Tetrahedron Letters,Vol.23,No.52,pp 5535-5538,1982 0040-4039/82/525535-04$03.00/0
Printed in Great Britain

DITERPENIC SKELETON TRANSFORMATIONS : ALUMINA CATALYSED REARRANGEMENTS OF EPOXIDES

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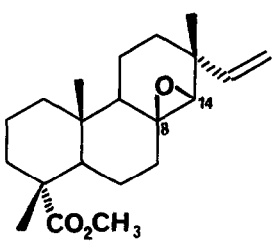
Abstract - The 8,14 β-epoxide of methyl sandaracopimarate undergoes new rearrangements on contact with active alumina, yielding labdane and another compound having the cycloisopimarane skeleton.

In an earlier paper[1] dealing with the reactivity of methyl sandaracopimarate 8,14 β epoxide **1** towards boron trifluoride etherate, the hydroxy-olefin **2** was obtained by a backbone rearrangement. The results obtained by Sukh Dev[2] and Ourisson[3] showing that the action of active alumina is different from that of BF_3:Et_2O when working with monoterpene and sesquiterpene derivatives prompted us to investigate the behaviour of epoxide **1** towards this reagent.



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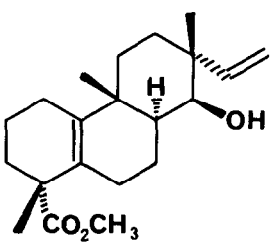

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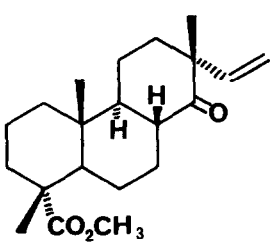
Thus treatment of **1** in cyclohexane solution, during 12 h with active neutral alumina yielded a mixture of carbonyl and hydroxy compounds whose structures were established on the basis of spectral data.



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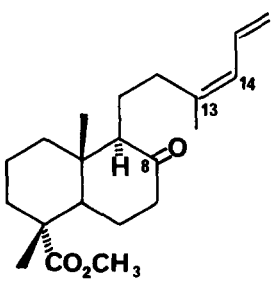

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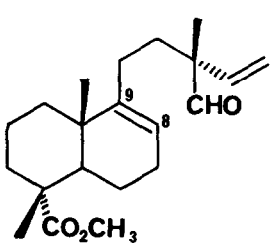

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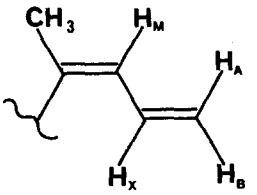
The carbonyl fraction included the ketones **3** (2 %), recently described[1], and **4** (11 %) and the aldehyde **5** (5 %).

* Compound 4

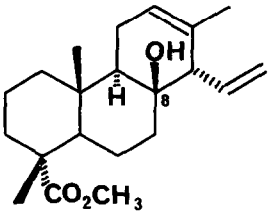
An ir band at 1710 cm^{-1} indicates the presence of a keto group. The ^1H nmr spectrum exhibited a singlet (3 H) at δ 1.75 ppm due to an olefinic methyl group, and olefinic proton signals (4 H) between δ 4,89 and 6.69 ppm. These low field resonances appeared as an ABX system with H_X further coupled to a one-proton doublet (H_M) at δ 5.89 ppm (J = 11 Hz) in agreement with the opposite partial structure.



Analysis of the ^{13}C nmr and mass spectra permitted us to propose a bicyclic structure and to locate the keto group at C-8 .A(Z) configuration of the double bond C_{13}-C_{14} was indicated by the chemical shift of the methyl group at C-13 (δ 23.5 ppm).

* Compound 5

The presence of an aldehyde function in 5 was indicated by its infrared spectrum (ν_{max} 1710 cm^{-1}) and its ^1H nmr spectrum (singlet at δ 9.44 ppm). In addition, a broad singlet at δ 5.24 ppm was consistent with the presence of a trisubstituted double-bond, located at C_8-C_9 by mass spectroscopic fragmentation data. The bicyclic structure 5 assigned to this compound is supported by these spectral data.



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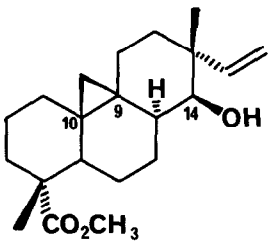

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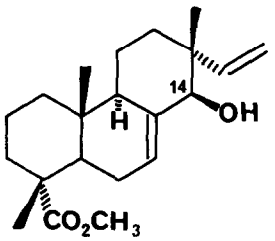

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The hydroxy compounds isolated are methyl-14 β-hydroxy-isopimarate 8 (43 %), recently described[4], 6 (3 %) and 7 (5 %).

* Compound 6

The most striking features of the ^1H nmr spectrum of compound 6 are a singlet (3 H) at δ 1.62 ppm (olefinic methyl group) and an ABX system between δ 4.92 and 5.80 ppm. Double irradiation experiments showed that H_X was coupled with a doublet proton resonating at δ 2.23 ppm (J = 9 Hz). The tertiary nature of the alcohol function at C-8 was supported by its ^{13}C nmr spectrum (singlet in "off resonance" at δ 72.5 ppm).

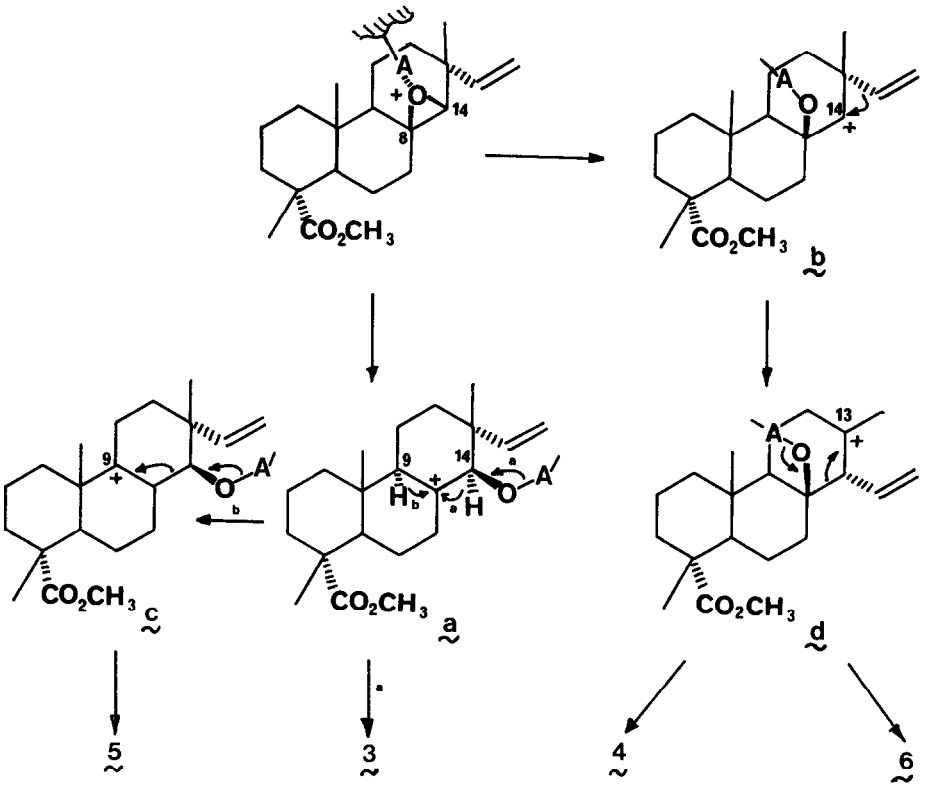

Fig. 1

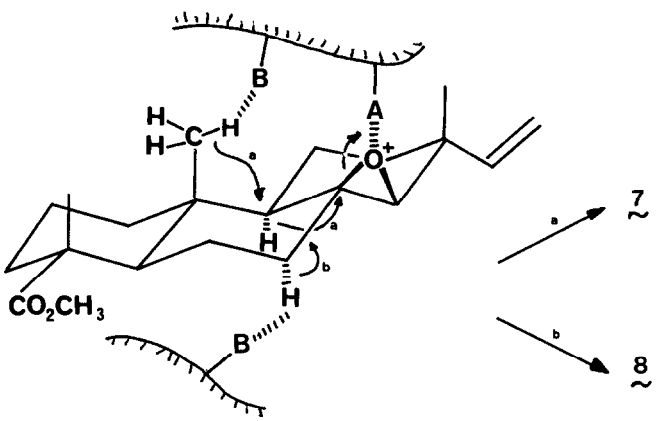

Fig. 2

* Compound 7

Hydroxy compound 7 possesses a three membered ring in its skeleton. As expected, the ^1H nmr spectrum showed an AB system (J = 4 Hz) at δ 0.11 and 0.92 ppm, and the ^{13}C nmr spectrum showed two high-field quaternary carbon atoms (δ 19.8 and 20.2 ppm). The absence of any signal corresponding to CH_3-20 permits us to locate the cyclopropane ring between C-9 and C-10. A broad ($W_{1/2}$ = 4 Hz) one proton signal at δ 3.20 ppm is in good agreement with a β-configuration for the hydroxyl group at C-14.

Sukh Dev[5] has demonstrated that the action of active alumina towards trisubstituted epoxides essentially leads to allylic alcohols and carbocationic rearrangement products. Most of the reactions described above are due to the dipolar character of Al_2O_3 which possesses on its surface both electron-donor and electron-acceptor sites.

Thus from epoxide 1 we can consider the formation of two carbo-cationic species a and b occuring after the coordination of epoxidic oxygen with an electron-acceptor site (Fig.1). The carbo-cation a may undergo a 1,2 shift of hydride ion H-14 to give ketone 3 . Alternatively, a hydride ion shift from C-9 to C-8 would give the tertiary carbo-cation c from which compound 5 is derived by a fragmentation reaction[6].From ion b a 1,2-vinyl shift from C-13 to C-14 followed by proton loss from C-12 would lead to the observed product 6 . The keto-labdane 4 can arise by fragmentation of the carbonium ion d . The formation of hydroxy compounds 7 and 8 can be interpreted by a mechanism[7] in which an epoxidic oxygen atom is adsorbed on an acidic site of the alumina surface while a hydrogen atom suitably located is adsorbed on a basic center (Fig. 2). This bifunctional mechanism involving acidic and basic sites of alumina matrix is analogous to the enzymatic scheme of cycloartenol biosynthesis proposed by Goodwin[8].

Acknowledgements

We thank Mr. M. PETRAUD and Mr. B. BARBE for nmr spectra and Mr. G. BOURGEOIS for mass spectra (Centre d'Etudes Structurales et d'Analyses des Molécules Organiques, Université de Bordeaux I).

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(Received in France 30 September 1982)