109. Reaction of Hydroxymethyl- and Alkyl-Substituted Azulenes with Manganese Dioxide

by **Reza-Ali Fallahpour**[1]), **Rolf Sigrist**, and **Hans-Jürgen Hansen***

Organisch-chemisches Institut der Universität, Winterthurerstrasse 190, CH–8057 Zürich

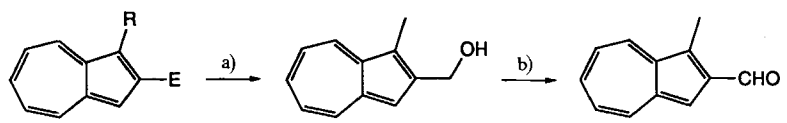
Dedicated to *Richard Neidlein* on the occasion of his 65th birthday

(21.VII.95)

It is shown that the 2-(hydroxymethyl)-1-methylazulenes **6** are being oxidized by activated MnO_2 in CH_2Cl_2 at room temperature to the corresponding azulene-1,2-dicarbaldehydes **7** (*Scheme 2*). Extension of the MnO_2 oxidation reaction to 1-methyl- and/or 3-methyl-substituted azulenes led to the formation of the corresponding azulene-1-carbaldehydes in excellent yields (*Scheme 3*). The reaction of unsymmetrically substituted 1,3-dimethylazulenes (*cf.* **15** in *Scheme 4*) with MnO_2 shows only little chemoselectivity. However, the observed ratio of the formed constitutionally isometric azulene-1-carbaldehydes is in agreement with the size of the orbital coefficients in the HOMO of the azulenes. The reaction of guaiazulene (**18**) with MnO_2 in dioxane/H_2O at room temperature gave mainly the expected carbaldehyde **19**. However, it was accompanied by the azulene-diones **20** and **21** (*Scheme 5*). The precursor of the demethylated compound **20** is the carbaldehyde **19**. Similarly, the MnO_2 reaction of 7-isopropyl-4-methylazulene (**22**) as well as of 4,6,8-trimethylazulene (**24**) led to the formation of a mixture of the corresponding azulene-1,5-diones and azulene-1,7-diones **20**/**23** and **25**/**26**, respectively, in decent yields (*Schemes 6* and *7*). No MnO_2 reaction was observed with 5,7-dimethylazulene.

Introduction. – One of the most versatile reagents for the dehydrogenation of allylic and benzylic alcohols leading to the corresponding carbaldehydes is MnO_2 in one or the other activated form (*cf.* [1] and especially [2])[2]). We have already reported that this method can successfully also be applied to 2-(hydroxymethyl)azulenes which give the corresponding azulene-2-carbaldehydes [4] [5]. A further example is shown in *Scheme 1*.

Scheme 1[a])



R = E : **1a**
R = Me : **1b**

2

3 (65%)

a) DIBAH in hexane/Et_2O, 0°; **1a** → **2**: 75%; **1b** → **2**: 92%. b) MnO_2 (10-fold excess by weight with respect to **2**)/CH_2Cl_2, room temperature, 10 min. All described reactions have been performed with 'Mangan(IV)-oxid, gefällt, aktiv' from *Merck-Schuchardt* (see also later remarks).

[a]) E = $COOCH_3$ in this and the following schemes.

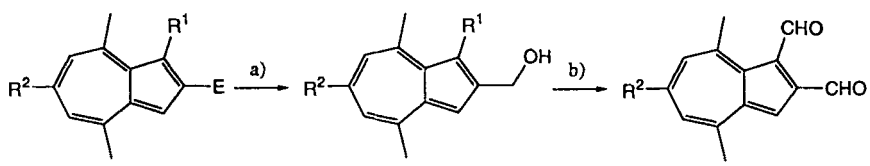
[1]) New address: Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH–4056 Basel.

[2]) Recently, it has been shown that such dehydrogenation reactions with MnO_2 may be improved or even made possible under ultrasound irradiation [3].

2-(Hydroxymethyl)-1-methylazulene (**2**), which is available by DIBAH reduction of azulene-1,2-dicarboxylate **1a** (*cf.* [6]) or methyl 1-methylazulene-2-carboxylate (**1b**) (*cf.* [7]), can be transformed by MnO_2 in CH_2Cl_2 into 1-methylazulene-2-carbaldehyde (**3**; *Scheme 1*).

Results and Discussions. – We were quite astonished to find that the MnO_2 reaction, when performed with the 4,6,8-trisubstituted 2-(hydroxymethyl)-1-methylazulenes **6**, did not stop at the azulene-2-carbaldehyde stage, but proceeded further to give the corresponding azulene-1,2-dicarbaldehydes **7** (*Scheme 2*). The best yields of **7** were obtained, when MnO_2 was applied in a 20-fold excess by weight with respect to **6**. Reduction of the amount of MnO_2 decreased the yields of **7**. On the other hand, no intermediate products could be observed by TLC or ^{1}H-NMR spectroscopy. However, we observed that **1b** was transformed in a yield of 20% into methyl 1-formylazulene-2-carboxylate upon usual treatment with MnO_2 in CH_2Cl_2. This finding could be interpreted in a way that an

Scheme 2

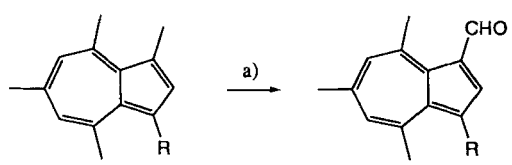


4a,b[a]**),5**[b]) **6a–c**[b]) **7a–c**[b]) (43 – 47%)

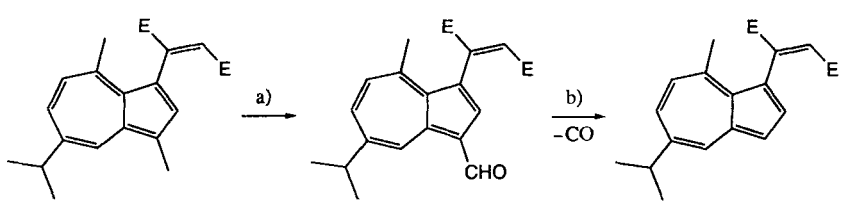
a) See *b*) in *Scheme 1*. b) MnO_2 (20-fold)/CH_2Cl_2, room temperature, 30 min.

[a]) **a** R^1 = E, R^2 = Me; **b** R^1 = E, R^2 = *t*-Bu.
[b]) **c** R^1 = Me, R^2 = Ph.

Scheme 3



R = H : **8** **10** (84%)
R = Me : **9** **11** (81%)



12 **13** (77%) **14**

a) See *b*) in *Scheme 2*. b) Distillation at 200°/0.02 mm Hg in a *'Kugelrohr'*.

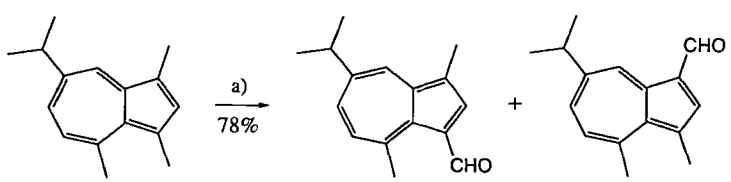
activation of a Me group at C(1) by σ- and π-acceptor substituents (*e.g.* CHO or MeOCO) at C(2) is necessary to allow the oxidation of this group by MnO_2. Therefore, we subjected some 1-methyl-substituted azulenes, having no such substituents at C(2), to the oxidation reaction with MnO_2 in CH_2Cl_2. To our surprise, we found that this type of azulenes (*cf. Scheme 3*) was easily oxidized by MnO_2 to give the corresponding azulene-1-carbaldehydes in remarkably good yields[3]).

The oxidation reaction of the pentamethylazulene **9** stopped completely after the formation of one CHO group. This observation is in agreement with the fact that strong σ- and π-acceptor substituents at C(1) lower the HOMO energy of the azulenes and, therefore, will change their reactivity pattern (*cf.* [9]). On the other hand, the oxidation of Me–C(3) of the 1-(azulen-1-yl)fumarate **12** shows that moderate σ- and π-acceptor[4]) substituents do not suppress the reaction with MnO_2[5]).

The oxidation reaction of Me-substituted azulenes with MnO_2 in CH_2Cl_2, so far described, shows that only Me groups at C(1) and/or C(3) are oxidized by MnO_2, *i.e.*, in positions exhibiting the largest orbital coefficients in the HOMO. Indeed, the attempt to oxidize 2,4,6,8-tetramethylazulene with MnO_2 under the applied conditions was not successful. The starting azulene was recovered unchanged.

AM1 Calculations indicate that 1,3,4,6,8-pentamethylazulene (**9**) and 1,3,4,7-tetramethylazulene possess similar HOMO energies (*cf.* [12] [13]). However, the tetramethyl derivative exhibits slightly different orbital coefficients at C(1) and C(3) in its HOMO with the larger value at C(3). Therefore, one would expect a certain chemoselectivity in the oxidation reaction of this azulene with MnO_2. As a substitute for the not easily available 1,3,4,7-tetramethylazulene, we chose 3-methylguaiazulene (**15**), which is easily

Scheme 4



a) See *b*) in *Scheme 2*.

15 **16** (1.5 : 1) **17**

[3]) It seems that, so far, only diarylmethanes have been oxidized at high temperatures with MnO_2 to the corresponding ketones (*cf.* Chapt. 3 in [2]). The oxidation of Me groups to CHO substituents by MnO_2 has been reported to occur in methylferrocenes (*cf.* Chapt. 4 in [2]). However, aromatic Me groups seem not be oxidizable by MnO_2 (*cf.* [8]).

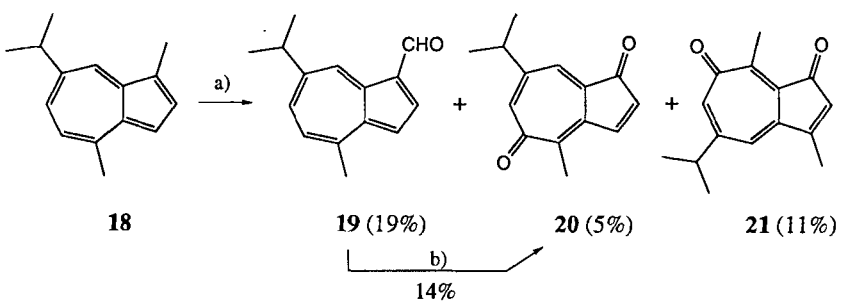
[4]) The X-ray crystal-structure analysis as well as the UV spectra of 1-(azulen-1-yl)fumarates of type **12**, *i.e.*, with a Me substituent at C(8), clearly indicate a largely orthogonal arrangement of the two involved π systems [10]. This means that the fumarate moiety in azulenes such as **12** cannot exert a strong π-acceptor effect.

[5]) On distillation *in vacuo*, we observed the decarbonylation of **13** (*cf.* [11]). This reaction shows that 3-methylazulenes can, in principle, be demethylated by selective oxidation and decarbonylation. With respect to the formation of **14**, it should be noted that **14** carries the fumarate moiety on its sterically more hindered site. The acid-catalyzed reaction of azulenes, substituted unsymmetrically at the seven-membered ring, with dimethyl acetylenedicarboxylate (ADM) leads, in general, to the introduction of the fumarate and maleate moiety on the sterically less uncumbered site at the five-membered ring [10].

accessible from guaiazulene (see *e.g.* [13]). Indeed, when **15** was reacted with MnO_2 in CH_2Cl_2, we observed a slight preponderance in the oxidation of the Me group at C(3) (*cf. Scheme 4*). Both carbaldehydes formed, namely **16** and **17**, could easily be separated by chromatography on silica gel. Carbaldehyde **16** represents the *Vilsmeier* formylation product of guaiazulene (see *e.g.* [13]). Carbaldehyde **17**, however, is new and difficult to obtain by other means.

In a control experiment, guaiazulene (**18**), which had been the matter of extensive autoxidation studies with O_2 in DMF [14] as well as with H_2O_2 in pyridine [15], was also subjected to the oxidation with MnO_2. Several experiments in CH_2Cl_2 with 10- to 40-fold amounts of MnO_2 showed that mainly three products were formed beside non-volatile materials, namely the expected carbaldehyde **19** and the two azulene-diones **20** and **21** (*cf. Scheme 5*). The best results were obtained with the 20-fold amount of MnO_2, which led to an average formation of 4% of carbaldehyde **19**, 13% of the azulene-1,7-dione **21**, and 3% of the demethylated form **20**[6]).

Scheme 5

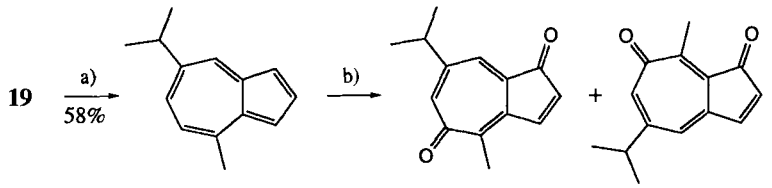


a) MnO_2 (40-fold)/dioxane + 2.5% H_2O, room temperature, 18 h; 5% of **18** were still present after 18 h (GC evidence). The same reaction, however, without the addition of H_2O gave 19% of **19**, 4% of **20**, and 4% of **21**. b) MnO_2 (40-fold)/dioxane, room temperature, 19 h; yield determined with GC and docosane as standard.

More reproducible results were obtained in dioxane as solvent, especially when small amounts of H_2O were present (*Scheme 5*). The carbaldehyde **19** was in these cases again the main product (*cf.* also *Exper. Part, Table 2*). The precursor of the demethylated azulene-1,5-dione **20** seems to be **19**, since it gave **20** under the applied reaction conditions (*cf. Scheme 5*). We suppose that **19** undergoes first a type of *Dakin* rearrangement under the reaction conditions, before it is further oxidized to **20**. Another possibility would be that **19** will undergo first decarbonylation or oxidative decarboxylation to form 7-isopropyl-4-methylazulene (**22**) as intermediate which is then further oxidized to give **20**. However, the control experiment with **22** – obtained by decarbonylation of **19** with *Wilkinson*'s catalyst – showed that this azulene gave, as expected, **20** in a 1:1 mixture with its regioisomer **23** (*Scheme 6*). Since the azulene-1,7-dione **23** was not present in the original reaction mixture starting from **18** (*Scheme 5*), **22** cannot be the precursor of **20** in this case. The isolated carbaldehyde **19** was identical with dihydrolactaroviolin (*cf.* [9]

[6]) The yields refer to GC analyses with docosane as standard. They were strongly dependent on the quality of the used MnO_2. In one experiment, we obtained an isolated yield of **19** and **21** of together over 70%. However, this yield could not be reproduced (see also *Exper. Part*, especially *Table 1*).

Scheme 6



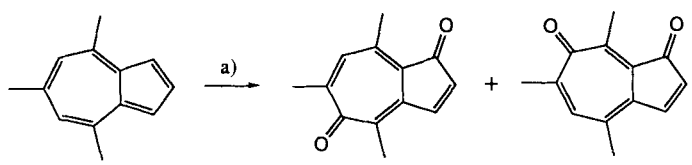
22 **20** (4%) **23** (4%)

a) $[RhCl(PPh_3)_3]$/toluene, 110°, 12 h. b) MnO_2 (30-fold)/CH_2Cl_2, room temperature, 2.5 h; the yields have not been optimized.

and lit. cit. there). Azulene-1,7-dione **21** has already been found in small amounts among several autoxidation products of guaiazulene (**18**; *cf.* [14] [15]). The two other azulene-diones **20** and **23**, the parent structures of which have been synthesized by *Scott* and *Adams* [16], were identified by their spectroscopic data, especially by their ^{1}H-NMR spectra and corresponding ^{1}H-NOE measurements (see *Exper. Part*).

It seems that for the first time azulene-diones have been formed in appreciable amounts by direct oxidation of its parent hydrocarbons (*cf.* the discussion in [17]). Therefore, we examined also the MnO_2 oxidation of 4,6,8-trimethylazulene (**24**), which carries, like **22**, no Me group at the five-membered ring. Indeed, this azulene also led in decent yields to the formation of two azulene-diones, namely **25** and **26**, with a clear preponderance of the corresponding 1,5-dione isomer **25** (*Scheme 7*).

Scheme 7



24 **25** (20%) **26** (3%)

a) MnO_2 (70-fold amount in three portions)/dioxane +2.5% H_2O, room temperature, 2 d. Optimization of the isolated yields by GC control.

Both azulene-diones had already been obtained by *Nozoe* and coworkers [14] [15] in small amounts among several other products in autoxidation experiments with **24**. However, according to ^{1}H-NOE measurements, we have to revise the structural assignments made by *Nozoe* and coworkers, *i.e.*, the reported data for the azulene-1,5-dione belong indeed to the azulene-1,7-dione and *vice versa*. The reasoning is quite clear: H–C(3) appears in both structures at lowest field (^{1}H-NMR ($CDCl_3$): 8.07 (**25**) and 7.96 ppm (**26**), as *d* with $^3J(2,3) = 6.0$ Hz)[7]). This H-atom shows a reciprocal ^{1}H-NOE effect

[7]) *Nozoe* and coworkers [14] [15] reported 4 Hz.

with the Me group, appearing as a *s* at 2.34 ppm in both azulene-diones. However, in the case of **25**, this Me group shows no further ^{1}H-NOE effect. In contrast to this finding, the Me group of the other isomer shows a ^{1}H-NOE effect with the H-atom which appears as a *s* at 7.07 ppm. Therefore, the second isomer, being the minor product in our experiments, must have the structure of the 1,7-dione **26** (for further details, see *Exper. Part*).

It is of interest to note that all three azulenes, **18**, **22**, and **24**, are oxidized by MnO_2 at those C-atoms which have the largest orbital coefficients in the HOMO. When both C-atoms at the seven-membered ring, which exhibit the second largest orbital coefficients at the HOMO, *i.e.*, C(5) and C(7), are occupied by Me groups, no oxidation reaction with MnO_2 in CH_2Cl_2 is observed. For example, 5,7-dimethylazulene was recovered unchanged after treatment with MnO_2 in CH_2Cl_2 at room temperature. This work will be continued.

We thank cand. chem. *Z. A. Molnar* and *Daniela Ziegler* for skilful help in laboratory work, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and ^{1}H-NOE measurements, and *H. Frohofer* and *J. Kessler* for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [5] [6].

Procedure for the Reduction of Azulene-2-carboxylates and Azulene-1,2-dicarboxylates with DIBAH (see also [6]). The esters were dissolved in Et_2O (30 ml/mmol of ester) and cooled to 0°. At this temp., DIBAH in hexane (*ca.* 0.7M soln.; 10 mol-equiv. excess) was slowly added. The mixture was stirred for an additional h at 0°. Then, AcOEt and H_2O were added dropwise. The deposited inorg. salts were dissolved in 2N NaOH. The org. phase was separated and the aq. phase extracted twice with Et_2O. The Et_2O phases were dried ($MgSO_4$), and their residue was purified by CC on silica gel (hexane/Et_2O).

Procedure for the Oxidation Reaction with MnO_2 in CH_2Cl_2. The corresponding azulene was dissolved in CH_2Cl_2 (10 ml/0.4 mmol of azulene) and the indicated amount of MnO_2[8]) was added in one portion if not otherwise stated. This mixture was stirred at r.t. for 30 min if not otherwise stated. The mixture was then filtered over a short silica-gel column with CH_2Cl_2 as eluant. CH_2Cl_2 was distilled off and the residue further purified by CC (silica gel; hexane/Et_2O mixtures), bulb-to-bulb distillation, and/or recrystallization.

1. Formation of Azulene-carbaldehydes. – 1.1. *1-Methylazulene-2-carbaldehyde* (**3**). 1.1.1. *2-(Hydroxymethyl)-1-methylazulene* (**2**): 0.8-mmol runs gave **2** in yields of 75% (from **1a** [18]) and 92% (from **1b** [7]). Blue crystals from hexane/Et_2O. M.p. 68°. R_f 0.19. IR (KBr): 3684*s*, 3602*s*, 3021*m*, 2923*m*, 1601*s*, 1575*s*, 1381*m*, 988*m*, 788*m*, 556*m*, 527*m*. ^{1}H-NMR: 8.23 (*d*, $J(7,8) = 9.8$, H–C(8)); 8.21 (*d*, $J(5,4) = 9.4$, H–C(4)); 7.52 (*t*-like, $J(5,6)) \approx J(7,6) = 9.9$, H–C(6)); 7.37 (*s*, H–C(3)); 7.10 (*t*-like, $J(8,7) \approx J(6,7) = 9.5$, H–C(7)); 7.07 (*t*-like, $J(4,5) \approx J(6,5) = 9.4$, H–C(5)); 5.07 (*s*, CH_2OH); 2.49 (*s*, Me–C(1)).

1.1.2. *Dehydrogenation of* **2**: 0.58 mmol of **2** were reacted with 2.0 g of MnO_2 to give 65% of **3**. Blue crystals from hexane/Et_2O. M.p. 119–120°. R_f 0.17. ^{1}H-NMR: 10.59 (*s*, CHO); 8.40 (*d*, $J(7,8) = 9.7$, H–C(8)); 8.33 (*d*, $J(5,4) = 9.4$, H–C(4)); 7.68 (*s*, H–C(3)); 7.60 (*t*-like, $J(7,6) \approx J(5,6) = 9.8$, H–C(6)); 7.09 (*t*-like, $J(8,7) \approx J(6,7) = 9.8$, H–C(7)); 7.04 (*t*-like, $J(4,5) \approx J(6,5) = 9.7$, H–C(5)); 2.88 (*s*, Me–C(1)).

1.2. *4,6,8-Trimethylazulene-1,2-dicarbaldehyde* (**7a**). 1.2.1. *2-(Hydroxymethyl)-1,4,6,8-tetramethylazulene* (**6a**). See [6]. 1.2.2. *Oxidation of* **6a**: 0.93 mmol of **6a** were reacted with 4.0 g of MnO_2 to give 47% of **7a**. Red needles from hexane/Et_2O. M.p. 142–143°. R_f 0.10. UV (hexane): λ_{max} 387 (sh, 3.53), 3.66 (3.79), 321 (4.35), 304 (4.31), 292 (sh, 4.19), 251 (3.95), 218 (4.09); λ_{min} 360 (3.77), 308 (4.30), 272 (3.92), 230 (3.98). ^{1}H-NMR: 10.91 (*s*, C(1)–CHO); 10.76 (*s*, C(2)–CHO); 7.81 (*s*, H–C(3)); 7.48 (*s*, H–C(7)); 7.43 (*s*, H–C(5)); 3.15 (*s*, Me–C(8)); 2.96 (*s*, Me–C(4)); 2.72 (*s*, Me–C(6)). CI-MS (NH_3): 227 (100, $[M + 1]^+$).

1.3. *6-(tert-Butyl)-4,8-dimethylazulene-1,2-dicarbaldehyde* (**7b**). 1.3.1. *6-(tert-Butyl)-2-(hydroxymethyl)-1,4,8-trimethylazulene* (**6b**). See [6]. 1.3.2. *Oxidation of* **6b**: 0.27 mmol of **6b** were reacted with 1.5 g of MnO_2 to give

[8]) If not otherwise stated, the oxidation reactions were performed with *ca.* 10-year-old batch of MnO_2 ('gefällt, aktiv') from *Merck-Schuchardt*.

41% of **7b**. Red crystals from hexane/Et_2O. M.p. 126–127°. R_f 0.17. UV (hexane): λ_{max} 386 (sh, 3.61), 365 (3.90), 322 (4.50), 258 (4.22), 220 (4.10); λ_{min} 358 (3.89), 276 (3.95), 232 (3.99), 211 (4.02). IR (CH_2Cl_2): 2971*m*, 1752*w*, 1633*s*, 1579*m*, 1523*m*, 1471*m*, 1421*m*, 1329*m*, 1244*m*, 1223*m*, 1098*w*, 896*m*, 866*m*. ^{1}H-NMR: 10.90 (*s*, C(1)–CHO); 10.77 (*s*, C(2)–CHO); 7.79 (*s*, H–C(3)); 7.72 (*s*, H–C(7)); 7.67 (*s*, H–C(5)); 3.19 (*s*, Me–C(8)); 3.00 (*s*, Me–C(4)); 1.50 (*s*, *t*-Bu).

1.4. *4,8-Dimethyl-6-phenylazulene-1,2-dicarbaldehyde* (**7c**). 1.4.1. *2-(Hydroxymethyl)-1,4,8-trimethyl-6-phenylazulene* (**6c**). It was obtained in a yield of 95% from methyl 1,4,8-trimethyl-6-phenylazulene-2-carboxylate (0.200 g, 0.66 mmol) [7]. Blue crystals from hexane/Et_2O. M.p. 101–102°. R_f 0.30. ^{1}H-NMR: 7.60–7.30 (*m*, 5 arom. H); 7.14 (*s*, H–C(5)); 7.11 (*s*, H–C(7)); 5.13 (*s*, CH_2OH); 3.15 (*s*, Me–C(8)); 3.06 (*s*, Me–C(4)); 2.54 (*s*, Me–C(1)).

1.4.2. *Oxidation of* **6c**: 0.36 mmol of **6c** were reacted with 2.0 g of MnO_2 to give 43% of **7c**. Red crystals from hexane/Et_2O. M.p. 151–152°. R_f 0.22. UV (hexane): λ_{max} 378 (sh, 3.45), 330 (3.89), 317 (3.90), 253 (3.75), 240 (3.76); λ_{min} 323 (3.88), 280 (3.59), 247 (3.75), 224 (3.70). IR (CH_2Cl_2): 2926*m*, 1672*s*, 1636*s*, 1579*s*, 1518*w*, 1422*w*, 1350*s*, 1334*s*, 896*m*, 860*m*. ^{1}H-NMR: 10.96 (*s*, C(1)–CHO); 10.79 (*s*, C(2)–CHO); 7.88 (*s*, H–C(3)); 7.75 (*s*, H–C(7)); 7.70 (*s*, H–C(5)); 7.67–7.64 (*m*, 2 arom. H); 7.55–7.51 (*m*, 3 arom. H); 3.24 (*s*. Me–C(8)); 3.05 (*s*, Me–C(4)).

1.5. *4,6,8-Trimethylazulene-1-carbaldehyde* (**10**). *1,4,6,8-Tetramethylazulene* (**8**; 0.10 g, 0.54 mmol) [9] was oxidized with MnO_2 (2.0 g) to give pure crystalline **10** (0.095 g, 84%), identical with an authentic sample [19].

1.6. *3,4,6,8-Tetramethylazulene-1-carbaldehyde* (**11**). *1,3,4,6,8-Pentamethylazulene* (**9**; 0.15 g, 0.75 mmol) [12] was oxidized with MnO_2 (4.5 g) to give pure crystalline **11** (0.130 g, 81%), identical with an authentic sample [12].

1.7. *Dimethyl (*E*)-1-(3-Formyl-5-isopropyl-8-methylazulen-1-yl)ethene-1,2-dicarboxylate* (**13**). *Dimethyl (*E*)-1-(5-isopropyl-3,8-dimethylazulen-1-yl)ethene-1,2-dicarboxylate* (**12**; 0.20 g, 0.59 mmol) [20] was oxidized with MnO_2 (4.0 g) to give pure crystalline **13** (0.160 g, 77%). Red crystals from hexane/Et_2O. M.p. 83°. R_f 0.16. UV (hexane): λ_{max} 394 (3.95), 310 (4.43), 242 (4.48), 231 (sh, 4.46), 214 (sh, 4.41); λ_{min} 351 (3.71), 270 (4.04), 207 (4.38). IR (KBr): 2952*m*, 1719*s*, 1641*s*, 1439*s*, 1392*m*, 1356*m*, 1295*m*, 1249*s*, 1203*m*, 1178*m*, 1146*m*, 1069*w*, 1020*w*, 915*w*. ^{1}H-NMR: 10.26 (*s*, CHO); 9.81 (*d*, J(6′,4′) = 1.9, H–C(4′)); 7.90 (*s*, H–C(2′)); 7.68 (*dd*, J(7′,6′) = 10.8, J(4′,6′) = 1.9, H–C(6′)); 7.44 (*d*, J(6′,7′) = 10.9, H–C(7′)); 7.18 (*s*, H–C(2)); 3.78, 3.56 (2*s*, COOMe); 3.22 (*sept.*, J = 6.9, Me_2CH); 2.80 (*s*, Me–C(8)); 1.41 (*d*, J = 6.9, Me_2CH). Anal. calc. for $C_{21}H_{22}O_5$ (354.41): C 71.17, H 6.26; found: C 71.39, H 6.54.

1.7.1. *Dimethyl (*E*)-1-(5-Isopropyl-8-methylazulen-1-yl)ethene-1,2-dicarboxylate* (**14**). Distillation of **13** in a *'Kugelrohr'* at 200°/2 · 10^{-4} Torr gave **14** in a yield of 90%. Green crystals from hexane/Et_2O. M.p. 77°. R_f 0.42. UV (hexane): λ_{max} 400 (3.57), 359 (sh, 3.58), 343 (3.80), 286 (4.58), 244 (4.46), 219 (4.32); λ_{min} 366 (3.52), 337 (3.78), 260 (4.17), 225 (4.31), 212 (4.30). IR (CH_2Cl_2): 2963*s*, 2871*m*, 1719*s*, 1606*m*, 1435*m*, 1371*m*, 1243*s*, 1204*m*, 1171*m*, 1113*m*, 1020*m*, 896*m*. ^{1}H-NMR: 8.25 (*d*, J(6′,4′) = 2.0, H–C(4′)); 7.54 (*d*, J(2′,3′) = 3.9, H–C(3′)); 7.39 (*dd*, J(7′,6′) = 10.8, J(4′,6′) = 1.9, H–C(6′)); 7.26 (*d*, J(3′,2′) = 3.9, H–C(2′)); 7.11 (*s*, H–C(2)); 7.05 (*d*, J(6′,7′) = 10.9, H–C(7′)); 3.75, 3.53 (2*s*, COOMe); 3.05 (*sept.*, J = 6.9, Me_2CH); 2.73 (*s*, Me–C(8′)); 1.35 (*d*, J = 6.9, Me_2CH). EI-MS: 327 (15, $[M + 1]^+$), 326 (78, M^+), 267 (28), 207 (18), 193 (20), 192 (17), 191 (25), 178 (28), 165 (74), 152 (26), 59 (100).

1.8. *5-Isopropyl-3,8-dimethyl- and 7-Isopropyl-3,4-dimethylazulene-1-carbaldehyde* (**16** and **17**, resp.). *3-Methylguaiazulene* (**15**; 0.060 g, 0.28 mmol) [13] was oxidized with MnO_2 (2.4 g). Careful CC on silica gel (hexane/Et_2O 4:1) gave in a first fraction **16** (0.030 g, 47%), followed by **17** (0.020 g, 31%). No other products were observed.

Data of **16**: R_f 0.38. Identical with those of an authentic probe [13].

Data of **17**: Violet oil. R_f 0.20. UV (hexane): λ_{max} 404 (4.07), 387 (4.04), 319 (sh, 4.38), 312 (4.55), 306 (4.52), 300 (sh, 4.48), 247 (4.44), 227 (4.41), 215 (4.39); λ_{min} 395 (4.00), 344 (3.67), 309 (4.51), 269 (4.03), 233 (4.38), 221 (4.37). IR (CH_2Cl_2): 2966*m*, 1703*m*, 1640*s*, 1537*w*, 1513*w*, 1445*s*, 1428*s*, 1394*s*. ^{1}H-NMR: 10.26 (*s*, C(1)–CHO); 9.62 (*d*, J(6,8) = 1.8, H–C(8)); 7.93 (*s*, H–C(2)); 7.55 (*dd*, J(5,6) = 10.7, J(8,6) = 1.8, H–C(6)); 7.29 (*d*, J(6,5) = 10.8, H–C(5)); 3.15 (*sept.*, J = 6.9, $(CH_3)_2CH$–C(7)); 3.08 (*s*, Me–C(4)); 2.84 (*s*, Me–C(3)); 1.39 (*d*, J = 6.9, $(CH_3)_2$CH–C(7)).

1.9. *Oxidation of Guaiazulene* (**1**). Since this azulene was readily available (*Fluka, puriss.*), and, beside the expected carbaldehyde **19** (dihydrolactaroviolin; *cf.* [9]), the formation of *7-isopropyl-4-methylazulene-1,5-dione* (**20**) as well as of *5-isopropyl-3,8-dimethylazulene-1,7-dione* (**21**, *cf.* [14] [15]) was observed, extensive screening studies were performed with respect to the influence of the provenance of MnO_2 and the solvent (*cf. Tables 1* and *2*). In first experiments with the old batch of MnO_2[8]) and CH_2Cl_2 as solvent, we obtained **19** and **21** in yields up to 70%. Compound **20** was not isolated in these cases. Later experiments with a new lot of MnO_2 (*Merck-Schuchardt*; Lot 45114980) gave much lower yields of **19–21**. The results of anal. screening experiments with docosane as GC standard are collected in *Table 1*. As can be seen, the oxidation reactions with MnO_2 in CH_2Cl_2 are only badly

Table 1. *Oxidation of Guaiazulene* (**18**) *with* MnO_2 *in* CH_2Cl_2 *at r.t.*[a])

Amount [g] of MnO_2[b])	Time [min]	Yields [%]			
		18	**19**	**20**	**21**
A 1.0	5	73	0	0	0
	20	63	1.3	0	2.9
	90	56	1.8	0	3.3
A 2.0	5	3	3.5	2.9	12.6
	30	0	4.4	3.3	13.6
A 2.5	5	31	2.0	0	6.8
	20	15	3.0	1.2	7.5
	30	14	3.2	1.2	8.0
A 4.0	5	7	3.0	1.5	9.6
	20	1	3.5	1.7	10.0
	30	0.5	4.0	1.9	10.0
B 1.0	5	72	0	0	2.3
	30	70	0	0	2.3
	90	48	1.7	0	3.2
B 2.5	5	36	1.4	0	5.4
	20	25	2.5	0	6.5
	30	21	2.8	0	5.6
B 4.0	5	15	2.6	0	8.2
	20	4	3.6	1.5	9.0
	30	2	3.8	1.5	9.3

[a]) *Ca.* 0.10 g of **18** were oxidized with MnO_2, added in one portion, in 11 ml of CH_2Cl_2 in the presence of 0.030–0.035 g docosane as GC standard. Analysis on a GC/MS instrument (*Hewlett-Packard*, model *5890*; with mass selective detector, model *5971*); column: *WCOT, HP-5* (25 m/0.2 mm). t_R (**20**) < t_R (**19**) < t_R (**21**).
[b]) *A*: 10-year-old batch of MnO_2 (*Merck-Schuchardt*); *B*: new batch of MnO_2 (*Merck-Schuchardt*).

Table 2. *Oxidation of Guaiazulene* (**18**) *with* MnO_2 *in Various Solvents at r.t.*[a])

Solvent	Time	Yields [%]			
		18	**19**	**20**	**21**
MeCN[b])	5 min	*ca.* 16	4	1	6
	30 min	*ca.* 5	4	0	5
DMSO[b])	5 min	*ca.* 66	< 1	0	0
	30 min	*ca.* 50	< 1	0	0
Benzene	5 min	12	4	3	7
	30 min	*ca.* 1	6	3	7
Pyridine	5 min	93	0	0	0
	30 min	84	1	0	0
	89 h	40	4.4	0	0
Acetone	5 min	42	5	1	5
	34 min	24	10	4	7
	1 h	20	11	4	8
Dioxane[c])	5 min	45 (39)	8 (9)	2 (2)	4 (5)
	30 min	29 (23)	12 (12)	3 (3)	4 (6)
	16.5 h	1 (1)	19 (18)	4 (4)	4 (3)

Table 2 (cont.)

Solvent	Time	Yields [%]			
		18	**19**	**20**	**21**
Dioxane	18 h	< 1	17	5	5
+ 1% H_2O[d])	18 h	0.6	18	7	14
+ 2.5% H_2O[e])	18 h	0.7 (5)	18 (19)	7 (5)	14 (11)
+ 10% H_2O	18 h	< 1	13	4	13
+ 50% H_2O	18 h	< 1	5	< 1	8

[a]) *Ca.* 0.15 g of **18** were oxidized with a new batch MnO_2 (6.0 g; *Merck-Schuchardt*, Lot. 45114980), added in one portion, in 15 ml of the solvent in the presence of docosane (*ca.* 0.05 g) as GC standard. See *a*) in *Table 1*.

[b]) No internal standard was added.

[c]) In parentheses the values obtained with a different batch of MnO_2 (*Merck-Schuchardt*).

[d]) Results of oxidation experiments with 20 mg of **18** in 2.0 g of dried dioxane to which the indicated percentage of H_2O was added. Standard: docosane; MnO_2: 0.80 g. The application of ultrasound did not improve the yields.

[e]) In parentheses the results of a prep. run with 1.50 g of **18** (see *1.9.1*).

reproducible. The best results were obtained with the > 10 year old batch of MnO_2, leading to *ca.* 13% of **21**, 4% of **19**, and 3% of **20**. Much better reproducible results were obtained with MnO_2 (Lot 45114980) in dioxane and varying small amounts of H_2O (*cf. Table 2*).

1.9.1. *Oxidation of* **18** *in Dioxane/*H_2O. The azulene (1.50 g, 7.56 mmol) and docosane (0.50 g as internal standard) were dissolved in dioxane (150 ml), and H_2O (3.75 ml, 2.5%) and MnO_2 (60 g; see *Table 2*) were added. The mixture was stirred under N_2 during 18 h at r.t. GC showed the presence of still 5% of **18**. MnO_2 was removed by centrifugation (4000 rpm) and the soln. filtered through *Celite*. The MnO_2 was washed 4-times with dioxane (70 ml) and the extracts also filtrated through the *Celite*. Further extraction overnight in a *Soxhlet* apparatus with CH_2Cl_2 showed that all products had been removed from MnO_2. The residue of the dioxane extracts (1.6 g) was subjected to CC (85 g silica gel; CH_2Cl_2) to give the mixture of **19**–**21** as a red-brown oil. The separation of **19**–**21** was realized by low-pressure chromatography on a *Lobar B* column (hexane/AcOEt 5:1). The first fractions gave pure **19** (GC: > 99%; 0.301 g, 19%), followed by **21** (GC: 97%; 0.198 g, 11%) and finally by **20** (GC: > 98%, 0.088 g, 5%).

Data of **19**: Dark red amorphous powder. M.p. 65–68°. R_f 0.45 (Alox; hexane/Et_2O 3:2). t_R 14.34 min[9]). All other data were identical with those of an authentic sample [9]. Anal. calc. for $C_{15}H_{16}O$ (212.29): C 84.87, H 7.60; found: C 84.61, H 7.61.

Data of **20**: Yelow-ochre microcrystalline powder after sublimation at 80–110°/2·10^{-4} Torr in a *'Kugelrohr'*. M.p. 111–113°. R_f 0.20 (Alox; hexane/Et_2O 3:2). UV (hexane): λ_{max} 400 (sh, 3.54), 380 (3.76), 361 (3.76), 343 (3.71), 310 (3.70), 270 (sh, 4.20), 256 (4.42), 250 (sh, 4.35), 240 (sh, 4.20); λ_{min} 370 (3.70), 350 (3.69), 334 (3.68), 284 (3.61), 225 (4.09). IR ($CHCl_3$): 3040*w*, 3008*m*, 2968*m*, 2930*m*, 1711*s*, 1647*s*, 1581*s*, 1569*s*, 1465*m*, 1417*m*, 1388*m*, 1378*m*, 976*w*, 926*w*, 900*w*, 833*s*. ^{1}H-NMR: 8.21 (*dd*, *J*(2,3) = 6.0, *J*(8,3) = 0.7, H–C(3)); 7.28 (*d*, *J*(8,6) = 1.9, H–C(6)); 6.90 (*dd*, *J*(6,8) = 1.9, *J*(3,8) = 0.7, H–C(8)); 6.53 (*d*, *J*(3,2) = 6.0, H–C(2)); 2.78 (*sept.*, *J* = 6.8, Me_2CH); 2.31 (*s*, Me–C(4)); 1.24 (*d*, *J* = 6.8, Me_2CH). ^{1}H-NOE (400 MHz, $CDCl_3$): 8.21 (H–C(3))→6.53 (*s*, H–C(2)), 2.31 (*m*, Me–C(4)); 6.90 (H–C(8))→2.78 (*s*, Me_2CH), 1.24 (*m*, Me_2CH); 2.31 (Me–C(4))→8.21 (*s*, H–C(3)). GC/MS (t_R 12.85 min[9])): 214 (36, M^+), 186 (21, $[M - CO]^+$), 171 (100), 143 (12), 141 (9), 128 (33), 115 (18). Anal. calc. for $C_{14}H_{14}O_2$ (214.27): C 78.48, H 6.59; found: C 78.76, H 6.72.

Data of **21** (*cf.* [14] [15]): Yellow-ochre crystals from hexane/Et_2O. M.p. 104–105° (94° [15]). R_f 0.15 (Alox; hexane/Et_2O 3:2). UV (hexane): λ_{max} 414 (sh, 3.28), 390 (sh, 3.59), 371 (3.65), 302 (3.92), 244 (4.36), 231 (4.37); λ_{min} 360 (3.63), 277 (3.85), 237 (3.65), 212 (4.12). IR (CH_2Cl_2): 2968*m*, 2928*m*, 1700*s*, 1638*m*, 1602*s*, 1582*s*, 1465*w*, 1381*w*, 1322*w*, 886*w*. ^{1}H-NMR: 6.75 (*d*, *J*(8,6) = 1.8, H–C(6)); 6.63 (*d*, *J*(6,8) = 1.8, H–C(8)); 6.23 (*q*-like, *J*(Me–C(3),2) = 1.3, H–C(2)); 2.75 (*sept.*, *J* = 6.8, Me_2CH); 2.63 (*s*, Me–C(8)); 2.29 (*d*, *J*(2, Me–C(3)) = 1.3, Me–C(3)); 1.25 (*d*, *J* = 6.8, Me_2CH). GC/MS (t_R 15.05[9])): 228 (41, M^+), 200 (21, $[M - CO]^+$), 185 (100), 157 (12), 142 (28), 141 (20), 128 (18), 115 (17). Anal. calc. for $C_{15}H_{16}O_2$ (228.29): C 78.92, H 7.06; found: C 78.92, H 7.07.

[9]) t_R refers to *HP-5* column (*cf. Footnote a* in *Table 1*) and a temp. program of 20°/min from 100 (2 min) to 240° (10 min), carrier gas: He.

1.9.2. *Oxidation of* **19** *in Dioxane:* The carbaldehyde (5 mg) and docosane (8 mg) were dissolved in dioxane (2 ml), MnO_2 (0.81 g) was added, and the mixture stirred under N_2 for 19 h at r.t. MnO_2 was removed by centrifugation, and the dioxane soln., the color of which had changed from red to yellow, subjected to GC analysis. Only the peak of **20** was found. The peak area corresponded to a yield of 14% of **20**.

2. Formation of Azulene-diones. 2.1. *Oxidation of 7-Isopropyl-4-methylazulene* (**22**). 2.1.1. *Decarbonylation of* **19**. The carbaldehyde (0.0457 g, 0.215 mmol) and $[RhCl(PPh_3)_3]$ (0.250 g, 0.245 mmol) were dissolved in dried toluene (3 ml), and the mixture was heated under Ar for 12 h at reflux. TLC showed only traces of **19**. Hexane (10 ml) was added and the precipitate filtered after 1 h. The filtrate was distilled in a rotatory evaporator. The residue (0.0232 g, 58%) represented pure **22**. R_f 0.60 (Alox; hexane/Et_2O 3:2). ^{1}H-NMR: 8.33 (*d*, $J(6,8) = 2.0$, H–C(8)); 7.82 (*t*, $J(1,2) = J(3,2) = 3.8$, H–C(2)); 7.48 (*dd*, $J(5,6) = 10.6$, $J(8,6) = 2.0$, H–C(6)); 7.33, 7.30 (2*dd*, $J(1,2) = J(3,2) = 3.8$, $J(1,3) = 1.5$, H–C(1), H–C(3)); 7.13 (*d*, $J(6,5) = 10.6$, H–C(5)); 3.09 (*sept.*, $J = 6.8$, Me_2CH); 2.89 (Me–C(4)); 1.37 (*d*, $J = 6.8$, Me_2CH). GC-MS (t_R 10.19 min[9])): 184 (59, $M^{+\cdot}$), 169 (100, $[M - Me]^+$), 154 (31, $[M - 2\,Me]^+$), 153 (28), 152 (17), 141 (12), 128 (13), 115 (13).

2.1.2. *Reaction of* **22** *with* MnO_2. Azulene **22** (0.023 g, 0.12 mmol) and docosane (0.0085 g) as standard were dissolved in CH_2Cl_2 (3 ml), MnO_2 (0.69 g) was added and the whole mixture stirred under Ar at r.t. GC Analysis showed that all **22** was consumed after 2.5 h. The mixture was filtered over *Celite* and the filter cake washed several times with CH_2Cl_2. The residue of the CH_2Cl_2 soln. was chromatographed on a short silica-gel column (hexane/Et_2O 3:2) and then subjected to low-pressure HPLC on a *Lobar B* column (hexane/AcOEt 5:1) to give *ca.* 1 mg (4%) of **20** and also *ca.* 1 mg (4%) of *5-isopropyl-8-methylazulene-1,7-dione* (**23**).

Data of **23**: R_f 0.20 (Alox; hexane/Et_2O 3:2). IR ($CHCl_3$): 3018*w*, 3008*w*, 2968*m*, 2931*w*, 2875*w*, 1705*s*, 1638*m*, 1584*s*, 1465*w*, 1370*w*, 1341*w*, 1306*w*, 1148*w*, 1013*w*, 887*w*, 834*m*. ^{1}H-NMR: 7.67 (*d*, $J(2,3) = 5.8$, H–C(3)); 6.73 (*d*, $J(4,6) = 1.8$, H–C(6))[10]); 6.61 (*d*, $J(6,4) = 1.8$, H–C(4))[10]); 6.37 (*d*, $J(3,2) = 5.8$, H–C(2)); 2.72 (*sept.*, $J = 6.8$, Me_2CH); 2.63 (*s*, Me–C(8)); 1.24 (*d*, $J(6.8$, Me_2CH–C(5)). GC-MS (t_R 12.99 min[9])): 214 (62, $M^{+\cdot}$), 199 (4, $[M - Me]^+$), 186 (16, $[M - CO]^{+\cdot}$), 171 (100), 143 (19), 141 (10), 128 (39), 115 (22).

2.2. *Oxidation of 4,6,8-Trimethylazulene* (**24**). The freshly distilled azulene (0.292 g, 1.72 mmol) [21] and docosane (0.0991 g) as internal standard were dissolved in dioxane (31 ml), and H_2O (0.72 ml) was added. The mixture was stirred under N_2 at r.t. and MnO_2 added within 2 d in three portions (in total 21.1 g). After this time, GC analysis showed the presence of *ca.* 2% **24**. The workup procedure was the same as described for **18** (*cf. 1.9.1*). The separation of the two azulene-diones **25** and **26** was realized on a *Lobar B* column with hexane/AcOEt 5:1 to give in a first fraction pure **25** (0.070 g, 20%; GC > 99%), followed by a small amount of **26** (0.011 g, 3%; GC > 99.5%).

Data of 4,6,8-Trimethylazulene-1,5-dione (**25**; *cf.* [14] [15]): Yellow-ochre needles from hexane/AcOEt and then toluene. M.p. 218–220° ([15]: 118°). R_f 0.25. IR (CH_2Cl_2): 2927*s*, 2855*s*, 1697*s*, 1585*m*, 1461*s*, 1377*s*, 1152*m*, 836*m*. ^{1}H-NMR: 8.07 (*d*, $J(2,3) = 6.0$, H–C(3)); 7.10 (*d*-like, J(Me–C(6,7) = 1.1, H–C(7)); 6.40 (*d*, $J(3,2) = 6.0$, H–C(2)); 2.66 (*s*, Me–C(8)); 2.34 (*s*, Me–C(4)); 2.28 (*d*, J(7, Me–C(6)) = 1.0, Me–C(6)). ^{1}H-NOE (400 MHz, $CDCl_3$): 8.07 (H–C(3))→6.40 (*s*, H–C(2)), 2.34 (*m*, Me–C(4)); 2.66 (Me–C(8))→7.10 (*s*, H–C(7)); 2.34 (Me–C(4))→8.07 (*s*, H–C(3)); 2.28 (Me–C(6))→7.10 (*s*, H–C(7)). Anal. calc. for $C_{13}H_{12}O_2$ (200.24): C 77.98, H 6.04; found: C 77.69, H 6.02.

Data of 4,6,8-Trimethylazulene-1,7-dione (**26**; *cf.* [14] [15]): Yellow-ochre crystals from toluene. M.p. 196–198° ([15]: 120°). R_f 0.23. IR (CH_2Cl_2): 2926*s*, 2855*m*, 1698*s*, 1587*s*, 1458*w*, 1375*w*, 1203*w*, 1152*w*, 836*m*. ^{1}H-NMR: 7.96 (*d*, $J(2,3) = 6.0$, H–C(3)); 7.07 (*d*-like, J(Me–C(6),5) = 1.1, H–C(5)); 6.28 (*d*, $J(3,2) = 6.0$, H–C(2)); 2.63 (*s*, Me–C(8)); 2.34 (*s*, Me–C(4)); 2.25 (*d*, J(7, Me–C(6)) = 1.0, Me–C(6)). ^{1}H-NOE (400 MHz, $CDCl_3$): 7.96 (H–C(3))→6.28 (*s*, H–C(2)), 2.34 (*m*, Me–C(4)); 7.07 (H–C(5))→2.34 (*m*, Me–C(4)), 2.25 (*s*, Me–C(6)); 6.28 (H–C(2))→7.96 (*s*, H–C(3)); 2.66 (Me–C(8))→no effect; 2.34 (Me–C(4))→7.96 (*s*, H–C(3)), 7.07 (*s*, H–C(5)); 2.25 (Me–C(6))→7.07 (*s*, H–C(5)). ^{1}H-NMR: (C_6D_6): 6.98 (*d*, H–C(3)); 6.32 (*q*-like, H–C(5)); 5.81 (*d*, H–C(2)); 2.90 (*s*, Me–C(8)); 2.10 (*s*, Me–C(6)); 1.51 (*s*, Me–C(4)).

On standing over several days in $CDCl_3$ soln., **26** was partly transformed into a new product with ^{1}H-NMR signals at: 7.28 (*d*, $J = 6.0$, 1 H); 6.68 (*d*, $J = 6.0$, 1 H); 5.93 (*q*-like, $J > 1$, 1 H); 2.28 (*s*, Me); 1.86 (*d*, $J > 1$, Me); 1.56 (*s*, Me).

[10]) Assignments according to the chemical shifts in the parent compound [16].

REFERENCES

[1] G. Procter, in 'Comprehensive Organic Synthesis', Vol. 7, 'Oxidation', Ed. S. V. Ley, Pergamon Press plc, Oxford, 1991, p. 305.

[2] a) A. J. Fatiadi, *Synthesis* **1976**, 65 and 133; b) A. J. Fatiadi, in 'Organic Synthesis by Oxidation with Metal Compounds', Eds. W. J. Mijs and C. R. H. I. de Jonge, Plenum Press, New York–London, 1986, p. 119.

[3] T. Kimura, M. Fujita, T. Ando, *Chem. Lett.* **1988,** 1387.

[4] A. A. S. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 1921.

[5] R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1995,** *78,* 231.

[6] R.-A. Fallahpour, H.-J. Hansen, *Helv. Chim. Acta* **1992,** *75,* 2210.

[7] A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1995,** *78,* 238; A. J. Rippert, Ph. D. Thesis, University of Zurich, 1994; R. Ostaszewski, H.-J. Hansen, *Helv. Chim. Acta* **1995,** *78,* in preparation.

[8] H. Offermanns, G. Pretscher, in 'Houben-Weyl, Methoden der organischen Chemie', 4th edn., Georg Thieme Verlag, Stuttgart, 1983, Bd. E3, p. 131ff.

[9] A. Magnussen, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1993,** *76,* 2887.

[10] P. Brügger, Ph. D. Thesis, No. 858, University of Fribourg, 1983; R.-A. Fallahpour, Ph. D. Thesis, University of Zurich, 1994; R.-A. Fallahpour, A. Linden, A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta,* in preparation.

[11] Y. N. Porshnev, E. M. Tereshenko, *Zh. Org. Khim.* **1975,** *11*(2), 462.

[12] Y. Chen, R. W. Kunz, P. Uebelhart, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1992,** *75,* 2447.

[13] P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1992,** *75,* 2493.

[14] Y. Matsubara, Sh. Takekuma, K. Yokoi, H. Yamamoto, T. Nozoe, *Bull. Chem. Soc. Jpn.* **1987,** *60,* 1415.

[15] Y. Matsubara, M. Morita, Sh. Takekuma, T. Nakano, H. Yamamoto, T. Nozoe, *Bull. Chem. Soc. Jpn.* **1991,** *64,* 3497.

[16] L. T. Scott, C. M. Adams, *J. Am. Chem. Soc.* **1994,** *106,* 4857.

[17] K.-H. Zeller, in 'Houben-Weyl, Methoden der organischen Chemie', 4th edn., Georg Thieme Verlag, Stuttgart, 1983, Bd. 5/2c, p. 408ff.

[18] K. Hafner, H. Diehl, H. U. Süss, *Angew. Chem.* **1976,** *88,* 121; *ibid. Int. Ed.* **1976,** *15,* 104.

[19] W. Bernhard, P. Brügger, J. J. Daly, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1985,** *68,* 415.

[20] R.-A. Fallahpour, H.-J. Hansen, *High Pressure Res.* **1992,** *11,* 125.

[21] K. Hafner, H. Kaiser, *Org. Synth. Coll. Vol.* **1973,** *5,* 1088.