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INFLUENCE OF THE STEREOCHEMISTRY ON THE 1,2-DIALKENYLCYCLOBUTANOLS BEHAVIOUR : OXY-COPE *VERSUS* RETRO-ENE REARRANGEMENTS

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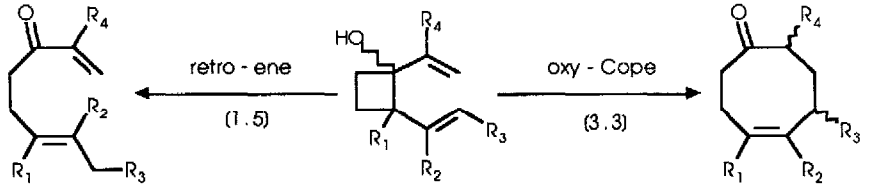
Summary : *From cyclobutanones* ***5a-j****,ten 1,2-divinylcyclobutanols* ***1a-j*** *were prepared. A stereochemical effect was clearly evidenced : while* trans *1,2-divinylcyclobutanols underwent a retro-ene ring opening, the* cis *isomers underwent an oxy-Cope ring enlargement.*

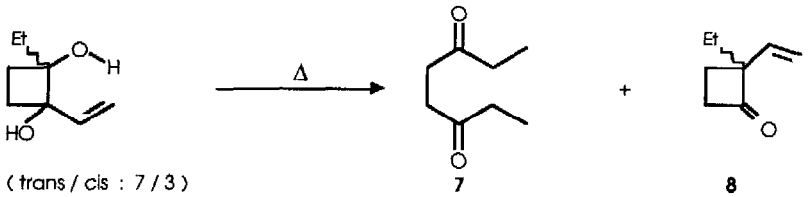
It is well known that *cis* 1,2-divinylcyclobutanes undergo thermal [3.3] sigmatropic rearrangement into *cis, cis* 1,5-cyclooctadienes (Cope rearrangement) [1] while the corresponding *trans* isomers react predominantly via [1.3] shift process to provide 4-vinylcyclohexenes [2]. On the other hand, it has been recently claimed that both *cis* and *trans* 1,2-dialkenylcyclobutanols **1** undergo upon treatment with potassium hydride (KH), anionic oxy-Cope C_4 -> C_8 ring expansion to give 4-cycloocten-1-ones **2** in good yields [3], opening up new ways to cyclooctanoid terpenes such as poitediol or dactylol [4]. No products resulting from [1.3] rearrangements were detected in these reactions [3]. Initial *trans - cis* isomerization was invoked, as previously suggested by Berson [5], to explain the surprising ring expansion of *trans* 1,2-divinylcyclobutanols [4]. Analogously, *cis* and *trans* homologous five-, six-, seven-, nine- and ten-membered 1,2-divinylcycloalkanols have been reported to provide 5-cycloalken-1-ones resulting from a four carbons ring enlargement [6].



3 **1** **2**

We report that contrary to the previous claim [3], the rearrangement of 1,2-dialkenylcyclobutanols **1** is highly depending on the *cis* or *trans* relationship of the two vinyl groups. We have recently disclosed a regio- and stereospecific way to racemic as well as optically active 2-alkenylcyclobutanones [7,8] highly competitive with the reaction of α-heterosubstituted cyclopropyllithium reagents with an enone or enal [9] or with the cycloaddition of vinylketenes to olefins [10]. Thus, addition of vinylic organometallic reagents to the readily available silylated 1-hydroxycyclopropanecarboxaldehyde or (1-hydroxycyclopropyl)methyl ketone [7,11] led to the cyclopropylvinylcarbinols **4a-f**, which underwent trifluoroborane etherate (BF_3-Et_2O) induced C_3 -> C_4 ring expansion into the 2-vinylcyclobutanones **5a-f** in high yields [7,8]. Then addition of vinyl- or prop-2-enylmagnesium bromides to **5a** (R_2 = H) and to **5b** (R_2 = Me) gave the 1,2-dialkenylcyclobutanols **1a-c**. However, these four-membered rings appeared to be very labile and underwent upon purification (l.c., SiO_2) or on standing in C_6D_6 at r.t., ready retro-ene ring opening (also termed β-hydroxy olefin cleavage or [1.5] hydrogen

shift) into the 1,6-octadien-3-ones **3a-c** respectively, with yields from **5a,b** superior to 90%. Such a retro-ene process had been observed previously but at rather higher temperatures [12] ; thus for instance, when a mixture of *trans* and *cis* (ratio 7:3) 1-ethyl-2-vinyl-1,2-cyclobutanediols **6** was heated in sealed tube at 220°C for 15 mn the 3,6-octanedione **7** (from retro-ene ring opening) and the 2-vinyl-2-ethylcyclobutanone **8** (from pinacolic transposition), where obtained (ratio 5:5), while the dione **7** was formed quantitatively upon heating **6** at 315°C for 2 h in the gas phase [13].Therefore the lability of the 1,2-divinylcyclobutanols **1a-c** implies a dramatic substituent effect on the behaviour of the vinylcyclobutane system (compare the stability of **1a-c** and **6**).



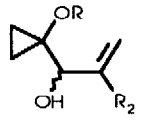
6 (trans / cis : 7 / 3) **7** **8**

220°C, 15mn. 50 50
315°C, 2h 100

Vinylation of **5d** prepared by BF_3-Et_2O induced ring expansion of the suitable cyclopropylvinylcarbinol **4d** [7,8], provided a 9:1 mixture of *trans* - **1d** and *cis* 2-(prop-1-enyl)-1-vinylcyclobutanol **1e**, which have been separated by l.c. (CH_2Cl_2/Et_2O : 97/3, SiO_2). Upon treatment with KH in THF at r.t., or on heating in C_6H_6 at 40°C, the major *trans* isomer **1d** underwent total retro-ene ring opening into the E 1,6-nonadien-3-one **3d**, exclusively ; while under the same conditions its *cis* isomer **1e** underwent total oxy-Cope ring expansion into the 6-methyl-4-cycloocten-1-one **2e**, exclusively in 78% yield. On the other hand, vinylation of **5f**, product of ring expansion of the cyclopropylvinylcarbinol **4f**, gave a 3:7 mixture of *trans*-**1f** and *cis* 2-methyl-2-(prop-1-enyl)-1-vinyl cyclobutanol **1g** in 83% yield. As recently suggested the presence of the methyl group on the four-membered ring favored the stereoproximal to stereodistal ratio [14]. Upon standing in C_6D_6 at r.t. the *trans* (distal) 1,2-divinylcyclobutanol **1f** underwent slow retro-ene ring opening, totally within one week as monitored by t.l.c., to provide the 6-methyl-1,6-nonadien-3-one **3f** ; while the *cis* (proximal) isomer **1g**, upon standing in C_6D_6 at 40°C led, to the 4,6-dimethyl-4-cycloocten-1-one **2g** [14].

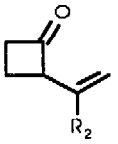
Addition of phenylethynylmagnesium bromide to **5d** yielded a 5:5 mixture of *trans* **1h** and *cis* 1-(2-phenylethynyl)-2-(prop-1-enyl) cyclobutanol **1i**, readily separated by l.c. (CH_2Cl_2/Et_2O : 97/3, SiO_2) .Upon heating in C_6H_6 at 50°C for 24 h or upon treatment with KH in THF at r.t. for 15 mn, the *cis* cyclobutanol **1i** underwent ring expansion into the 5-methyl-3-phenyl-2,5-cyclooctadien-1-one **2i**, exclusively as monitored by t.l.c. ; while, unrearranged under these conditions, the *trans* isomer **1h** underwent total ring opening into the (2-ethynylphenyl) 3-hexenyl ketone **3h** on further heating in refluxing benzene for 24 h.

Addition of 5-methyl-1-cyclopentenyllithium [15] to 2,2-dimethyl-1-siloxycyclopropanecarboxaldehyde (prepared from 2,2-dimethylsuccinate according to ref. 11) yielded the cyclopropylvinylcarbinol **4j** and on subsequent BF_3-Et_2O induced ring expansion the cyclobutanone **5j** which was treated with prop-2-enylmagnesium bromide to lead to the cyclobutanol **1j**. In spite of many attempts *i.e.*, treatment with KH [3], with $(Me_3Si)_2NK$ [16], ... under various conditions, **1j** did not undergo the anionic oxy-Cope rearrangement into the cyclopentacyclooctenone **2j**, a suitable precursor of precapnelladiene [17]. Once again the expected C_4 -> C_8 ring expansion was precluded by the *trans* relationship of the two vinyl groups of **1j**.

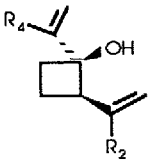


4a R_2 = H
b = Me

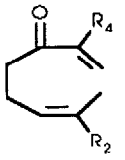
R = Si t-Bu Me_2 or Si t-Hex Me_2



5a,b

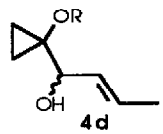


1a R_2, R_4 = H
b R_2 = Me, R_4 = H
c R_2, R_4 = Me

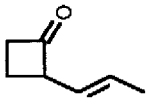


3a
b
c

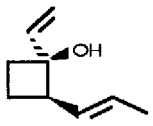
Ref. (22) (18) (23)



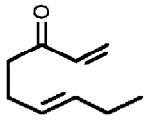
4d



5d



1d (20)



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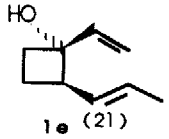
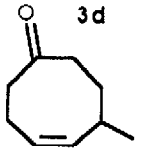


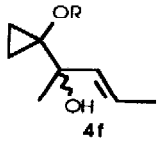
1e (21)



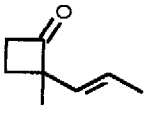
2e

3d

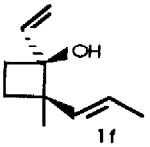
(24)



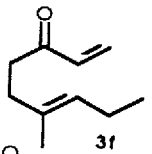
4f



5f

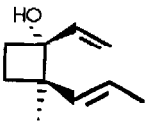


1f

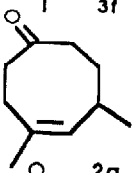


3f

(25)

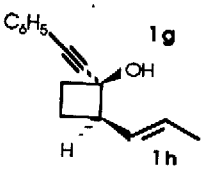


1g

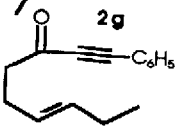


2g

(14)

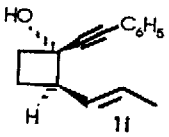


1h

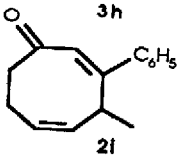


3h

(26)

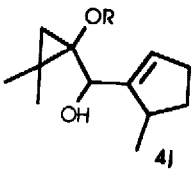


1i

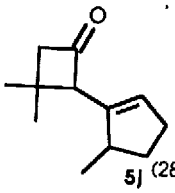


2i

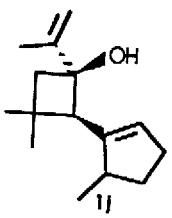
(27)



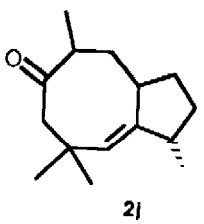
4j



5j (28)



1j



2j

(17)

REFERENCES

1) E. Vogel, Ann., 1958, **615**, 1.

2) G.S. Hammond and C.D. de Boer, J. Am. Chem. Soc., 1964, **86**, 899 ; D.J. Treckker and J.P. Henry, J. Am. Chem. Soc., 1964, **86**, 902. J.A. Berson and P.B. Dervan, J. Am. Chem. Soc., 1973, **95**, 267, 269.

3) R.C. Gadwood and R.M. Lett, J. Org. Chem., 1982, **47**, 2268.

4) R.C. Gadwood, R.M. Lett and J.E. Wissinger, J. Am. Chem. Soc., 1984, **106**, 3869 ; 1986, **108**, 6343.

5) J.A. Berson and P.B. Dervan, J. Am. Chem. Soc., 1972, **94**, 8949.

6) E.N. Marvell and W. Whalley, Tetrahedron Lett., 1970, 509 ; T. Kato, H. Kondo, M. Nishino, M. Tanaka, G. Hata and A. Miyake, Bull. Chem. Soc. Jpn., 1980, **53**, 2958.

7) J. Ollivier and J. Salaün, Tetrahedron Lett., 1984, **25**, 1269 ; J.P. Barnier, B. Karkour and J. Salaün, J. Chem. Soc. Chem. Comm., 1985, 1270.

8) J. Salaün and B. Karkour, Tetrahedron Lett., 1987, **28**, 4669 ; 1988, **29**, 1537 ; J. Salaün, B. Karkour and J. Ollivier, Tetrahedron, in press.

9) R.C. Gadwood, M.R. Rubino, S.C. Nagarajan and S.T. Michel, J. Org. Chem., 1985, **50**, 3255 and references cited therein.

10) R.L. Danheiser, C. Martinez-Davila and H. Sard, Tetrahedron, 1981, **37**, 3943 ; D.A. Jackson, M. Rey and A.S. Dreiding, Helv. Chim. Acta, 1983, **66**, 2230 ; Tetrahedron Lett., 1983, **24**, 4817.

11) J. Salaün and Y. Almirantis, Tetrahedron, 1983, **39**, 2421 ; J.P. Barnier and J. Salaün, Tetrahedron Lett., 1984, **25**, 1273 ; J. Ollivier and J. Salaün, J. Chem. Soc. Chem. Comm., 1985, 1269.

12) A. Viola, E.J. Iorio, K. Chen, G.M. Glover, V. Nayak and P.J. Kiocienski, J. Am. Chem. Soc., 1967, **89**, 3462 ; P. Leriverend and J.M. Conia, Bull. Soc. Chim. Fr., 1970, 1040.

13) J.P. Barnier and J.M. Conia, Bull. Soc. Chim. Fr., 1975, 1659.

14) S.A. Miller and R.C. Gadwwod, J. Org. Chem., 1988, **53**, 2214.

15) W. Barth anb L.A. Paquette, J. Org. Chem., 1985, **50**, 2438 ; N.E. Schore and M.J. Kundsen, J. Org. Chem., 1987, **52**, 569.

16) L.A. Paquette and M.A. Poupart, Tetrahedron Lett., 1988, **29**, 273.

17) W.A. Kinney, M.J. Coghlan and L.A. Paquette, J. Am. Chem. Soc., 1984, **106**, 6868 ; 1985, **107**, 7352.

18) R. Bloch, Tetrahedron, 1983, **39**, 639.

19) P. Dubs and R. Stüssi, Helv. Chim. Acta, 1978, **61**, 990.

20) **1d** IR (CCl_4) 3600, 3100, 1640 cm^{-1} ; ^1H NMR 250 MHz (C_6D_6) : 5.95 (dd, J = 16, 12 Hz, 1H), 5.5 (m, 2H), 5.25 (dd, J = 16, 2 Hz, 1H), 4.92 (dd, J = 12, 2 Hz, 1H), 3.09 (m, 1H), 2.0 (m, 3H), 1.80 (m, 2H), 1.44 (d, J = 6 Hz, 3H). CIMS (NH_3) m/e (rel. int.) : 138 (100), 129 (100). MS m/e (rel. int.) 123 (6.7), 109 (35.5), 95 (28.8), 81 (14.4), 68 (34.6), 55 (100), 41 (38.4).

21) **1e** IR (CCl_4) 3600, 3100, 1640 cm^{-1} ; ^1H NMR 250 MHz (C_6D_6) : 5.92 (dd, J = 20, 12 Hz, 1H), 5.42 (m, 2H), 5.22 (dd, J = 20, 2 Hz, 1H), 5.02 (dd, J = 12, 2 Hz, 1H), 3.12 (m, 1H), 1.95(m, 3H), 1.80 (m, 2H), 1.6 (d, J = 7 Hz, 3H). CIMS (NH_3) m/e (rel. int.) : 138 (100), 109 (100).

22) **3a** IR (CCl_4) 1710, 1690, 1620 cm^{-1} ; ^1H NMR 250 MHz (C_6D_6) : 6.30 (m, 2H), 5.85 (dd, J = 10, 2 Hz), 5.42 (m, 2H), 2.65 (t, J = 8 Hz, 2 H), 2.38 (m, 2H), 1.62 (d, J = 6 Hz, 3H). MS m/e (rel. int.) : 124 (M^+, 1), 41 (30), 55 (100), 69 (17).

23) **3c** ^1H NMR 250 MHz (C_6D_6) : 5.45 (s, 1H), 5.22 (s, 1H), 5.12 (m, 1H), 2.35 (m, 4H), 1.75 (s, 3H), 1.60 (s, 3H), 1.50 (s, 3H).

24) **2e** IR (CCl_4) 1700, 1450 cm^{-1} ; ^1H NMR 250 MHz (C_6D_6) : 5.5 - 5.3 (m, 2H),3.3 (m, 1H), 2.10 (m, 3H), 1.62 (m, 2H), 1.38 (m, 2H), 1.10 (m, 1H), 0.80 (d, J = 6.5 Hz, 3H). MS m/e (rel. int.) : 138 (3), 123 (33.8), 110 (75.7), 95 (57.5), 81 (71.2), 68 (80.8), 67 (100).

25) **3f** IR (CCl_4) 1710, 1690, 1620 cm^{-1} ; ^1H NMR 250 MHz ($CDCl_3$) : 6.30 (m, 2H), 5.85 (dd, J = 8 , 2 Hz, 1H), 5.90 (m, 1H), 2.65 (t, J = 6 Hz, 2 H), 2.35 (t, J = 6 Hz, 2H), 2.00 (t, J = 6 Hz, 2H), 1.70 (s, 3H), 0.95 (t, J = 6 Hz, 3H).

26) **3h** IR (CCl_4) 2200,1715, 1670 cm^{-1} ; ^1H NMR 250 MHz ($CDCl_3$) : 7.3 - 7.6 (m, 5H), 5.25 - 5.6 (m, 2H), 2.6 - 2.8 (m, 2H), 2.4 - 2.6 (m, 2H), 1.9 - 2.15 (m, 2H), 0.98 (t, J = 7 Hz, 3H). MS :m/e (rel. int.) : 212 (M^+, 2.8), 155 (34), 144 (22.8), 141 (26), 129 (100), 75 (24.2).

27) **2i** IR (CCl_4) : 1665, 1620 cm^{-1} ;^1H NMR 250 MHz ($CDCl_3$) : 7.2 - 7.45 (m, 5H), 6 (s, 1H), 5.55 - 5.8 (m, 2H), 4.3 (dq, J = 7,7 Hz, 1H), 3.2 - 3.38 (m, 1H), 2.37 - 2.8 (m, 3H), 1.05 (d, J = Hz, 3H). MS : m/e (rel. int.) : 212 (M^+, 56.4), 169 (80.6), 156 (46), 155 (100), 144 (53.4), 141 (56.4), 115 (55.4), 91 (74.3), 77 (67).

28) **5j** IR (CCl_4) : 1785, 1620 cm^{-1} ; ^1H NMR 250 MHz ($CDCl_3$) : 5.7 (m, 1H), 3.6 (m, 1H), 3 - 1 (m, 7H), 1.5 (s, 6H), 1.1 (d, J = 4 Hz, 3H). MS : m/e (rel. int.) : 178 (M, 6.5), 136 (89), 122 (52), 121 (100).

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