

## Short Communication

# Rearrangement products derived from $\beta$ -patchoulene epoxide: Structure of a novel ketone having tricyclo[5.2.2.0<sup>4,8</sup>]undecane skeleton<sup>†</sup>

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### Abstract

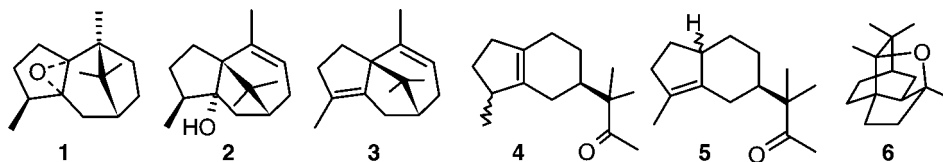
Structure of the unidentified ketone obtained by  $\text{BF}_3$ -catalyzed rearrangement of  $\beta$ -patchoulene epoxide (**1**) has been assigned as 4,8,9,9-tetramethyltricyclo[5.2.2.0<sup>4,8</sup>]undecane-3-one (**7**).

**Keywords:**  $\beta$ -Patchoulene epoxide,  $\text{BF}_3$ -catalyzed multistep rearrangement, 4,8,9,9-tetramethyltricyclo[5.2.2.0<sup>4,8</sup>]undecane-3-one.

Molecular rearrangement is one of the fascinating aspects of terpenoid chemistry. The structures of several rearrangement products **2**, **3**, **4**, **5** and **6** of  $\beta$ -patchoulene epoxide (**1**) with  $\text{BF}_3$  and  $\text{SnCl}_4$  under different solvent and experimental conditions have been elegantly explicated.<sup>1,2</sup> We report here an unusual type of rearranged structure **7** for the uncharacterized crystalline ketone,  $\text{C}_{15}\text{H}_{24}\text{O}$ , m. p.  $80^\circ\text{C}$  obtained by treatment of **1** with  $\text{BF}_3$  gas and using benzene as solvent.<sup>2</sup> The available spectral ( $\nu_{\text{max}}$   $1700\text{ cm}^{-1}$ ,  $^1\text{H NMR}$ : four methyl singlets at  $\delta$  0.81, 0.90, 3H each, 0.95, 6H) and analytical data indicate that the rearrangement product must be tricyclic with four tertiary methyl groups and most probably contains an  $\alpha$ ,  $\alpha$ -disubstituted cyclohexanone functionality.

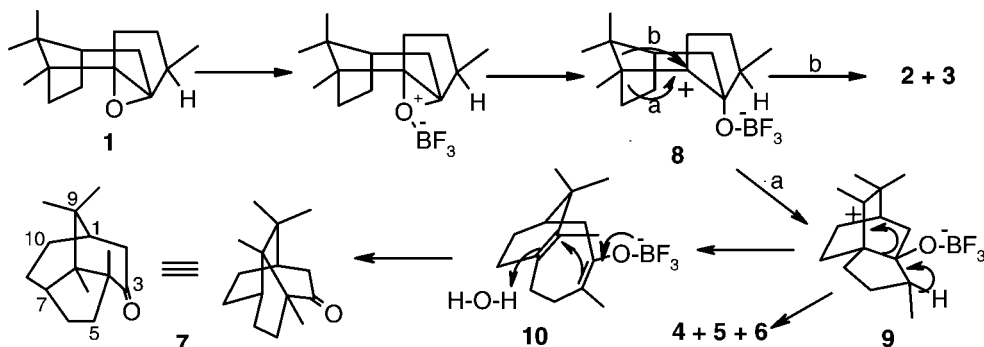
The mechanistic reasoning used by Ourisson and coworkers<sup>1</sup> to rationalize the formation of rearrangement products **2–6** gave us a clue to the structure of the unidentified ketone. We propose that this should be represented by **7**, a compound with a tricyclo[5.2.2.0<sup>4,8</sup>]undecane skeleton, so far not reported in terpenoids.

To explain the formation of the unidentified ketone **7** (Scheme 1), we invoke the same cationic intermediate **8**, earlier proposed by Ourisson and coworkers<sup>1,2</sup> which leads to products



<sup>†</sup> Dedicated to Prof. S. C. Bhattacharyya

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Scheme 1.

**4, 5 and 6.** Cation **8** gets transformed into enol ether intermediate **10**, via fragmentation of **9** (Scheme 1), in which the disposition of the double bonds is such as to about a facile overlap and interaction as shown in **10**. Protonation of the double bond and bond formation with participation of the oxygen function leads to the desired product possessing the four tertiary methyls and the saturated ketone on a six-membered ring. The simplicity of the reaction mechanism leading to the structure 4,8,9,9-tetramethyltricyclo[5.2.2.0<sup>4,8</sup>]undecan-3-one (**7**) and its compatibility with other pathways leading to structures **2–6**<sup>1,2</sup> argues for its correctness.

Though the carbon skeleton of **7** is unprecedented in terpenoid chemistry, there are previous reports describing the formation of tricyclo[5.2.2.0<sup>4,8</sup>]undecane through an acid catalyzed multistep rearrangement of tricyclo[5.2.2.0<sup>2,6</sup>]undecane.<sup>3,4</sup> The basic hydrocarbontricyclo[5.2.2.0<sup>4,8</sup>]undecane has been synthesized.<sup>5</sup>

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