHz ^{1}H-NMR spectra ($CDCl_3$). As compared to **11a** and **11b**, respectively, the following spectral changes were manifest: [1′,*exo*-6′-D_2]-**11a**: the signals at δ = 1.24 and 2.66 were missing; the signals of 2′-H, 5′-H (br. d, $J_{5',6'endo}$ = 3.4 Hz), and *endo*-6′-H (d) were shifted upfield by ca. 0.005, 0.011, and 0.011 ppm, respectively. − [1′-D]-**11a**: the signal at δ = 2.66 was missing; the signals of 2′-H, 5′-H (reduced multiplicity), and 6′-H_2 (reduced multiplicity) were shifted upfield by ca. 0.005 ppm. − [*exo*-6′-D]-**11a**: the signal at δ = 1.24 was missing;

the signals of 1′-H, 5′-H, and *endo*-6′-H showed reduced multiplicities and were shifted upfield by ca. 0.005 ppm. − [1′,*exo*-6′-D_2]-**11b**: the signals at δ = 1.23 and 1.84 were missing; the signals of 2′-H, 5′-H (br. d), and *endo*-6′-H (d, $J_{5',6'endo}$ = 3.1 Hz) were shifted upfield by ca. 0.005, 0.015, and 0.013 ppm, respectively. − [1′-D]-**11b**: the signal at δ = 1.84 was missing; the signals of 2′-H, 5′-H (reduced multiplicity), and 6′-H_2 (reduced multiplicity) were shifted upfield by ca. 0.005 ppm. − [*exo*-6′-D]-**11b**: the signal at δ = 1.23 was missing; the signals of 1′-H, 5′-H, and *endo*-6′-H showed reduced multiplicities and were shifted upfield by ca. 0.005 ppm.

☆ Dedicated to Professor *John D. Roberts* on the occasion of his 80th birthday.

[1] S. Masamune, N. T. Castellucci, *Proc. Chem. Soc.* **1964**, 298; S. Masamune, *Tetrahedron Lett.* **1965**, 945−951.

[2] [2a] A. Small, *J. Am. Chem. Soc.* **1964**, *86*, 2091−2092. − [2b] A. Small Monahan, *J. Org. Chem.* **1968**, *33*, 1441−1445.

[3] A. Kraft, Dissertation, Universität Würzburg, **1989**.

[4] [4a] M. Christl, *Angew. Chem.* **1981**, *93*, 515−531; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 529−546. − [4b] M. Christl, E. Brunn, F. Lanzendörfer, *J. Am. Chem. Soc.* **1984**, *106*, 373−382; M. Christl, S. Freund, *Chem. Ber.* **1985**, *118*, 979−999; M. Christl, P. Kemmer, B. Mattauch, *Chem. Ber.* **1986**, *119*, 960−970; M. Christl, M. Braun, *Angew. Chem.* **1989**, *101*, 636−638; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 601−603; M. Christl, S. Krimm, A. Kraft, *Angew. Chem.* **1990**, *102*, 704−706; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 675−677. − [4c] M. Christl, M. Türk, E.-M-Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1994**, *106*, 1719−1720; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1639−1641.

[5] [5a] S. Krimm, Dissertation, Universität Würzburg, **1990** (addition of two nitrile *N*-oxides). − [5b] T. Fischer, Dissertation, Universität Würzburg, **1996** (Pauson-Khand reaction).

[6] T. J. Katz, K. C. Nicolaou, *J. Am. Chem. Soc.* **1974**, *96*, 1948−1949.

[7] J. Yoshida, S. Nakatani, S. Isoe, *J. Chem. Soc., Chem. Commun.* **1988**, 1468−1470; *J. Org. Chem.* **1993**, *58*, 4855−4865.

[8] M. Christl, B. Mattauch, H. Irngartinger, A. Goldmann, *Chem. Ber.* **1986**, *119*, 950−959 and references cited; O. Ermer, P. Bell, J. Schäfer, G. Szeimies, *Angew. Chem.* **1989**, *101*, 503−506; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 473.

[9] A. L. Spek, P. van der Sluis, *Acta Crystallogr., Sect. C* **1990**, *46*, 1357−1358.

[10] R. L. Cook, T. B. Malloy, Jr., *J. Am. Chem. Soc.* **1974**, *96*, 1703−1707.

[11] R. Hoffmann, *Tetrahedron Lett.* **1970**, 2907−2909; H. Günther, *Tetrahedron Lett.* **1970**, 5173−5176.

[12] M. Christl, *Adv. Strain Org. Chem.* **1995**, *4*, 163−224.

[13] D. W. T. Griffith, J. E. Kent, M. F. O′Dwyer, *J. Mol. Spectrosc.* **1975**, *58*, 427−435.

[14] T. J. Katz, E. J. Wang, N. Acton, *J. Am. Chem. Soc.* **1971**, *93*, 3782−3783; T. J. Katz, R. J. Roth, N. Acton, E. J. Carnahan, *Org. Synth.* **1973**, *53*, 157.

[15] W. H. Mueller, P. E. Butler, *J. Am. Chem. Soc.* **1968**, *90*, 2075−2081; P. B. Hopkins, P. L. Fuchs, *J. Org. Chem.* **1978**, *43*, 1208−1217.

[16] R. J. Roth, T. J. Katz, *J. Am. Chem. Soc.* **1972**, *94*, 4770−4771.

[98208]