

Synthesis and Structure of 7-Methyl-2-(4'-methyl-2',3'-dihydro-1'H-inden-1'-yl)-1H-indene†

Albertina G. Moglioni, Dora G. Tombari and Graciela Y. Moltrasio Iglesias*

Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, (1113), Buenos Aires, Argentina

We report research to find better conditions for the dehydration of 4-methylindan-1-ol to render 4-methylindene and 7-methyl-2-(4'-methyl-2',3'-dihydro-1'H-inden-1'-yl)-1H-indene.

A suitable starting material for the preparation of several pterosines¹ is the 4-methylindene **1**. We have previously reported the synthesis of 5,6-dimethoxyindene from 5,6-dimethoxyindan-1-ol with thionyl chloride in benzene at 0 °C,² so the same reaction was performed with 4-methylindan-1-ol **2**, but the reactions products were a complex mixture from which a compound of molecular weight 260 was isolated. Bearing in mind that a dimeric compound had been obtained when 5,6-dimethoxyindan-1-ol was treated with toluene-*p*-sulfonic chloride or mesityl chloride,² and comparing MS and NMR spectra, the structure of 7-methyl-2-(4'-methyl-2',3'-dihydro-1'H-inden-1'-yl)-1H-indene **3** was assigned tentatively to the compound of M_w 260. The formation of such a product was rationalized within the framework of the previously proposed mechanism for similar compounds (see Scheme 1).³

But, taking into account that the benzylic carbocations involved in the reaction could be transposed, several other isomers are possible (e.g. **4–7**).

Structure **3** was confirmed by employing 2D NMR techniques (Fig. 1). The ¹H–¹H and ¹H–¹³C correlation spectra were measured using COSY and HSQC procedures

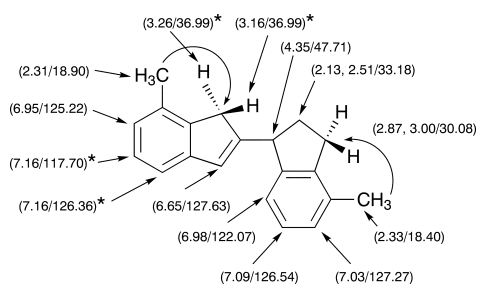
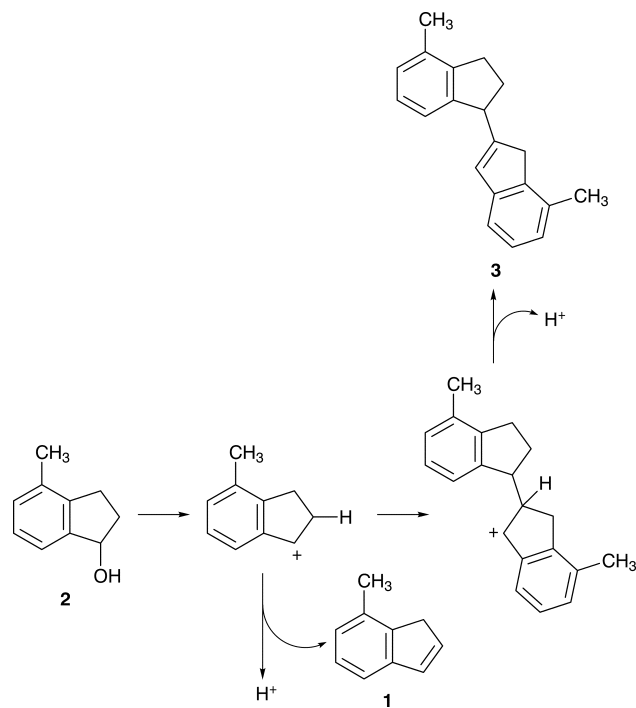


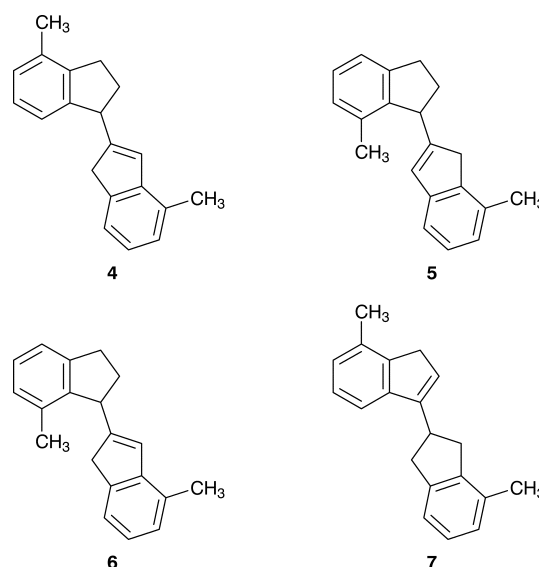
Fig. 1 *Interchangeable

respectively. With these techniques were elucidated the connectivity of the carbon atoms to which the protons were attached. The HH NOESY experiment showed the proximity of the two methyl-H atoms (at δ 2.31 and 2.33) to the benzylic methylene protons. This confirmed the substitution system of **3**. The position of the double bond was also evaluated with an HH NOESY experiment. The lack of spatial connectivity between the olefinic proton and the benzylic methylene H-atom let us rule out isomer **7**.

Smooth conditions have been described for the dehydration of indan-1-ols.⁴ In 1963, Elvidge and Foster,⁵ suggested the preparation of indenenes from the reaction of indan-1-ols with a few crystals of toluene-*p*-sulfonic acid (PTSA). However, when we repeated the procedure only the dimeric product **3** was obtained. In 1977, Woodward *et al.*⁶ quantified the amount of PTSA for several tetrasubstituted indan-1-ols, but when we employed their conditions with the 4-methylindan-1-ol **2**, the alcohol was recovered without modification.



Scheme 1



*To receive any correspondence.

†This is a Short Paper as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1

Experiment	M (PTSA)/mg ^a	Benzene/ml	Reflux time	Products (%)
1	30	75	10 min	Polymers
2	20	75	10 min	3 (35), 2 (25), 1 (14)
3	4	100	10 min	2 (100)
4	4	100	100 min	2 (40), 3 (40)
5	4	200	150 min	1 (60)
6	10	100	180 min	1 (80)
7	100	100	24 h	3 (90)

^aFor each reaction 1 g of 4-methylindan-1-ol was used.

We now report research to find better conditions under which the yields of the dimeric compound and the indene could be maximized and Table 1 summarizes our results.

Experimental

Melting points are uncorrected, and were determined on a Thomas Hoover apparatus. ¹H NMR and ¹³C NMR were recorded on a Bruker AC400 spectrometer. The mass spectrum was recorded on a Varian CH7A. Satisfactory microanalysis was obtained for compound **3**.

4-Methylindene 1.—4-methylindan-1-ol (1 g), PTSA (10 mg) and benzene (100 ml) were heated at reflux for 180 min. Benzene was then distilled off (30 °C, 30 mmHg) and the residual product was isolated by distillation *in vacuo* (64–66 °C, 2 mmHg, lit.,⁵ 88 °C, 13 mmHg).

δ_{H} (CDCl₃) 2.50 (3 H, s, CH₃); 3.40 (2 H, br s, HC-3); 6.65 (1 H, br d, *J*_{1,2} 5.60, HC-2); 7.00–7.60 (4 H, m, HC-1 and ArH). δ_{C} (CDCl₃) 18.4; 37.7; 118.5; 125.6; 126.4; 132.6; 133.4; 142.1; 144.3.

7-Methyl-2-(4'-methyl-2',3'-dihydro-1'H-inden-1'-yl)-1H-indene 3.—To a solution of 4-methylindan-1-ol (1 g, 6.75 mmol) in benzene (100 ml), PTSA (100 mg) was added. The solution was stirred at reflux for 24 h, then washed with 5% aqueous NaHCO₃ (2 × 30 ml) and water (2 × 30 ml), dried (Na₂SO₄) and evaporated to dryness. The residue was purified by flash chromatography (hexane:ethyl acetate, 4:1) to give 790 mg (yield 90%). Mp (ethanol) 98–99 °C. ν/cm^{-1} (neat): 2900, 1580 and 1450. MS, EI 261 (M⁺+1, 11.4); 260 (M⁺, 50.5); 259 (2.0), 131 (100) (Found: C, 92.40; H, 7.91. C₂₀H₂₀ requires C, 92.26; H, 7.74%).

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