Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Epoxides from Myrcene: Selective Obtention

Valéry Fauchet [b], Bernadette Arreguy-San Miguel [c], Martine Taran [c] & Bernard Delmond [a]

[a] Laboratoire de Chimie Organique et Organométallique (URA 35), Université Bordeaux, 1, 351, cours de la Libération 33405, TALENCE Cedex, FRANCE

[b] Institut du Pin, Université Bordeaux, 1 351, cours de la Libération 33405, TALENCE Cedex, FRANCE

[c] UER des Sciences Pharmaceutiques, Université, Bordeaux II

Published online: 24 Sep 2006.

To cite this article: Valéry Fauchet , Bernadette Arreguy-San Miguel , Martine Taran & Bernard Delmond (1993): Epoxides from Myrcene: Selective Obtention, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:18, 2503-2510

To link to this article: http://dx.doi.org/10.1080/00397919308012583

SYNTHETIC COMMUNICATIONS, 23(18), 2503-2510 (1993)

EPOXIDES FROM MYRCENE : SELECTIVE OBTENTION

Valéry Fauchet[b], Bernadette Arreguy-San Miguel[c], Martine Taran[c] and Bernard Delmond*[a]

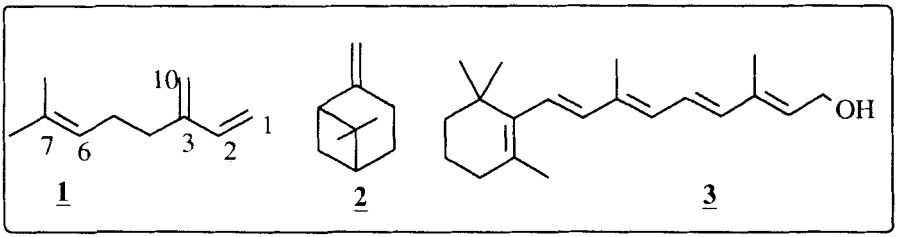
[a] Laboratoire de Chimie Organique et Organométallique (URA 35)
Université Bordeaux 1, 351, cours de la Libération
33405 TALENCE CEDEX FRANCE
[b] Institut du Pin, Université Bordeaux 1
351,cours de la Libération 33405 TALENCE CEDEX FRANCE
[c] UER des Sciences Pharmaceutiques, Université Bordeaux II

Abstract : 1,2-and 3,10-epoxy myrcene are selectively obtained from dihydroxy derivatives prepared by an oxidation reaction of myrcene with potassium permanganate.

Myrcene **1** is a monoterpene compound, easily obtained according to an industrial process by pyrolysis[1] of β-pinène **2** one of the two major constituents of Pine turpentine. On account of its availability, myrcene is a widely used intermediate in the chemistry of perfumes[2-5], vitamin A[6] **3** and other terpenoïds.

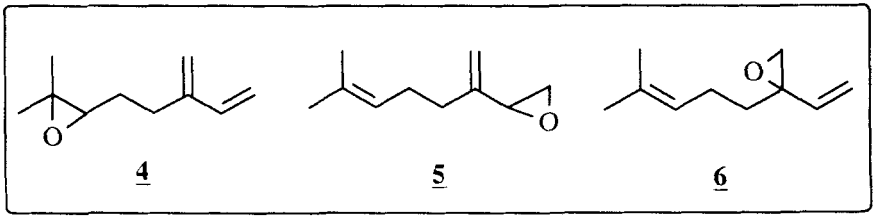
---

*To whom correspondence should be addressed.



1 2 3

Epoxides being versatile synthetic tools, we wish to report in this communication a method for the selective obtention of mono epoxides **5** and **6** from myrcene **1**.

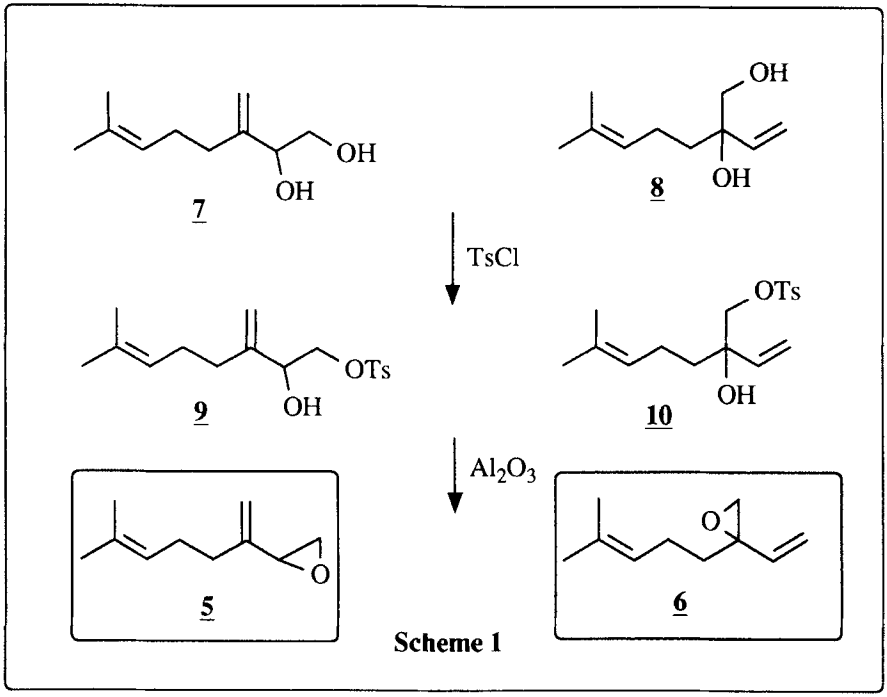


4 5 6

When the oxidation reaction of myrcene **1** is performed by means of peracids[7] (metachloroperbenzoïc acid), 6,7-epoxy myrcene **4** was almost exclusively produced. This epoxide could also be prepared, by a cycloalcoxydehalogenation[8] reaction, from 6-halogeno-7-hydroxy derivatives, obtained by treatment of myrcene **1** with N-halosuccinimide/H_2O system.

In order to obtain mono epoxides on 1,3-diene moiety of myrcene, we have thought use dihydroxy compounds as precursors of epoxidic function, via hydroxy-tosylates (scheme 1).

Thus, by oxidation of myrcene **1** with potassium permanganate, at low temperature for one hour, in the presence of benzyltributylammonium chloride, we have obtained after purification with 56% yield, a mixture of hydroxy



Scheme 1

compounds **7** and **8** which can be easily separated by column chromatography (silica gel), then caracterized.

From each corresponding diols, the selective reaction of tosyl chloride with primary hydroxyl group gave hydroxy-tosylates **9** and **10**.

The treatment of hydroxy-tosylates **9** and **10** in cyclohexane solution with alumina oxide[9] led to 1,2-epoxy myrcene **5** and 3,10 epoxy myrcene **6** respectively.

Thus from myrcene **1**, the three mono epoxides could be selectively prepared. The oxidation of **1** with peracids gave 6,7-epoxy, while 1,2- and 3,10 epoxy were obtained via hydroxy-tosylates after oxidation with potassium permanganate.

These new compounds exhibited interesting structural features, in particular a vinyl-epoxy moiety, and would be used as intermediates to access to highly functionalized acyclic terpenoids, key precursors in the chemistry of perfumes and vitamins.

EXPERIMENTAL SECTION

Column chromatography was performed with MERCK silica gel 60, 70-230 mesh ASTM. ^{1}H and ^{13}C NMR spectra were recorded at 250 MHz on a BRUKER AC 250 spectrometer using $CDCl_3$ as solvent. Chemical shifts are recorded as δ values in ppm from internal tetramethylsilane.

Solvents were freshly distilled from drying agent in a nitrogen atmospher. Myrcene was a generous gift of "Dérivés Résiniques et Terpéniques" (DRT) DAX (France).

Oxidation of myrcene

A solution of 2,61g (16.5mmol) of potassium permanganate[11] and 5.32g (16.5mmol) of benzyltributylammonium chloride in 500ml of methane dichloride was stirred during three hours. The solution was cooled to -5°C, then 5g (36mmol) of myrcene was added, under stirring for one hour.

The reaction mixture was successively treated with NaOH (5g in 80mL H_2O), $NaHSO_3$ (5g in 80mL H_2O), H_2SO_4 (10g in 100mL H_2O), then extracted with Et_2O.

The organic solution was washed with H_2O, dried ($MgSO_4$) and evaporated under reduced pressure.

A rapid column chromatography (SiO_2) in order to eliminate excess myrcene and light products, gave 2.09g of (1 :1) dihydroxylated[10] compounds 7 and 8 which were separated by column chromatography (SiO_2).

Elution with 6 : 4 petroleum ether-ether as an eluent gave :

1,2-dihydroxy myrcene 7 (818mg)

^1H NMR ($CDCl_3$) δ : 1,60 (3H,s),1.68 (3H,s), 3.46-3.71 ($C\underline{H}_2OH$, m), 4.16-4.20 ($C\underline{H}$-OH,m), 4.96 and 5.13 ($C\underline{H}_2$=C,m), 5.10 ($C\underline{H}$=C,t)

^{13}C NMR ($CDCl_3$), δ : 17.8 (C-9), 25.7 (C-8), 26.6 (C-5), 32.7 (C-4), 65.9 (C-1), 75.4 (C-2), 110.5 (C-10), 124.0 (C-6), 131.8 (C-7), 148.3 (C-3)

3,10-dihydroxy myrcene 8 (755mg)

^1H NMR ($CDCl_3$) δ : 1.57(3H,s), 1.65 (3H,s), 3.46 ($C\underline{H}_2$OH,m), 5.08 ($C\underline{H}$=C,t) 5.20-5.36 ($C\underline{H}_2$=CH,m), 5.72-5.84 ($C\underline{H}$=CH_2,m)

^{13}C NMR ($CDCl_3$) : 17.7 (C-9), 22.0 (C-5), 25.7 (C-8), 36.8 (C-4), 68.8 (C-10), 76.3 (C-3), 115.1 (C-1), 124.2 (C-6), 132.1 (C-7), 140.7 (C-2).

Obtention of 1,2-epoxy myrcene 5 and 3,10-epoxy myrcene 6

* To a solution of 1,2 dihydroxy myrcene 7 (2.3g, 13.5mmol) in pyridine (10mL) was added at 0°C tosyl chloride (3.11g, 16mmol). After stirring for three hours, the reaction mixture was hydrolysed with 10% HCl, extracted with

Et_2O, washed with 5% aqueous hydrochloric acid, H_2O and dried over $MgSO_4$.

Removal of the solvent gave tosyl derivative **9** (3.55g, 81% yield)

^1H NMR ($CDCl_3$) δ : 1.57 (3H,s), 1.66 (3H,s), 2.43 (3H,s), 3.88-4.11 ($C\underline{H}_2O$-m), 4.30 ($C\underline{H}$-O,m) , 4.96 and 5.11 ($C\underline{H}_2$ = C,m), 5.04 ($C\underline{H}$ = C,t), 7.30-7.76 (Ar,m).

According to the same procedure, from 3,10-dihydroxy myrcene **8** (1.62g, 9.5 mmol) and tosyl chloride (2.19g, 11.5 mmol) we have obtained tosyl derivative **10** (2.43g , 79% yield).

^1H NMR ($CDCl_3$) δ : 1.52 (3H,s), 1.61 (3H,s), 2.41 (3H,s), 3.86 ($C\underline{H}_2O$-,s),5.00 ($C\underline{H}$= C,t) , 5.15-5.33 ($C\underline{H}_2$=CH,m), 5.64-5.75 ($C\underline{H}$ = CH_2,m), 7.28-7.77 (Ar,m).

* A solution of 2-hydroxy-1-tosyl derivative **9** (3.55g, 11 mmol) in cyclohexane (30 mL) was stirred during 12 hours with desactivated neutral alumina (37g). After filtration and washing of alumina with Et_2O, the organic layers were evaporated off under reduce pressure to give 1,2-epoxymyrcene **5** (1.5g , 90% yield).

^1H NMR ($CDCl_3$) δ :1.53 (3H,s), 1.61 (3H,s), 2.55-2.81 ($C\underline{H}_2$-O,m), 3.25-3.28 ($C\underline{H}$-O,m), 4.89-5.08 ($C\underline{H}_2$=C,m), 5.03 ($C\underline{H}$ = C,t).

^{13}C NMR ($CDCl_3$) δ : 17.7 (C-9), 25.7 (C-8), 26.7 (C-5), 30.8 (C-4), 47.9 (C-1), 53.8 (C-2), 112.3 (C-10), 123.7 (C-6), 132.0 (C-7), 145.3 (C-3).

According to the same procedure, from 3-hydroxy-10-tosyl myrcene **10** (2.43g 7.5 mmol) and 25g of alumina oxide, we have obtained 3,10-epoxy myrcene **6** (1.1g, 93% yield).

^{1}H NMR ($CDCl_3$) δ : 1.60 (3H,s), 1.68 (3H,s), 2.66 - 2.80 ($C\underline{H}_2O$,m)5.10 ($C\underline{H}$ = C,t), 5.18 - 5.38 ($C\underline{H}_2$ = CH, m), 5.71 - 5.82 ($C\underline{H}$ = CH_2,m)

^{13}C NMR ($CDCl_3$) δ : 17.7 (C-9), 23.7 (C-5), 25.7 (C-8), 33.6 (C-4), 55.1 (C-10), 58.5 (C-3), 116.5 (C-1), 123.6 (C-6), 132.1 (C-7), 137.5 (C-2).

Acknowledgements

We thank M. PETRAUD and B. BARBE for recording the NMR spectra and "Dérivés Résiniques et Terpéniques" (Dax, France) for a generous gift of myrcene.

References :

1. GOLDBLATT, L.A. and PALKIN,S.
Patent US - 2420131 (1947)
2. WEISS, R., (Van Ameringen-Haebler, Inc.)
Patent US - 2882323 (1959)
3. WEBB, R.L. (The Glidden Company)
Patent US - 3016408 (1962)
4. KANE, B.J. and VAN GENK R.A. (SCM Corp.)
Patent US - 4 244 890 (1981)
5. FUJITA, T., SUGA, K. and WATANABE, S.,
Aust. J. Chem., (1974), 27, 531-546
6. LIU, R.S.H. and ARSATO, A.E.
Tetrahedron, (1984), 40, 1931-1969 and references therein
7. MOUSSERON-CANET, M. ,MOUSSERON, M., and LEVALLOIS, C.
Bull. Soc. Chim. Fr., (1963), 376-378

8. SCHULZE, K., HAUFE, G. and KOHLER, G.

Z. Chem.(1980), 20, 293-294

9. ARREGUY-SAN MIGUEL, B., TARAN, M., PICARD, P. and DELMOND, B.

Synth. Commun., (1989), 19, 979-986

10. YAMAZAKI, Y., HAYASHI, Y., HORI, N. and MIKAMI, Y.

Agric. Biol. Chem., (1988), 52, 2921-2922

11. FOGLIA, T.A., BARR, P.A. and MALLOY, A.J.

J. Am. Oil Chem. Soc. (1977), 54, 858.

(Received in the UK 15 April 1993)