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STABLE 3a-METHYL-3a<u>H</u>-INDENES

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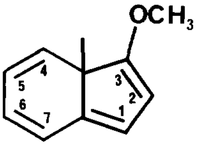
Abstract: A "push-pull" stabilized 3a-methyl-3aH-indene **1** and the first 3aH-indenoquinone **7** have been synthesized and characterized.

3-methoxy-3a-methyl-3aH-indenes have both theoretical and practical importance. We have demonstrated their utility in recent syntheses of tricyclic [10]-annulene and [10]-annulenol[1] . Investigation of their physical properties has been impeded, however, by their facile decomposition in air and thermal instability above room temperature. The reactivity of 3aH-indenes would decrease, we reasoned, if an electron withdrawing substituent was added to the parent structure in order to remove electron density from the electron rich, hence reactive ring system. Ideally, we wanted to place such a substituent onto C-4, so that electron release from the methoxy group and the highest degree of electron delocalization throughout the periphery would be achieved.



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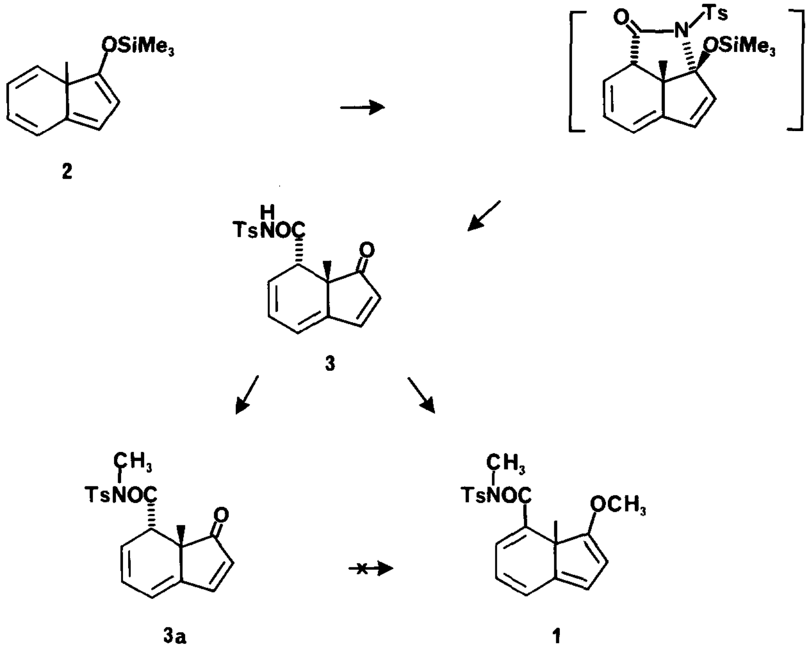
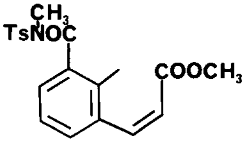
We obtained such a "push-pull" stabilized 3a-methyl- 3aH-indene **1** in a two step synthesis from the parent compound **2**, which was generated in situ at 0°C, as we described before. Thus addition of excess tosylisocyanate to the etheral solution of **2** and then reflux for 2 hours gave, after standard work-up, 46% yield of **3**[2], which was then treated with 2.2 eq of KH/18-crown-6 in dry DME at -23°C. Quenching of the deep blue dianion with 2.2 eq. of methyl fluorosulphonate generated a red solution, which upon reaching room temperature was filtered through celite, evaporated to a small volume, diluted with ether and washed with water. Chromatography on basic alumina gave a low yield (15%) of **1**, as a red oil[3]. Interestingly, quenching of the anion generated from **3a**[4] with methyl fluorosulphonate did not result in the formation of **1**.



In accord with the prediction, compound **1** was stable in chloroform solution for a few days, but when neat it decomposed to the cis-cinnamic acid 4[5] within a few hours. Otherwise, it underwent the range of reactions typical of 3a-methyl-3aH-indenes like [1,5] sigmatropic methyl shift in refluxing benzene leading to the indene **5**[6] and formation of the [8+2] cycloadduct **6**[1] on treatment with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).



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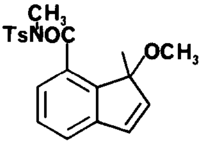

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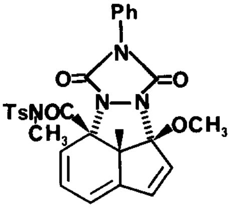

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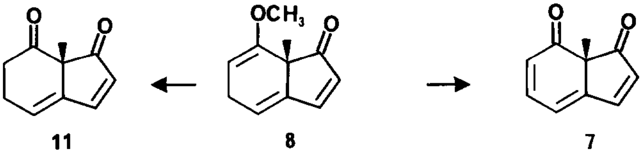
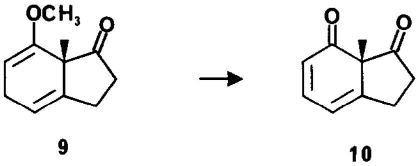
The 3aH-indenoquinone 7[8] was obtained in 25-35% yield as yellow crystals mp.99°C from trienone 8[9] by reaction with PhSeCl in dry DMSO containing 2.2 eq. of water and subsequent treatment of the crude selenide with 10 eq. of 30% hydrogen peroxide at 0°C in methylene chloride. This compound proved to be remarkably stable, considering the lability of indenes having a fully unsaturated periphery broken by the sp^3 hybridised brigdehead carbon. A similar protocol applied to dienone **9**[9] resulted in generation of **10**[10] in $CDCl_3$. Interestingly, this compound was not sufficiently stable to permit isolation, while isomeric **11**[11] obtained from **8** by acidic hydrolysis in THF was isolated in 77% yield and characterized.





Acknowledgements: This project was carried out under the auspices of Prof. C. W. Rees to whom the author is greatly in debt.

References and Notes:

1. Z. Lidert, R. McCague, C. J. Moody, C. W. Rees, JCS Perkin I, **1984**, 383 and R. McCague, C. J. Moody, C. W. Rees, JCS Perkin I,**1984**, 165

2. Compound **3**: mp.(acetone-ether)171°C NMR($CDCl_3$)δppm 1.04 (3H,s,7a-CH_3) 2.41 (3H,s) 3.48 (1H,d,J=6.8Hz,H-7) 6.05 (1H,d,J=4.7,H-4) 6.19 (1H,dd,J=6.8,9 3Hz, H-6) 6.32 (1H,dd,J=4.7,9.3Hz,H-5) 6.32 (1H,d,J=5.7Hz,H-2) 7.27 (2H,d,J=7.8Hz) 7.72 (1H,d,J=5.7Hz,H-3) 7.76 (2H,d,J=7.8Hz)

3. Compound **1** NMR($CDCl_3$)δppm 1.50 (3H,s,3a-CH_3) 2.44 (3H,s,Ts-CH_3) 3.13 (3H,s,NCH_3) 3.68 (3H,s,OCH_3) 5.12 (1H,d,J=2.5Hz,H-2) 5.74 (1H,dd,J=8.8, 6.3Hz,H-6) 5.80 (1H,dd,J=1.2,6.3Hz,H-5) 6.28 (1H,dd,J=2.5,1.0Hz,H-1) 6.48 (1H,ddd,J=8.8,1.2,1.0Hz,H-7) 7.28 (2H,d,J=8.1Hz) 7.73 (2H,d,8.1Hz)

4. Compound **3a**: mp.(ether)144.5°C NMR($CDCl_3$) δppm 1.12(3H,s,7a-CH_3) 2,46(3H,s,Ts-CH_3) 2.95 (3H,s,NCH_3) 4,56 (1H,d,J=5.0Hz,H-7) 6.14 (1H,dd,J=5.0,1.2Hz,H-4) 6.35 (1H,ddd,J=1.2,5.0,7.5Hz,H-6) 6.38 (1H,d,J=5.0Hz,H-2) 6.39 (1H,dd,J=5.0, 7.5Hz,H-5) 7.42 (2H,d,J=8.3Hz) 7.77 (1H,d,J=5.0Hz,H-3) 7.84 (2H,d,J=8.3Hz) calc.($C_{19}H_{19}NO_4S$) C 63.85 H 5.36 N 3.92 found C 64.03 H 5.36 N 3.99 was obtained from **3** in quantitative yield by an overnight reflux in acetone containing a large excess of methyl iodide and potasium carbonate, followed by a standard work-up in ether.

5. Compound **4**: mp. 100-103°C NMR($CDCl_3$)δppm 2.01 (3H,s,Ar-CH_3) 2.45 (3H,s,Ts-CH_3) 3.31 (3H,s,NCH_3) 3.63 (3H,s,OCH_3) 6.08 (1H,d,J=12.1Hz) 7.04 (1H,d,J=12.1Hz) 7.04 (1H,d,J=7.5Hz,Ar-H) 7.15 (1H,t, J=7.5Hz,Ar-H) 7.30 (2H,d,J=8.3Hz,Ts-H) 7.32(1H,d,J=7.5Hz) 7.75 (2H,d,J=8.3Hz,Ts-H)

6. Compound **5**: NMR($CDCl_3$)δppm 1.38 (3H,s,1-CH_3) 2.47 (3H,s,Ts-CH_3) 2.97 (3H,s,NCH_3) 3.18 (3H,s,OCH_3) 6.23 (1H,d,J=5.6Hz,H-3) 6.66 (1H,d,J=5.6Hz,H-2) 7.02 (1H,dd,J=2.5,6.2Hz,H-5) 7.27 (1H,d,J=2.5Hz,H-4 or 6) 7.28 (1H,d,J=6.2Hz,H-4 or 6) 7.36 (2H,d,J=8.1Hz,Ts-H) 7.94 (2H,d,J=8.1Hz,Ts-H)

7. Compound **6**: mp.136-140°C NMR($CDCl_3$)δppm 1.08 (3H,s,7b-CH_3) 2.44 (3H,s,Ts-CH_3) 3.53 (3H,s,NCH_3) 3.64 (3H,s,OCH_3) 5.92 (1H,d,J=9.4Hz,H-7) 6.02 (1H,dd,J=0.5, 5.2Hz,H-5) 6.41 (1H,dd,J=5.2,9.4Hz,H-6) 6.47 (1H,dd,J=0.5,5.7Hz, H-4) 6.90 (1H, d,J=5.7Hz,H-3) 7.3-7.4 (7h,m,ArH) 7.93 (2H,d,J=8.3Hz,ArH) Calc ($C_{28}H_{26}N_4O_6S$) C 61.5 H 4.79 N 10,25 found C 61.5 H 4.77 N 10.16

8. Compound **7**: NMR($CDCl_3$)δppm 1.55 (3H,s,7a-CH_3) 6.23 (1H,d,J=9.5Hz,H-6) 6.40 (1H,d,J=5.6Hz,H-2 or 4) 6.46 (1H,d,J=5.6Hz,H-2 or 4) 7.13 (1H,dd,J=9.5, 5,6Hz,H-5) 7.79 (1H,d,J=5.6Hz,H-3) calc. ($C_{10}H_8O_2$) C 74.99 H 5.10 found C 74.91 H 5.03

9. Z. Lidert and C. W. Rees JCS Chem. Commun.**1982,** 499

10. Compound **10**: NMR($CDCl_3$) δppm 1.48 (3H,s,7a-CH_3) 2.45-2.85 (4H,m,H-2 and 3) 5.85 (1H,d,J=9.6Hz,H-6) 6.21 (1H,dd,J=1.9,5.6Hz,H-4) 7.00 (1H,dd,J=9.6,5.6Hz, H-5)

11. Compound **11**: NMR($CDCl_3$) δppm 1.47 (3H,s,CH_3) 2.25-2.70 (4H,m,H-5 and 6) 6.09 (1H,d,J=5.7Hz,H-2) 6.33 (1H,dd,J=7.0,2.5Hz,H-4) 7.72 (1H,d,J=5.7Hz,H-3)

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