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One -Pot Synthesis of Optically Pure Tricyclo[5.3.1.0 ^{3,8}]undecanes Involving a Novel Triple Michael-Dieckmann Reaction

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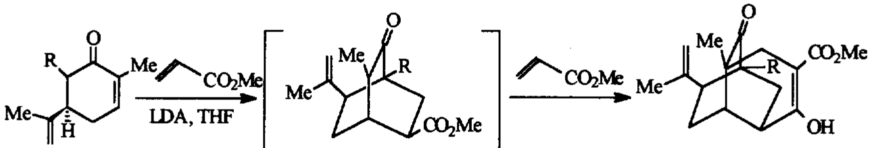
Abstract : Tricyclo-undecane **5** or **6** has been synthesised through sequential triple Michael-Dieckmann reaction of carvone (**1**) or methylcarvone (**2**) with methyl acrylate.

The importance of one-pot synthesis of complex, stereochemically defined structural frameworks involving multi-step and multi-component reactions cannot be overemphasised. Tandem Michael or Diels-Alder reactions have proved very useful in this context, allowing easy access to a number of bridged ring carbocyclic compounds.[1] The application of such reactions to the readily available, optically pure α, β-unsaturated ketones like carvone (**1**) or methyl carvone (**2**) is potentially useful for the construction of the desired optical isomers of complex natural products.

Herein we report an unusually efficient one-pot synthesis of the tricyclo[5.3.1.0 ^{3,8}]undecane system, the structural framework of seychellane, patchouli alcohol and related natural products.

When methyl carvone (**2**) [a mixture of diastereomers prepared from (-)-**1**] was treated with two equivalents of methyl acrylate in presence of one equivalent each of lithiumdiisopropylamide and hexamethylphosphoramide,[2] **6** could be isolated in 44% yield. The structure, initially established by spectral analysis, [3] was confirmed by a single crystal X-ray diffraction study [4] (An ORTEP diagram is presented in Fig. 1). Similarly **5** was prepared from (-)-**1** in 40% yield (**Scheme - 1**).



1, R =H
2, R =Me

3, R = H
4, R = Me

5, R= H
6, R= Me

Scheme-1

The formation of the undecane keto-enol ester **5** or **6** from the substrate **1** or **2**, as shown in **Scheme-1**, conceivably arises through the respective intermediate bicyclo[2.2.2]octanone **3** or **4**. The intermolecular Michael addition of **1** or **2** with methyl acrylate followed by an intramolecular Michael addition of the resulting anion generates the respective intermediate[5] **3** or **4**, which undergoes an additional Michael reaction with methyl acrylate and successive Dieckmann cyclisation leading to the tricyclic system **5** or **6**.

In essence, the effective sequence of single-pot reactions occurring in a co-operative manner, reported in the present communication, represents a remarkably simple synthetic entry to the functionalised tricyclic system *en route* to a few complex natural products.

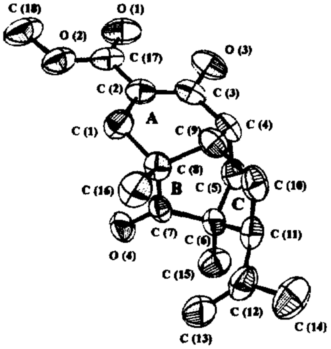


Fig1: **ORTEP** diagram of **6**

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REFERENCES AND NOTES

1. Ihara, M.; Fukumoto, K. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1010-1022.
2. Reaction carried out in tetrahydrofuran at -20 °C to room temperature for 6 hrs.
3. Selected data for **5** and **6:**
   5: m.p. 103-104° C; $[\alpha]_D^{25} = -43.52°$ (*c* 0.85, $CHCl_3$) ; IR (KBr, cm^{-1}): 1716, 1663, 1625; δ_H ($CDCl_3$) : 1.10 (s,3H),1.75 (s, 3H), 1.75-1.86 (m, 1H), 1.93 and 2.80 (2x1H d, *J* 16Hz), 1.95-2.01 (m, 3H), 2.24 (ddd, *J* 1.6, 11.4 and 14.0 Hz, 1H), 2.47-2.65 (m, 3H), 3.73 (s, 3H), 4.73 and 4.75 (2x1H s) and 11.88 (s, 1H); δ_C ($CDCl_3$) : 220.0, 174.2, 172.3, 147.2,109.7, 94.0, 51.3, 45.7, 44.8, 42.3, 37.3, 36.0, 33.4, 24.4, 22.5 and 21.8; EI-MS : m/z 290 (M^+).
   6: m.p. 104-105° C; $[\alpha]_D^{25} = -42.58°$ (c 1.47, $CHCl_3$); IR (KBr, cm^{-1}): 1708, 1663, 1626; δ_H ($CDCl_3$) : 1.03 (s, 3H), 1.19 (s, 3H), 1.69 (s, 3H), 1.52 (dd, *J* 14 and 3 Hz, 1H), 1.85 (ddd, *J* 14, 5 and 3 Hz, 1H), 1.94-2.22 (m,3H), 2.00 and 2.84 (2x1H d, J 16Hz), 2.35 (dd, *J* 12 and 5 Hz, 1H), 2.60 (dt, J 12 and 3 Hz, 1H) 3.73 (s, 3H), 4.46 and 4.77 (2x1H s) and 11.86 (s, 1H):δ_C ($CDCl_3$) : 221.2, 174.5, 172.2,146.2, 110.8, 93.7, 51.3, 49.0, 45.6, 44.6, 43.0, 37.3, 36.8, 34.2, 26.8, 23.2 and 18.3; EI-MS: m/z 304 (M^+).
4. Details will be published elsewhere.
5. Zhao, R.-B. , Zhao, Y.-F., Song, G.-Q.; Wu, Y.-L. *Tetrahedron Lett.* **1990**, *31*, 3559-3562.

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