

The dimerisation of 5,6-dimethoxy-indene

Braulio M. Fraga* and Inmaculada Cabrera

Instituto de Productos Naturales y Agrobiología, CSIC, PO Box 195, 38206 La Laguna, Tenerife, Canary Islands, Spain and Instituto Universitario de Bio-Orgánica 'Antonio González', Universidad de La Laguna, Tenerife, Spain

J. Chem. Research (S),
2003, 252-253
J. Chem. Research (M),
2003, 0530-0540

The reaction of 5,6-dimethoxy-indanol with acids or with triphenylphosphine-carbon tetrachloride afforded several dimeric compounds; in the dimerisation of 5,6-dimethoxy-indene with $\text{SiO}_2\text{-AgNO}_3$ only a single dimer was obtained.

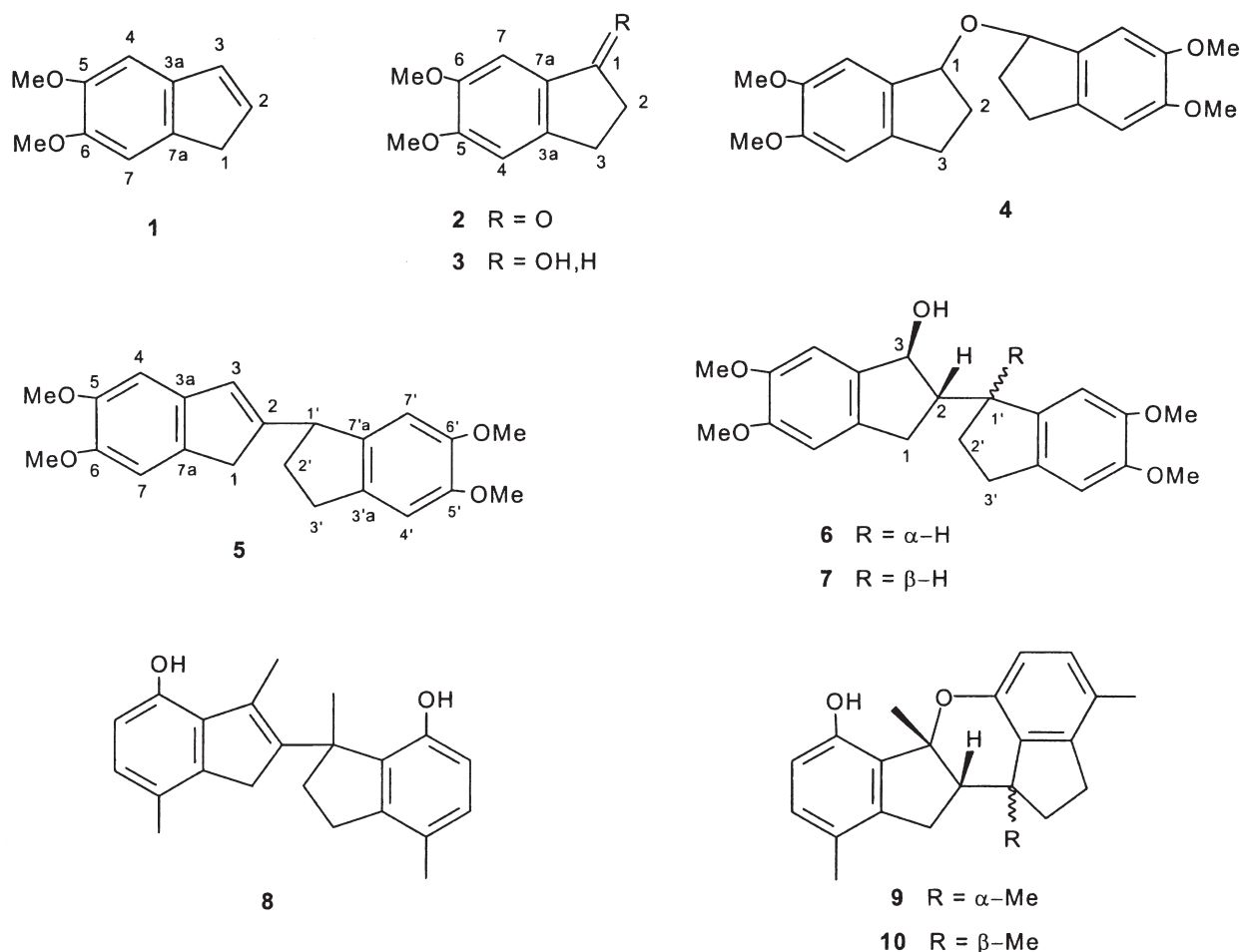
Keywords: 5,6-dimethoxy-indene, triphenylphosphine-carbon tetrachloride, $\text{SiO}_2\text{-AgNO}_3$

In previous work we have studied the dimerisation of precocene II (6,7-dimethoxy-chromene) with Lewis acids.¹ Continuing with this work we have carried out studies of the dimerisation of 5,6-dimethoxy-indene (**1**), which are described herein.

Compound **1** was prepared as follows: (a) reduction of 5,6-dimethoxy-1-indanone (**2**) with lithium aluminum hydride and treatment of the alcohol **3** formed with 4M HCl gave 5,6-dimethoxy-indene (**1**) and the dimers **4-7**. (b) The indanone **2** was reduced with lithium aluminum hydride to give dimethoxy-1-indanol² (**3**) and a small amount of the symmetrical dimer **A** (**4**). Chromatography on silica gel of the mixture increased the formation of **4**. Treatment of the alcohol **3** with triphenylphosphine in carbon tetrachloride-pyridine gave **1** and dimer **B** (**5**). On the other hand, when 5,6-dimethoxy-indene (**1**) was treated with silica gel impregnated with silver nitrate, a Lewis acid, only the dimer **5** was obtained.

The ¹H NMR spectrum of the symmetrical dimer **A** (**4**) ($\text{C}_{22}\text{H}_{26}\text{O}_5$) was very similar to that of the alcohol **3**. Thus, H-4 resonates at δ 6.77 in both compounds, H-7 at δ 6.88 (6.95 in the alcohol), and one of the H-2 appears at δ 2.15 (m) (1.96 in **3**). The other H-2 is at δ 2.49 (m) (2.51 in the alcohol). The geminal proton to the ether function appears as a doublet of doublets at δ 5.12 with couplings of 9 and 5 Hz (δ 5.21, br s, in **3**). Other signals observed in the spectrum were H-3 at δ 2.79(m) and 3.05 (m), H-4 at δ 6.77 and the methoxy groups at δ 3.86 and 3.87. ¹H NMR proof of the dimeric structure of this compound was provided by the observation in the HMBC spectrum of a two bonds correlation between H-1 and C-1. Structure **4** represents the *meso* and/or racemic forms.

Dimer **B** (**5**) showed in the HRMS spectrum the molecular ion at 352.1647 ($\text{C}_{22}\text{H}_{24}\text{O}_4$). This compound had been prepared by dehydration of **3** with thionyl chloride or oxalyl chloride and an erroneous structure had been assigned.^{2,3} Later,⁴



* To receive any correspondence. E-mail: bmfraga@ipna.csic.es

this dimer was obtained by treatment of the indanone **2** with aluminum trichloride and subsequent Clemmensen reduction, and its structure was corrected to **5**, which has now been confirmed herein by assignment of the ^1H and ^{13}C NMR spectra, using 2D NMR data (COSY, HSQC and HMBC).

The other two dimeric compounds, dimers C (**6**) and D (**7**), were isomers ($\text{C}_{22}\text{H}_{24}\text{O}_5$) and had a similar ^1H NMR spectrum. Structure **6** was assigned to the more abundant of them. Its ^1H NMR spectrum showed four aromatic protons and four methoxy groups, which explained the existence of four oxygens of the five present in the molecule. The fifth oxygen must be part of a secondary alcohol group, because its geminal proton was observed at δ 5.09 (t, $J = 6.4$ Hz). Irradiation of this hydrogen, using double resonance experiments, transformed a septet at δ 2.70 into a double doublet. Alternatively, irradiation of this second signal collapsed the first into a broad singlet, transformed two double doublets, resonating at δ 2.51 and 2.88, into two doublets and converted a double doublet at δ 3.60 into a triplet. This indicated a partial structure of the type $-\text{CHOH}-\text{CH}(\text{CHR}_2)-\text{CH}_2-$. The corresponding carbon resonances of this group appear at δ 79.9 (C-3), 54.3 (C-2) and 32.6 (C-1), respectively. These data fixed the structure of the hydroxylated indane part of the molecule. Other non-aromatic carbons resonated at δ 46.5 (C-1), 28.6 (C-2) and 31.4 (C-3). Their corresponding hydrogen resonances were H-1' at δ 3.60 (dd, $J = 13.4$ and 6.7 Hz), H-2' at δ 1.81 (m) and 2.21 (m) and H-3' at δ 2.51 (dd, $J = 15.5$ and 8 Hz) and 2.88 (dd, $J = 15.5$ and 8.5 Hz), indicating the existence of a $-\text{CH}-\text{CH}_2-\text{CH}_2-$ group. Furthermore, the resonance parameters of the hydrogens at C-2' and C-3' were similar to those described for 6-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene.⁵ Thus, the structure of this dimer was determined as the racemate **6** and confirmed by 2D NMR data.

The chemical shift and form of resonance of H-4, H-7 and H-3 in the second isomer **7** (dimer D), which also represents a racemate, were identical with those of **6**, indicating a similar stereostructure for the 3α -hydroxy-indane part in both molecules. Consequently these two isomers must be epimeric at C-1'.

In relation to the relative stereochemistry of dimers C (**6**) and D (**7**), a *cis* relationship was assigned to H-2(β) and H-3(β), considering the coupling value ($J = 6.4$ Hz) observed in the ^1H NMR spectra of both compounds. The calculated coupling constants were 7.4 and 8.3 Hz for the *cis* and *trans* stereochemistry, respectively. Both dimers C (**6**) and D (**7**) were transformed into dimer B (**5**) over time.

New Zealand authors⁶ have studied the dimerisation of 3,7-dimethyl-1H-inden-4-ol with acids obtaining the dimers **8–10**, which in the acid medium are in an equilibrium mixture. These dimers are comparable to compounds **5–7** now obtained by us. On the other hand, dimers **9** and **10** have the same stereochemistry at C-2,C-3 and are epimeric at C-1'. The change of stereochemistry of the methyl over this carbon from **9**(α) to **10**(β) produced in the ^{13}C NMR spectrum shifts to lower field of C-1 (from δ 31.5 to 34.0) and at higher field of C-2 (from δ 58.8 to 56.1). These effects have now also been observed for the change of stereochemistry of H-1' of (**6**)(α) to (**7**)(β), from δ 32.6 to 35.2 at C-1 and from δ 54.3 to 50.3 at C-2, respectively. Thus, dimers C (**6**) and D (**7**) should have the same stereochemistry at C-1' as **9** and **10**, respectively.

Received 15 October 2002, accepted 20 May 2003

Paper 02/1604

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