J. Chem. Research (S), 1998, 606–607†

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

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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)-1*H*-indene.

A suitable starting material for the preparation of several pterosines[1] 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)-1*H*-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–^{13}C correlation spectra were measured using COSY and HSQC procedures 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**.

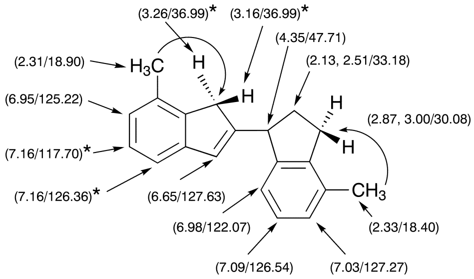
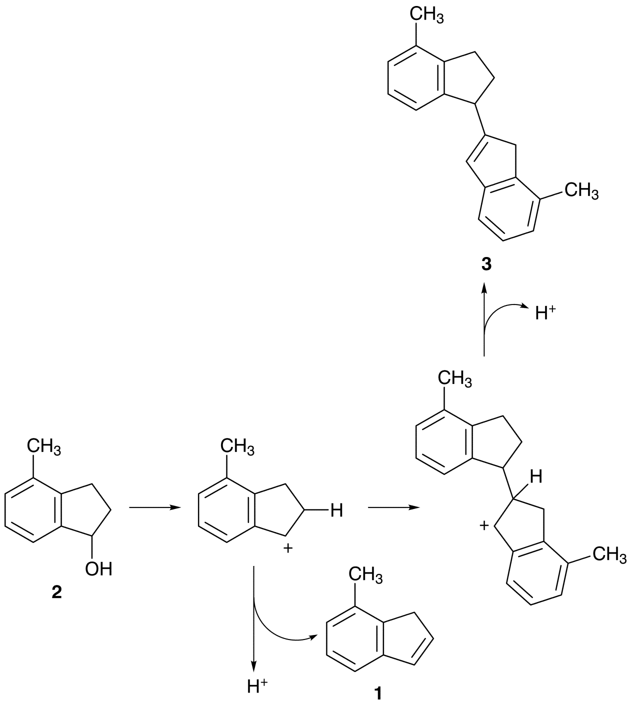
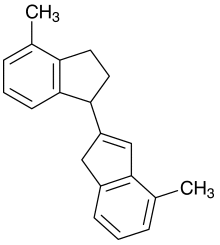


Fig. 1 *Interchangeable



Scheme 1

Smooth conditions have been described for the dehydration of indan-1-ols.[4] In 1963, Elvidge and Foster,[5] suggested the preparation of indenes 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.



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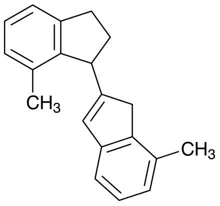

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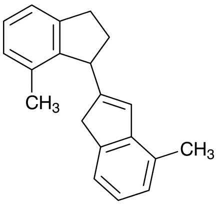

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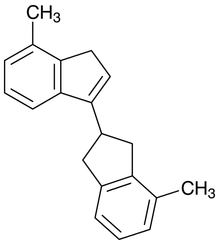

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

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)

[a] For 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. ^{1}H NMR and ^{13}C 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 ($CDCl_3$) 2.50 (3 H, s, CH_3); 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 ($CDCl_3$) 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 $NaHCO_3$ (2 × 30 ml) and water (2 × 30 ml), dried (Na_2SO_4) 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. $C_{20}H_{20}$ requires C, 92.26; H, 7.74%).

We express our sincere gratitude to Dr Teodor Parella from Universitat Autonoma de Barcelona, Spain, for the NMR spectra. This work is part of a Research Project supported by the CONICET and SECYT (UBA).

Received, 9th December 1997; Accepted, 1st June 1998
Paper E/7/08862K

References

1 (*a*) D. G. Tombari, A. G. Moglioni and G. Y. Moltrasio Iglesias, *Org. Prep. Proc. Int.*, 1995, **27**, 679; (*b*) A. G. Moglioni and G. Y. Moltrasio Iglesias, *An. Asoc. Quim. Argent.*, 1997, **85**, 77.
2 (*a*) W. Huckel, M. Sachs, J. Yantschulewitsch and F. Nerdel, *Liebigs. Ann. Chem.*, 1935, **518**, 155. (*b*) Z. Gorin, M. J. Heeg and S. Mobashery, *J. Org. Chem.*, 1991, **56**, 7186. (*c*) D. G. Tombari, A. G. Moglioni and G. Y. Moltrasio Iglesias, *An. Quim. de la Real Sociedad Españula de Quimíca.*, 1992, **88**, 722.
3 (*a*) W. E. Noland, L. L. Landucci and J. C. Darling, *J. Org. Chem.*, 1979, **44**, 1358; (*b*) B. R. Davies, S. J. Johnson and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2545.
4 (*a*) M. Braun and C. Bernard, *Liebigs. Ann. Chem.*, 1985, 435; (*b*) F. McCapra, P. D. Leeson, V. Donovan and G. Perry, *Tetrahedron*, 1986, **42**, 3223.
5 (*a*) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1963, 590; (*b*) 1964, 981.
6 R. B. Woodward and T. R. Hoye, *J. Am. Chem. Soc.*, 1977, **99**, 8007.