The structure of **3a** was determined by X-ray structure analysis (Fig. 1). **3a** is the first example of a (*Z*)-diphosphene as a ligand of a mononuclear carbonylmetal complex. It should be noted that P1, P2, Cr, and Cl are coplanar, whereas the dihedral angle C1–P1–P2–C10 is 12.1°. The bond distance P1–Cr (2.354 Å) is shorter than that for pentacarbonyl(triphenylphosphane)chromium (2.422 Å)[5].

In the absence of these transition metals, the energy barrier for the isomerization of diphosphene (HP=PH) is considerable, the rotational transition state being preferred to the inversion transition state (Fig. 2). On complexation, however, the rotational barrier could be lowered both sterically and electronically.

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CAS Registry numbers:
2a, 95342-12-4; **2b**, 95342-13-5; **2c**, 95342-14-6; **3a**, 95250-88-7; **3b**, 95250-89-8; **3c**, 95250-90-1.

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[2] Selected physical data: **2a**: m.p. = 166°C, δ(P) = 500.9, 412.3 (AB, ^1J(PP) = 517.6 Hz), UV (cyclohexane): λ_{max} = 460 nm; **3a**: 136°C, δ = 393.9, 384.9 (603.0 Hz), 473 nm; **2b**: 163°C, δ = 486.3, 395.0 ppm (518.8 Hz), 435 nm; **3b**: 123°C, δ = 398.4, 359.0 (585.9 Hz), 456 nm; **2c**: 177°C, δ = 461.9, 352.4 (528.8 Hz), 436 nm; **3c**: 128°C, δ = 393.1, 322.4 (576.8 Hz), 459 nm. *Note added in proof* (March 22, 1985): We have meanwhile found a new synthesis of **2**: M. Yoshifuji, T. Hashida, K. Shibayama, N. Inamoto, *Chem. Lett.*, in press.

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Synthesis and Dynamic Properties of Chiral Heptalenes**

By *Klaus Hafner**, *Günter L. Knaup*, *Hans Jörg Lindner*, and *Hans-Christian Flöter*

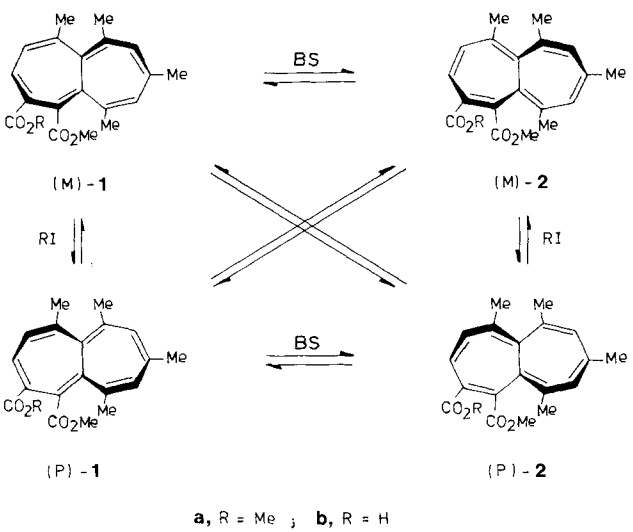
Dedicated to Professor Günther Wilke on the occasion of his 60th birthday

Mono- and bicyclic non-benzenoid systems with a 4n perimeter possess localized double bonds in the ground state. Their antiaromatic structures[1] with delocalized double bonds are transition states on the potential surfaces that connect the localized bond systens with one another. The results of experimental investigations on the 4nπ-electron systems tetra-*tert*-butylcyclobutadiene[2a], 1,3,5-tri-*tert*-butylpentalene[2b], cyclooctatetraene[2c], and heptalene[2d] are in agreement with this.

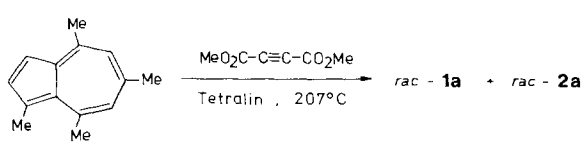
In contrast to cyclobutadiene and pentalene, their higher homologues cyclooctatetraene and heptalene are characterized by a nonplanar structure. X-ray structure analysis[3] of heptalene derivatives confirms a C_2 geometry for the bicyclic system with the two annelated seven-membered rings in boat conformations. For heptalenes, according to *Oth* et al.[4], four axially chiral isodynamic structures should be in equilibrium with one another via two dynamic processes [bond shift (BS) and ring inversion (RI)]. A study of both processes should provide information on their transition states and, therefore, also on the antiaromaticity of the delocalized heptalene system.

For the π-bond shift in heptalenes, *Vogel* et al.[2d, 5] determined an activation energy of 3.5 kcal·mol^{-1} by ^{13}C-NMR spectroscopy; for its 1,6-dialdehyde and dimethyl 1,6-dicarboxylate, a free energy of activation of 9.9 and 14 kcal·mol^{-1}, respectively. *Klärner*[6] found $\Delta G^{\ddagger}_{3°C}$ = 21.7 and 21.0 kcal mol^{-1} for the isomerization of the bond-shift isomers of dimethyl 6,8,10-trimethyl-1,2-heptalenedicarboxylate[7], which can be separated by low-temperature chromatography. The kinetic parameters for the ring inversion of the heptalene system have not yet been determined.

We have succeeded for the first time in isolating in pure form all four possible isomers, (M)-**1**, (P)-**1**, (M)-**2**, and (P)-**2**, of a substituted heptalene, dimethyl 5,6,8,10-tetramethyl-1,2-heptalenedicarboxylate[8], and in investigating the kinetics of both dynamic processes for this heptalene derivative.



In analogy to the reaction[7] of azulene with dimethyl acetylenedicarboxylate, the reaction of 1,4,6,8-tetramethylazulene **3** with dimethyl acetylenedicarboxylate in boiling tetralin affords both isomers of *rac*-heptalene **1a** (yellow crystals, m.p. = 130°C) and **2a** (orange crystals, m.p. = 89–91°C) in 38 and 4% yield, respectively; the two compounds could be separated by chromatography on alumina at room temperature[9].



rac-**1a** and *rac*-**2a** differ characteristically in their electron and NMR spectra (Table 1). The position of the double bonds is determined from the ^{1}H-NMR spectra and the

[*] Prof. Dr. K. Hafner, Dipl.-Ing. G. L. Knaup, Prof. Dr. H. J. Lindner, Dipl.-Ing. H. C. Flöter
Institut für Organische Chemie der Technischen Hochschule
Petersenstrasse 22, D-6100 Darmstadt (FRG)

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X-ray structure analyses[10] (Fig. 1), which confirm the double boat structure and thus the chirality of these compounds.

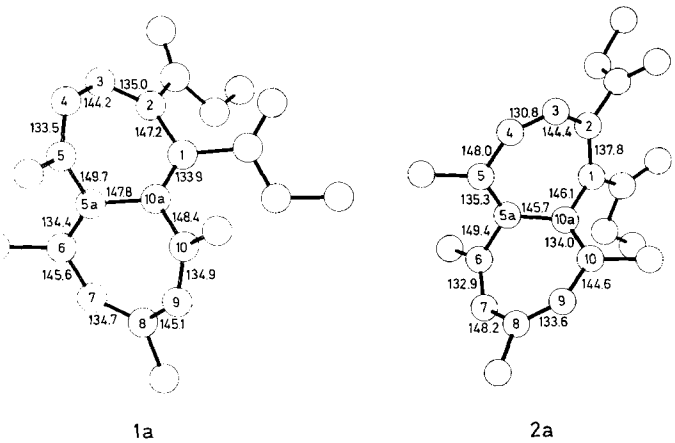

Fig. 1. Molecular structure of **1a** and **2a** with bond lengths [pm] (standard deviation **1a**: $\sigma_r = 0.6$ pm, **2a**: $\sigma_r = 1.0$ pm) [10].

Table 1. Spectroscopic data for racemic heptalenes **1** and **2**.

rac-**1a**: 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta = 1.74$ (s, 3 H, 6-Me), 1.96 (d, $J = 1.2$ Hz, 3 H, 10-Me), 2.00 (dd, $J = 1.4$, 1.0 Hz, 3 H, 5-Me), 2.04 (d, $J = 1.2$ Hz, 3 H, 8-Me), 3.69, 3.70 (2 s, each 3 H, 2 CO_2Me), 6.01 (quint., $J = 1.1$ Hz, 1 H, 9-H), 6.14 (s, 1 H, 7-H), 6.27 (dq, $J = 6.9$, 1.4 Hz, 1 H, 4-H), 7.53 (dq, $J = 6.9$, 1.0 Hz, 1 H, 3-H); UV (*n*-hexane): $\lambda_{max}(\lg\varepsilon) = 211$ (4.38), 264 (4.21), 322 sh (3.46) nm.

rac-**1b**: 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta = 1.73$ (s, 3 H, 6-Me), 1.95 (d, $J = 1.1$ Hz, 3 H, 10-Me), 2.00 (br. s, 3 H, 5-Me), 2.03 (d, $J = 1.2$ Hz, 3 H, 8-Me), 3.67 (s, 3 H, 1-CO_2Me), 6.01 (s, 1 H, 9-H), 6.14 (s, 1 H, 7-H), 6.28 (dq, $J = 5.9$, 1.4 Hz, 1 H, 4-H), 7.61 (dq, $J = 5.9$, 1.1 Hz, 1 H, 3-H), 11.10 (s, 1 H, 2-CO_2H); UV (dioxane): $\lambda_{max}(\lg\varepsilon) = 265$ (4.20), 318 sh (3.50), 369 sh (2.92) nm.

rac-**2a**: 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta = 1.68$ (s, 3 H, 10-Me), 1.77 (s, 3 H, 5-Me), 1.99 (d, $J = 1.2$ Hz, 3 H, 8-Me), 2.02 (d, $J = 1.3$ Hz, 3 H, 6-Me), 3.71, 3.82 (2 s, 3 H each, 2 CO_2 Me), 6.01 (s, 1 H, 9-H), 6.10 (s, 1 H, 7-H), 6.55 (d, $J = 11.8$ Hz, 1 H, 3-H), 6.59 (d, $J = 11.8$ Hz, 1 H, 4-H); UV (*n*-hexane): $\lambda_{max}(\lg\varepsilon) = 210$ (4.34), 230 sh (4.21), 270 (4.31), 308 sh (3.54), 378 (2.74) nm.

rac-**2b**: 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta = 1.72$ (s, 3 H, 10-Me), 1.77 (s, 3 H, 5-Me), 1.99 (d, $J = 1.0$ Hz, 3 H, 8-Me), 2.03 (d, $J = 1.2$ Hz, 3 H, 6-Me), 3.73 (s, 3 H, 1-CO_2Me), 6.01 (s, 1 H, 9-H), 6.10 (s, 1 H, 7-H), 6.57 (d, $J = 11.8$ Hz, 1 H, 3-H), 6.70 (d, $J = 11.8$ Hz, 1 H, 4-H), 11.00 (s, 1 H, 2-CO_2H). UV (dioxane): $\lambda_{max}(\lg\varepsilon) = 231$ sh (4.21), 271 (4.30), 309 sh (3.56), 381 (2.75) nm.

The saponification of *rac*-**1a** and *rac*-**2a** with CH_3OH/KOH affords the *rac*-acids **1b** (yellow crystals, m.p. = 150—155 °C (decomp.)) and **2b** (yellow crystals, m.p. 156—157 °C (decomp.)), respectively, which could be reconverted quantitatively into *rac*-diester **1a** and **2a**, respectively, with diazomethane. The resolution of **1b** is achieved by fractional crystallization of the cinchonine and (+)-α-phenylethylamine salts followed by liberation of the acids with 2 N sulfuric acid; that of **2b** in a corresponding way with (+)- and (−)-ephedrine[11].

The enantiomeric purity of the heptalenes so obtained, (+)- and (−)-**1b**, and (+)- and (−)-**2b**, is greater than 98%, as shown on the basis of the signals of the methoxy group in the ^{1}H-NMR spectra of the ephedrine salts. The enantiomerically pure acids, (+)- and (−)-**1b**, and (+)- and (−)-**2b**, and the enantiomerically pure esters obtained from these with diazomethane, (+)- and (−)-**1a** and (+)- and (−)-**2a**, have the high specific optical rotations typical for molecules with chiral chromophores (Table 2).

Table 2. Specific optical rotations of the heptalenes (+)-**1** and (+)-**2** (in $CHCl_3$) [12].

	$[\alpha]^{20}_{546}$	$[\alpha]^{20}_{578}$
(+)-**1a**	+1930 ($c = 1.028$)	+1460 ($c = 1.028$)
(+)-**1b**	+2550 ($c = 1.004$)	+1910 ($c = 1.004$)
(+)-**2a**	+1860 ($c = 0.921$)	+1310 ($c = 0.921$)
(+)-**2b**	+2140 ($c = 0.514$)	+1430 ($c = 1.029$)

The kinetic parameters for the bond shift, starting from *rac*-**2a**, were determined by ^{1}H-NMR spectroscopy in [D_{14}]-diglyme at temperatures between 50 and 80 °C. The rate constants for the reverse reactions were calculated from the equilibrium constants, which were determined in the temperature range of 50 to 170 °C, since the equilibrium ratio *rac*-**1a** : *rac*-**2a** is about 10 : 1 and therefore the measurements starting from *rac*-**1a** afford only very inaccurate data (Table 3).

Table 3. Kinetic parameters for the bond shift (BS) and ring inversion (RI) of the heptalenes **1a** and **2a** [13].

	$\Delta H^{\ddagger}_{25\,°C}$ [kcal·mol^{-1}]	$\Delta S^{\ddagger}_{25\,°C}$ [cal·mol^{-1}·K^{-1}]
BS **2a** → **1a**	22.8 ± 0.6	−11.1 ± 2.0
BS **1a** → **2a**	25.7 ± 0.6	−7.8 ± 1.7
RI (−)-[**1a** ⇌ **2a**] → *rac*-[**1a** ⇌ **2a**]	28.3 ± 0.4	−11.6 ± 0.9

The rates of racemization were determined on the basis of the decrease in optical rotation of solutions of optically active heptalenes **1a** and **2a** in diglyme at 130 to 150 °C. Since the same rate constants are obtained starting from **1a** and **2a**, the bond shift may occur in a preceding equilibrium.

The kinetic data for the dynamic processes of the heptalenes **1a** and **2a** are not in accord with a planar transition state for the bond shift. For the bond shift, which proceeds with retention of configuration, a helical chiral transition state with a delocalized π-electron system must be assumed. In the case of planar transition states, like those assumed by *Paquette*[14] for the analogous processes of substituted cyclooctatetraenes, the energy barrier for the bond shift should be higher than that for ring inversion by the amount of energy required for the delocalization of the anti-aromatic π-electron system.

According to π-SCF force-field calculations[15] for the dynamics of both processes of 1,5,6,10-tetramethylheptalene, which are in agreement with experimental results, the bond shift should proceed via a helical, delocalized transition state ($\Delta H^{\ddagger}$: 30 kcal·mol^{-1}); the ring inversion, on the other hand, should occur via an only partly planar and localized transition state ($\Delta H^{\ddagger}$: ca. 31 kcal·mol^{-1}). In contrast to this, the corresponding processes with planar transition states require activation enthalpies of more than 50 kcal·mol^{-1}.

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(±)-**1a**, 95045-18-4; (+)-**1a**, 95045-19-5; (−)-**1a**, 95045-20-8; (±)-**1b**, 95045-21-9; (+)-**1b**, 95045-22-0; (−)-**1b**, 95045-23-1; **3**, 830-55-7; dimethyl acetylenedicarboxylate, 762-42-5.

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[8] The IUPAC rule A-21.1, according to which the parent system is to be called a heptalene, is not suitable for the correct designation of the bond-shift isomers. Rule A-31.3 makes it possible to give the structures unequivocal names. **1a**: dimethyl 6,8,10,12-tetramethylbicyclo[5.5.0]dodeca-1,3,5,7,9,11-hexaene-2,3-dicarboxylate; **2a** is the corresponding 2,4,6,8,10,12(1)-hexaene.
[9] In addition to *rac*-**1a** and *rac*-**2a**, 2% *rac* dimethyl 5,6,8,10-tetramethyl-2,3-heptalenedicarboxylate (orange needles, m.p. 125–127°C; 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta = 1.78$ (d, $J = 1.0$ Hz, 3H, 10-Me), 1.79 (s, 3H, 5-Me), 1.97 (s, 3H, 6-Me), 2.00 (d, $J = 1.3$ Hz, 3H, 8-Me), 3.76, 3.77 (2s, 3H each, $2CO_2Me$), 5.97 (s, 1H, 7-H), 6.09 (s, 1H, 9-H), 6.75 (s, 1H, 1-H), 7.40 (s, 1H, 4-H); UV (*n*-hexane): λ_{max}(lgε): 219 sh (4.24), 232 (4.25), 271 (4.30), 328 (3.75) nm) and 23% dimethyl 4,6,8-trimethyl-1,2-azulenedicarboxylate [8] are obtained.
[10] X-ray structure analysis: **1a**: monoclinic, space group $P2_1/c$, $Z = 8$, $a = 2394.5(4)$, $b = 922.9(3)$, $c = 1671.6(9)$ pm; $\beta = 105.04(5)°$, $V = 3567 \times 10^6$ pm^3; $\rho_{calc} = 1.22$ g/cm^3; $5° \leq 2\theta \leq 60°$; ($Cu_{K\alpha}$, $\lambda = 154.18$ pm), 4330 independent reflections, Lorentz and polarization correction, position of the hydrogen atoms calculated and optimized according to ideal geometry, $R_1 = 0.0667$, $R_2 = 0.0509$ for 4322 structure factors ($|F_0| \geq 0.5\sigma_F$). **2a**: triclinic, space group $P\bar{1}$, $Z = 4$, $a = 1840.7$, $b = 1197.9$, $c = 860.9$ pm; $\alpha = 102.75(1)$, $\beta = 98.57(2)$, $\gamma = 80.24(4)°$; $V = 1812 \times 10^6$ pm^3; $\rho_{calc} = 1.20$ g/cm^3; $5° \leq 2\theta \leq 60°$; ($Cu_{K\alpha}$, $\lambda = 154.18$ pm); 4830 independent reflections, Lorentz and polarization correction, position of the hydrogen atoms calculated and optimized according to ideal geometry, $R_1 = 0.1417$, $R_2 = 0.0981$ for 4317 structure factors ($|F_0| \geq 0.5\sigma_F$). Further details of the crystal structure investigation can be obtained on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-51084, the names of the authors, and the journal citation.
[11] By a similar route (H.-J. Hansen, private communication, 1981), an enantiomeric enrichment was achieved for *rac* dimethyl 7-isopropyl-5,10-dimethyl-1,2-heptalenedicarboxylate (W. Bernhard, H.-R. Zumbrunnen, H.-J. Hansen, *Chimia 33* (1979) 324).
[12] Corresponding optical rotations were found for (−)-**1** and (−)-**2**. Note added in proof (February 6, 1985): Recently the absolute configuration of (+)-**1b** was determined as M by an X-ray structure analysis of the (1*S*,2*R*)-(+)-ephedrine salt of (+)-**1b**.
[13] Details on the kinetic measurements: G. L. Knaup, Dissertation, TH Darmstadt 1985.
[14] L. A. Paquette, *Pure Appl. Chem. 54* (1982) 987.
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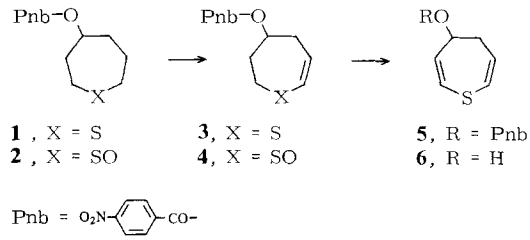
The Homothiopyrylium Ion; Generation and Characterization

By *Kagetoshi Yamamoto, Shoko Yamazaki,* and *Ichiro Murata**

Recently we succeeded in identifying several homothiopyrylium ions generated by protonation of 2,7-di-*tert*-butylthiepines[1] and 1-benzothiepine[2]. We describe now the parent homothiopyrylium ion **7**. Since the use of the protonation sequence to generate **7** requires the hitherto unknown unsubstituted thiepine, which is expected to be an extremely unstable compound[3], we have considered the ionization route for the preparation of **7** and synthesized the precursor 4,5-dihydrothiepin-4-ol **6** using a double Pummerer reaction.



Oxidation of *p*-nitrobenzoyl-protected hexahydro-4-thiepinol **1** (prepared from hexahydro-4-thiepinol[5]) with sodium periodate in aqueous methanol afforded the sulfoxide **2**[4] quantitatively. Interestingly, **2**, on treatment with acetic anhydride, afforded the protected tetrahydro-4-thiepinol **3** as the sole isolable product[4]. The structure of **3** was determined by ^{1}H-NMR (Table 1). After oxidation of **3** with sodium periodate in aqueous methanol or *m*-chloroperbenzoic acid in dichloromethane to the sulfoxide **4**[4], the second double bond was introduced by a modified Pummerer reaction[6]. When **4** was treated with diisopropylethylamine in dichloromethane followed by addition of freshly distilled trimethylsilyl iodide under nitrogen, protected 4,5-dihydro-4-thiepinol **5** was obtained. Finally, the alcohol **6** was smoothly liberated from **5** by hydrolysis with KOH in aqueous *tert*-butyl alcohol.

Table 1. Some physical data for the new compounds. In order to facilitate comparison, the atoms in **3** and **6** are numbered as in **7**.

1, colorless crystals, m.p. = 85.0–85.5°C

3, m.p. = 79.5–80.5°C, 37% yield based on **1**. ^{1}H-NMR (100 MHz, $CDCl_3$): $\delta = 5.36$ (dddd, $J = 9.0$, 7.5, 4.5, 3.0 Hz, H-5); 6.05 (ddd, $J = 9.5$, 7.5, 6.0 Hz, H-3); 6.42 (d, $J = 9.5$ Hz, H-2); 8.26 (AA′BB′, 4 Aryl-H); 2.14–2.56 (m, 2H-6); 2.60–3.14 (m, 2H-4, 2H-7)

5, yellow crystals, m.p. = 107–108°C, 56% yield based on **3**.

6, colorless crystals, m.p. = 42–43°C (hexane/ether). ^{1}H-NMR (360 MHz, $CDCl_3$): $\delta = 2.20$ (bs, OH); 2.66 (dddd, $J(4a,4b) = 13.6$, $J(4a,5) = 8.7$, $J(4a,3) = 6.2$, $J(4a,6) = 1.3$ Hz, H-4a); 2.73 (dddd, $J(4a,4b) = 13.6$, $J(4b,3) = 7.8$, $J(4b,5) = 3.0$, $J(4b,2) = 1.4$ Hz, H-4b); 4.43 (dddd, $J(5,4a) = 8.7$, $J(5,6) = 3.2$, $J(5,4b) = 3.0$, $J(5,7) = 1.5$ Hz, H-5); 5.98 (ddd, $J(7,6) = 11.2$, $J(7,2) = 1.6$, $J(7,5) = 1.5$ Hz, H-7); 6.01 (ddd, $J(3,2) = 9.6$, $J(3,4b) = 7.8$, $J(3,4a) = 6.2$ Hz, H-3); 6.05 (ddd, $J(6,7) = 11.2$, $J(6,5) = 3.2$, $J(6,4a) = 1.3$ Hz, H-6); 6.24 (ddd, $J(2,3) = 9.6$, $J(2,7) = 1.6$, $J(2,4b) = 1.4$ Hz, H-2). IR (KBr): ν(OH) = 3175 cm^{-1}. MS (70 eV): M^+, m/z 128 (100%)

7, ^{1}H-NMR (100 MHz, $CD_2Cl_2 + SO_2 + HFSO_3$, −80°C, standard Me_4Si with $\delta_{CHDCl_2}(Me_4Si) = 5.30$): $\delta = 7.99$ (d, $J(2,3) = 7.5$ Hz, H-2); 6.32 (dt, $J(2,3) = J(3,4a) = J(3,4b) = 7.5$ Hz, H-3); 1.16 (m, H-4a); 4.44 (m, H-4b); 7.15 (dt, $J(5,6) = J(5,4a) = J(5,4b) = 7.9$ Hz, H-5); 7.99 (m, H-6); 10.04 (d, $J(7,6) = 6.1$ Hz, H-7). ^{13}C-NMR (22.5 MHz, $CD_2Cl_2 + SO_2 + HFSO_3$, −70°C, standard Me_4Si with $\delta_{CH_2Cl_2}(Me_4Si) = 53.8$): $\delta = 131.2$ (C-2 or C-6); 133.4 (C-2 or C-6); 129.7 (C-3); 33.76 (C-4); 150.5 (C-5); 178.9 (C-7)

The hydroxy group of **6** can be cleaved off as follows: 10 mg **6** in 0.2 mL CD_2Cl_2 was mixed with 0.2 mL SO_2, containing three drops of fluorosulfuric acid, in an NMR

[*] Prof. Dr. I. Murata, Dr. K. Yamamoto, Dipl.-Chem. S. Yamazaki
Department of Chemistry, Faculty of Science
Osaka University, Toyonaka, Osaka 560 (Japan)