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OXIDATION OF SUBSTITUTED BICYCLO[4.4.0]DECEN-3-ONES

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Abstract. The results of the oxidation of 6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3-one and its derivative 6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-10-en-3-one by O_2, H_2O_2, and *t*-BuOOH under basic conditions in the presence of K_2CO_3, Et_3N, and *t*-BuOK are reported. The relevant γ-hydroxyenones, 1,4-diketoenone, and 1,2-diketoenone were isolated. The oxidation was found to proceed through the dienolate formation. A possible mechanism for α- and γ-oxidation is discussed.

Key words: oxidation, regioselectivity, dienolate, enone.

INTRODUCTION

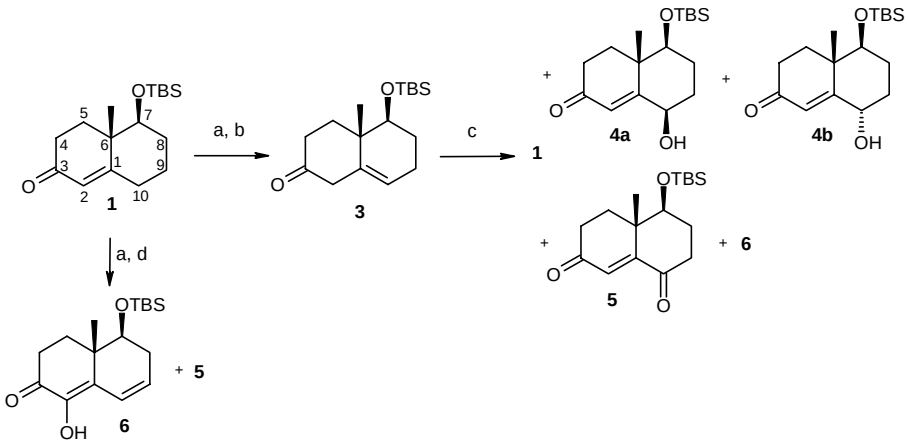
The functionalization of bicyclic[4.4.0] systems has been an important issue in the synthesis of many naturally occurring bioactive compounds. As shown in Scheme 1, similar enone fragments are present in the intermediate of cytotoxic 9,11-secosterol [1], decipienin [2], batrachotoxinin [3], and an HIV integrase inhibitor integric acid [4].

Several methods have been used to obtain γ-hydroxyenones. These include oxidation of homoallylic alcohols with permanganate ion [5] or pyridinium chlorochromate [6], allylic oxidation of enone by SeO_2 [7], oxidation of dienolethers or -esters with oxone® [8] or with *m*-chloroperbenzoic acid [9, 10], and oxidation of enones by oxygen [2, 11, 12] or hydrogen peroxide [13] in the presence of a strong base. In several cases, a strong substrate dependence on the chemo- and regioselectivity of the reaction has been observed.

In this paper we report the results of oxidation of enones **1** and **3** (Scheme 1) and discuss a possible mechanism of the reaction.

RESULTS AND DISCUSSION

Compounds **1** and **3** (Scheme 1) are the intermediates of the AB-ring of 9,11-secosterols, whose synthesis was recently published by us [1]. A partial auto-γ-hydroxylation of alkene **3** was detected in the course of the synthesis. Therefore a more detailed investigation of the reaction was carried out to find a mild method for the generation of these useful bicyclic γ-hydroxyenones.



Scheme 1. a: *t*-BuOK, *t*-BuOH, r.t.; b: 10% AcOH; c: O_2, *t*-BuOOH or H_2O_2, see Table 1; d: *t*-BuOOH, see Table 1.

It was found that compound **3** oxidizes easily by air in the presence of K_2CO_3 at room temperature, affording a mixture of alcohols **4a** and **4b** (26%, at a ratio of 3:1 as determined by NMR) as the main products (Table 1, No. 1). In the case of a complete conversion of the starting alkene **3**, alcohols **4a** and **4b** were still the main isolated products (24%, at a ratio of 2.4:1, respectively), but the relative amount of 1,4-diketone **5** increased (Table 1, No. 2). The moderate total yield of the oxidation products (42%) refers to the possible over-oxidation in the course of the process.

An isolated double bond in compound **3** is prone to migrate back to the conjugated form, resulting in **1**. Therefore, some isomerization was always detected. (For example, the slightly acidic $MgSO_4$ and SiO_2, as well as K_2CO_3 in methanol caused isomerization.) It is interesting to note that enone **1** is nonreactive under the conditions that caused the oxidation of compound **3**.

In the following experiments oxidizing agents other than O_2 were used, to have a more selective reaction. No reaction occurred with *t*-BuOOH in the absence of the basic component. However, after the addition of 2 eq of Et_3N substrate **3** was completely oxidized (Table 1, No. 3). The main isolated products were again alcohols **4a** and **4b** (35%, at a ratio of 2.8:1). As the oxidation of compound **3** with *t*-BuOOH was quite slow, a stronger oxidant, H_2O_2, was used. Being aware of the need for the presence of a base for oxidation, we added pyridine to the reaction mixture. After a 24-hour reaction the starting alkene **3** had remained mainly unchanged (the minor oxidation products appeared during the sample preparation in the air (Table 1, No. 4)). The reaction started only after 1 eq of Et_3N was added (Table 1, No. 4).

As the ratio of **4a**:**4b** does not depend much on the oxidant, it is very likely that the diastereoselectivity of the oxidation is controlled by the substrate.

Table 1. Oxidation of enones **1** and **3**

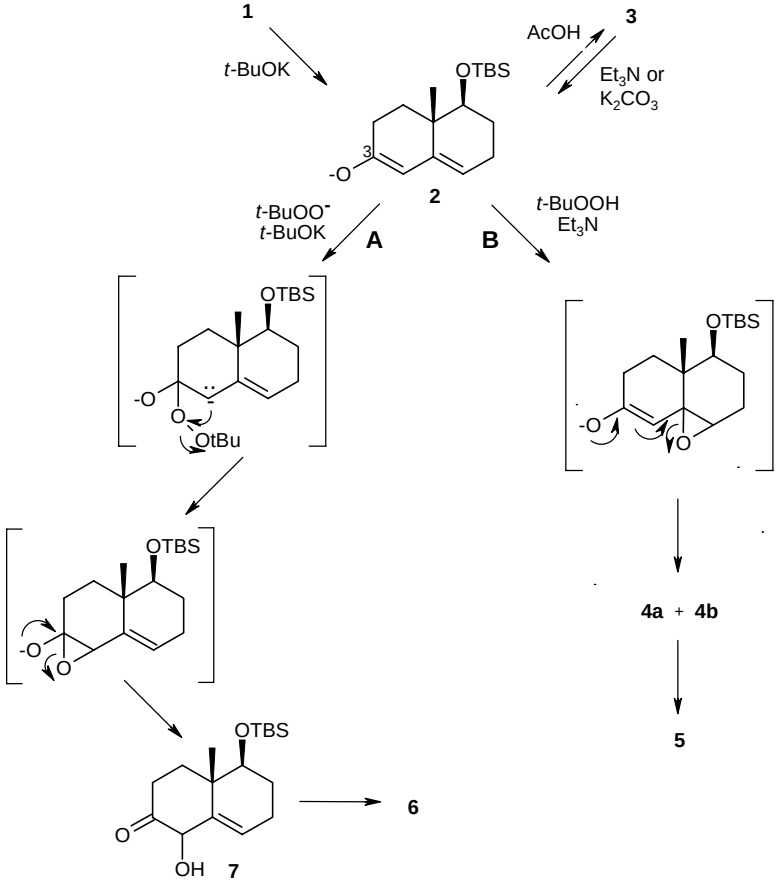
No.	Reaction (see Scheme 1)	Conditions	Products determined by GC form crude mixture (or isolated yields), %						
			3	**1**	**4a**	**4b**	**4a** : **4b**	**5**	**6**
1	**c**	Air, K_2CO_3, CH_2Cl_2, obscure, 0 °C, 16 h	(**36**)	(16)	(**26**)		3 : 1	(7)	
2	**c**	Air, K_2CO_3, EtOAc, r.t., 2 d	4	13 (7)	**22** (17)	9 (7)	2.4 : 1	**28** (11)	14
3	**c**	1.2 eq *t*-BuOOH, 2 eq Et_3N, toluene, r.t., 6 d	–	17 (7)	**39** (26)	10 (9)	3.9 : 1	**26** (14)	1
4	**c**	1,2 eq H_2O_2, pyridine,THF, r.t., 24 h, then 1 eq Et_3N added, 5 h[a]	**42** 11	4 7	13 **27**	5 11	2.5 : 1	14 9	11 15
5	**d**	1.1 eq *t*-BuOOH, 10 eq *t*-BuOK, *t*-BuOH, r.t., 4 h	–	–	–	–	–	7	**69** (21)

[a] Isolated yields were **1** + **3** + **6** 10%, **4a** 6%, **4b** 4%, and **5** 9%.

The fact that the presence of a base ($pK_b \approx 10$) is necessary for the reaction is indicative of the formation of intermediate dienolate, which then is oxidized. Therefore, the oxidation of the potassium dienolate (**2**) obtained from **1** was separately investigated. When a molecular oxygen was passed through the reaction mixture, dienolate oxidized readily ending up in a complex mixture of products during 30 min. Similar results were obtained in MeOH/KOH by Massanet et al. [2]. Then 1.1 eq of *t*-BuOOH was used as an oxidant (Table 1,

No. 5). Surprisingly enough, in that case an α-oxygenated product, the enolized 1,2-diketone **6**, was isolated as the main product.

These results led us to the assumption that to obtain α- and γ-oxidation products two competitive reaction schemes, **A** and **B**, exist (Scheme 2). There are two important factors to consider: first, the selectivity of the dienolate formation (thermodynamic versus kinetic) and, second, the regioselectivity of oxidation. Under the conditions used only a thermodynamic dienolate was formed leading to α- and γ-oxidation products. The formation of possible kinetic enolization products (4-oxygenated products) was not observed.



Scheme 2. Path **A** dominates when 10 eq *t*-BuOK and *t*-BuOOH are used (Table 1, No. 5). Path **B** dominates when 2 eq Et_3N and *t*-BuOOH are used (Table 1, No. 3).

The reaction of dienolate (**2**) with *t*-BuOOH is the most impressive example of the regioselectivity of oxidation. In the presence of 2 eq of Et_3N we obtained 75% of γ-oxygenated products (**4a** + **4b** + **5**, by GC) versus 1% of α-oxygenated

1,2-diketone **6** (Table 1, No. 3). When the oxidation was carried out in the presence of 10 eq of *t*-BuOK, the ratio of γ-oxygenated **5** to α-oxygenated **6** was nearly 1:10 (7% of **5** versus 69% of **6**) (Table 1, No. 5). In the case of 30% aqueous H_2O_2 the ratio of regioisomers was only 3:1 (47% of γ-oxygenation versus 15% of α-oxygenation) (Table 1, No. 4). The lower regioselectivity refers to the possible influence of water as a protic solvent, shifting the selectivity toward α-oxidation, while Et_3N has a tendency to shift the oxidation toward γ-oxidation like in the case of *t*-BuOOH described above.

It is interesting to note that α,β-unsaturated ketones epoxidize under strongly alkaline conditions by peroxides [14] and in these cases peroxide reacts as a nucleophile. It is also known that *t*-BuOOH is ineffective toward enones in the presence of Et_3N [15]. Therefore, we propose that the α-oxygenation (path **A**) proceeds as a result of a nucleophilic attack of the peroxide anion *t*-$BuOO^-$ to the most electrophilic carbon 3, via the 2,3-epoxy-intermediate. In the case of the γ–attack (path **B**) *t*-BuOOH reacts with the second double bond, affording the 1,10-epoxy-intermediate. After the generation of epoxides the oxirane rings open and the allylic alcohols **4a** and **4b** (in the case of the γ–attack) are formed. As a result of the α-attack, probably through intermediate **7**, which may oxidize completely to 1,2-diketone by air during the work-up procedure, 1,2-diketoenone, existing only in the enolized form **6,** is produced. γ–Hydroxyenones (**4a** and **4b**) are more stable than α-hydroxyenones. Under these conditions, however, further oxidation of γ–hydroxyenones is still possible.

The present study demonstrated that we are able to control the regio-selectivity of oxidation of dienolate **2** toward either the α- or γ-product. The diastereoselectivity of hydroxylation was found to be mainly substrate-dependent.

EXPERIMENTAL

The 6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3-one (**1**) was synthesized according to the literature [1]. Reactions were followed on TLC and GC (nonpolar column). All NMR spectra were recorded on a Bruker AMX500 instrument. Determination of the structures and configurations of the obtained compounds was based on the use of 2D FT NMR methods. Mass spectra were recorded on a Hitachi M80B spectrometer.

6-Methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-10-en-3-one (3)

Potassium *tert*-butoxide (193 mg or 1.72 mmol) was added to 0.1 M solution of 6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3-one (**1**) (52 mg or 0.176 mmol) in dry *tert*-butanol and stirred at room temperature under argon atmosphere for 2 h. The produced dienolate (2) was quenched by 5 mL of 10%

acetic acid and neutralized with saturated aliquot solution of $NaHCO_3$ at 0 °C, then extracted 5 times with diethyl ether, filtered through a K_2CO_3 layer, and the solvent was evaporated. The obtained compound **(3)** was used in oxidations without any additional purification.

CIMS (isobutane): m/z 295($M + H^+$), 237, 163, 75.

Procedure for oxidation of (3) by air

The compound **3**, prepared directly before the oxidation, was dissolved in aprotic solvent (0.05 M) and left in the open air on K_2CO_3 (10 eq). After filtration and evaporation of the solvent, the products were isolated by flash chromatography on SiO_2 (3% up to 15% of acetone in petroleum ether). In the case of full conversion the main products were alcohols (**4a**) in yield 17% and (**4b**) 7%, diketone (**5**) 11%, and enone (**1**) 11% (see Table 1).

10β-Hydroxy-6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3-one (4a)

^{1}H NMR ($CDCl_3$): δ 0.05 and 0.08 (2s, 6H, 2 × $SiCH_3$), 0.91 (s, 9H, *t*-BuSi), 1.38 (s, 3H, 6-CH_3), 1.57 and 2.10 (m, 2H, H-8), 1.63 and 2.00 (m, 2H, H-9), 1.77 and 2.08 (m, 2H, H-5), 2.38 and 2.41 (m, 2H, H-4), 3.38 (dd, 1H(α,ax), J_{aa} = 11.6 Hz, J_{ae} = 4.0 Hz, H-7), 4.25 (t, 1H(α,eq), $J_{ee} = J_{ea}$ = 2.5 Hz, H-10), 5.86 (s, 1H, H-2).

^{13}C NMR ($CDCl_3$): δ −4.95 and −3.96 (2 × $SiCH_3$), 17.38 (6-CH_3), 18.03 (Si**C**$(CH_3)_3$), 25.28 (C-8), 25.77 (SiC(**C**$H_3)_3$), 29.96 (C-9), 34.19 (C-4), 36.12 (C-5), 41.48 (C-6), 72.07 (C-10), 79.03 (C-7), 127.64 (C-2), 166.80 (C-1), 200.63 (C-3).

CIMS (isobutane): m/z 311($M + H^+$), 293, 235, 179, 161, 119, 75.

10α-Hydroxy-6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3-one (4b)

^{1}H NMR ($CDCl_3$): δ 0.04 and 0.06 (2s, 6H, 2 × $SiCH_3$), 0.90 (s, 9H, *t*-BuSi), 1.18 (s, 3H, 6-CH_3), 1.40 and 2.14 (m, 2H, H-9), 1.77 and 2.07 (m, 2H, H-5), 1.78 (m, 2H, H-8), 2.39 and 2.41 (m, 2H, H-4), 3.42 (dd, 1H(α,ax), J_{aa} = 9.2 Hz, J_{ae} = 4.0 Hz, H-7), 4.34 (ddd, 1H(β,ax), ^4J = 1.2 Hz (to H-2), J_{ae} = 5.5 Hz, J_{aa} = 11.6 Hz, H-10), 6.18 (d, 1H, ^4J = 1.2 Hz (to H-10), H-2).

^{13}C NMR ($CDCl_3$): δ −4.93 and −4.02 (2 × $SiCH_3$), 16.56 (6-CH_3), 17.98 (Si**C**$(CH_3)_3$), 25.75 (SiC(**C**$H_3)_3$), 28.80 (C-8), 32.16 (C-9), 33.58 (C-4), 35.21 (C-5), 42.08 (C-6), 68.11 (C-10), 78.21 (C-7), 121.44 (C-2), 169.31 (C-1), 199.81 (C-3).

CIMS (isobutane): m/z 311($M + H^+$) 293, 235, 179, 161, 75, 58.

6-Methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1-en-3,10-dione (5)

^{1}H NMR ($CDCl_3$): δ 0.08 and 0.10 (2s, 6H, 2 × $SiCH_3$), 0.90 (s, 9H, *t*-BuSi), 1.16 (s, 3H, 6-CH_3), 1.88 (dt, 1H, J = 5.7 and 2 × 14 Hz, H-5α), 2.02 and 2.07

(m, 2H, H-8), 2.23 (ddd, 1H, J = 2.9, 5.1 and 13.5 Hz, H-5β), 2.49 (m, 1H, H-9α), 2.51-2.53 (m, 2H, H-4$\alpha\beta$), 2.70 (ddd, 1H, J = 2.4, 5.1 and 17.3 Hz, H-9β, 3.82 (dd, 1H, J = 4.5 and 11.3 Hz, H-7α), 6.26 (s, 1H, H-2).

^{13}C NMR ($CDCl_3$): δ −4.83 and −4.03 ($2 \times SiCH_3$), 15.83 (6-CH_3), 18.02 (Si**C**$(CH_3)_3$), 25.74 (SiC(**C**$H_3)_3$), 27.76 (C-8), 33.90 (C-4), 34.72 (C-5), 38.07 (C-9), 42.04 (C-6), 75.87 (C-7), 127.52 (C-2), 157.89 (C-1), 199.59 and 200.56 (C-3 and C10).

CIMS (isobutane): m/z 309($M + H^+$), 251, 177, 75, 28.

Procedure for the oxidation of (3) with *t*-BuOOH

Compound **3** (0.21 mmol or 61 mg), prepared directly before the oxidation, was dissolved in 4 mL of toluene under argon atmosphere, then 0.25 mmol of *t*-BuOOH in toluene (46 μL of 4.6 M) and 0.5 mmol (50 μL) of Et_3N added. The reaction mixture was stirred at room temperature for 4 days. After evaporation of the solvent the products were isolated by flash chromatography on SiO_2 (3% up to 15% of acetone in petroleum ether). The main isolated products were alcohols (**4a**) in yield 26% and (**4b)** 9%, (**5**) 14%, and (**1**) 7% (see Table 1).

Procedure for the oxidation of (3) with H_2O_2

Compound **3** (0.19 mmol or 56 mg), prepared directly before the oxidation, was dissolved in 2 mL of THF under argon atmosphere, then 0.5 mmol (40 μL) of pyridine and 0.22 mmol (25 μL) of 30% H_2O_2 in water were added. The reaction mixture was stirred at room temperature overnight, then 0.2 mmol (20 μL) of Et_3N was added, and the reaction mixture was stirred at room temperature for 2 days. After the evaporation of the solvent the products were isolated by flash chromatography on SiO_2 (3% up to 15% of acetone in petroleum ether). The main isolated products were alcohols (**4a + 4b**) in yield 10% and 1,4-diketone (**5**) 9% (see Table 1).

Procedure for the oxidation of (1) with *t*-BuOOH

Dienolate (**2**) (0.17 mmol) was prepared as compound (**3**), described above. Then 0.18 mmol (40 μL) of *t*-BuOOH was added and the reaction mixture was stirred under argon atmosphere for 4 h. The reaction mixture was quenched with 10% aliquot solution of acetic acid and extracted 4 times with diethyl ether, the organic phase was washed with brine and dried on K_2CO_3. After the filtration and evaporation of the solvents the crude product was purified by flash chromatography on SiO_2 (3% up to 5% of ethyl acetate in petrol ether). 21% of enolized 1,2-diketone (**6**) was obtained (see Table 1).

2-Hydroxy-6-methyl-7-*tert*-butyldimethylsilyloxybicyclo[4.4.0]dec-1,9-dien-3-one (6)

^{1}H NMR ($CDCl_3$): δ −0.03 and 0.00 (2s, 6H, $2 \times SiCH_3$), 0.83 (s, 9H, *t*-BuSi), 1.01 (s, 3H, 6-CH_3), 1.58 (dt, 1H, J = 5.2 and 2×14 Hz, H-5α), 2.08 (dddd,

J = 0.5, 2.1, 5.2 and 13.3 Hz, H-5β), 2.23 (tdd, 1H, J = 2 × 2.8, 9.7 and 19.0 Hz, H-8β), 2.32 (dtd, 1H, J = 1.0, 2 × 5.7 and 19.0 Hz, H-8α), 2.53 (ddd, 1H, J = 2.1, 5.2 and 18.2 Hz, H-4α), 2.60 (ddd, 1H, J = 5.2, 14.0 and 18.2 Hz, H-4β), 3.57 (dd, 1H, J = 9.7 and 5.7 Hz, H-7α), 5.96 (ddd, 1H, J = 2.8, 5.9 and 9.8 Hz, H-9), 6.55 (mdd, 1H, J = 2.6 and 9.8 Hz, H-10).

^{13}C NMR ($CDCl_3$): δ −4.89 and −3.98 (2 × $SiCH_3$), 14.55 (6-CH_3), 17.99 (Si**C**$(CH_3)_3$), 25.78 (SiC(**C**$H_3)_3$), 31.88 (C-4), 32.36 (C-5), 32.85 (C-8), 38.46 (C-6), 74.95 (C-7), 121.68 (C-10), 132.51 (C-9), 132.84 (C-1), 140.85 (C-2), 194.06 (C-3).

EIMS (70 eV): m/z 308(M^+), 251, 233, 176, 131, 106, 91, 75.

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REFERENCES

1. Aav, R., Kanger, T., Pehk, T. & Lopp, M. Synthesis of the AB-ring of 9,11-secosterols. *Synlett*, **2000**, 529–531.
2. Aladro, F. J., Guerra, F. M., Moreno-Dorado, F. J., Bustamante, J. M., Jorge, Z. D. & Massanet, G. M. Enantioselective synthesis of (+)-decipienin A. *Tetrahedron*, 2001, **57**, 2171–2178.
3. Kurosu, M., Marcin, L. R., Grinsteiner, T. J. & Kishi, Y. Total synthesis of (±)-batrachotoxinin A. *J. Am. Chem. Soc.*, 1998, **120**, 6627–6628.
4. Singh, S. B., Zink, D., Polishook, J., Valentino, D., Shafiee, A., Silverman, K., Felock, P., Teran, A., Vilella, D., Hazuda, D. J. & Lingham, R. B. Structure and absolute stereochemistry of HIV-1 integrase inhibitor integric acid. A novel eremophilane sesquiterpenoid produced by a *Xylaria* sp. *Tetrahedron Lett.*, 1999, **40**, 8775–8779.
5. Parish, E. J. & Li, S. A one-step synthesis of 6β-hydroxy-Δ^4-3-ketones. Novel oxidation of homoallylic sterols with permanganate ion. *J. Org. Chem.*, 1996, **61**, 5665–5666.
6. Korde, S. S., Udasi, R. A. & Trivedi, G. K. Oxidation of steroidal 5-en-3β-ol with pyridinium chlorochromate: Isolation of key intermediate, steroidal 6β-hydroxy-4-en-3-one. *Synth. Comm.*, 1997, **27**, 3419–3430.
7. Rücker, G., Kretzschmar, U. Darstellung von 1.8.9.10-Tetradehydro-aristolanon-(2) und 9-Hydroxy-1(10)-aristolenon-(2) (Debilon). *Liebigs Ann. Chem.*, 1971, 748, 211–213.
8. Jansen, B. J. M., Kreuger, J. A. & de Groot, A. The conversion of (-)- and (+)-dihydrocarvone into chiral intermediates for the synthesis of (-)-poligodial, (-)-warburganal and (-)-muzigadial. *Tetrahedron*, 1989, **45**, 1447–1452.
9. Wijnberg, J. B. P. A., Vader, J. & de Groot, A. Stereospecific synthesis of selectively C-7-acetalized substituted 4aβ-methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*), 7(8*H*)-diones. A short total synthesis of (±)-β-eudesmol, (±)-β-selinene, and (±)-β-dictyopterol. *J. Org. Chem.*, 1983, **48**, 4380–4387.

10. Holland, H. L. & Auret, B. J. The mechanism of the microbial hydroxylation of steroids. Part 2. Hydroxylation of a Δ^4-3-ketosteroid analog by *Rhizopus arrhizus* ATCC 11145. *Can. J. Chem.*, 1975, **53**, 2041–2044.
11. Theobald, D. W. The chemistry of some 7β(H)-eudesm-11-en-3,6-diones and related compounds. *Tetrahedron*, 1963, **19**, 2261–2267.
12. Shimizu, T., Hiranuma, S. & Yoshioka, H. Regio- and stereoselective functsionalisations of the Wieland–Miescher ketone derivatives at the C-8 position. *Chem. Pharm. Bull.*, **1989**, 1963–1965.
13. Büchi, G., Matsumoto, K. E. & Nishimura, H. The total synthesis of (±)-vindorosine. *J. Am. Chem. Soc*., 1971, **93**, 3299–3300.
14. Yamaguchi, K., More, K., Mizugaki, T., Ebitani, K. & Kaneda, K. Epoxidation of α,β-unsaturated ketones using hydrogen peroxide in the presence of basic hydrocalcite catalysts. *J. Org.Chem.*, 2000, **65**, 6897–6903.
15. Yadav, V. K. & Kapoor, K. K. 1,8-Diazabicyclo[5.4.0]undec-7-ene: A remarkable base in the epoxidation of α,β-unsaturated-δ-lactones and other enones with anhydrous *t*-BuOOH. *Tetrahedron*, 1995, **51**, 8573–8584.

ASENDATUD BITSÜKLO[4.4.0]DETSEN-3-OONIDE OKSÜDEERIMINE

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On uuritud 6-metüül-7-*tert*-butüüldimetüülsilüüloksübitsüklo[4.4.0]dets-1-en-3-ooni ja selle derivaadi 6-metüül-7-*tert*-butüüldimetüülsilüüloksübitsüklo-[4.4.0]dets-10-en-3-ooni oksüdatsiooni O_2, H_2O_2 ja *t*-BuOOH-ga leeliselistes tingimustes, K_2CO_3, Et_3N ja *t*-BuOK manulusel. Reaktsioon kulgeb dienolaadi kaudu, mille oksüdeerimisel tekivad γ-hüdroksüenoonid, 1,4-diketoenoon ja 1,2-diketoenoon. On käsitletud α- ning γ-oksüdatsiooni produktide tekke-mehhanismi ja selektiivsust suunavaid tegureid.