



S0040-4039(96)00634-X

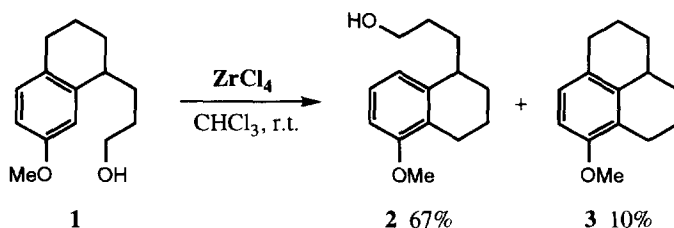
## A Sliding Cyclohexane Rearrangement Mediated by Zirconium Tetrachloride.

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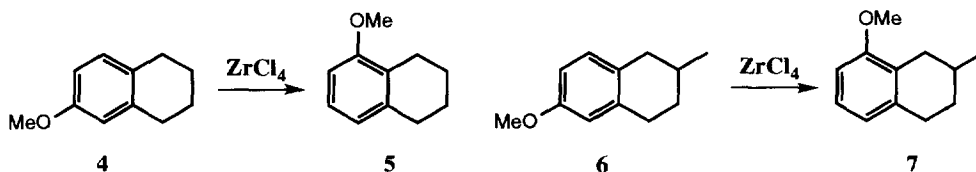
**Abstract:** 6-methoxytetralins may be smoothly transformed into 5-methoxytetralins through the action of zirconium tetrachloride. The rearrangement occurs at ambient temperature in chloroform and proceeds via fragmentation of the carbon - carbon bond para to the methoxy substituent followed by an intramolecular Friedel-Crafts alkylation. Copyright © 1996 Elsevier Science Ltd

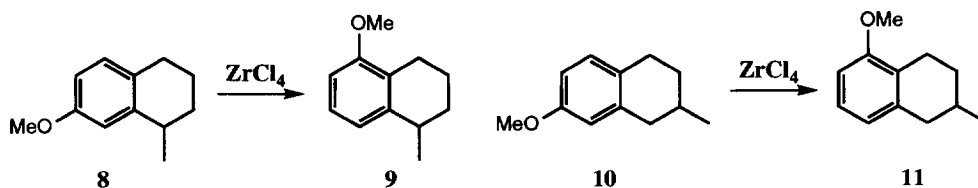
During some investigations directed towards the synthesis of the pseudopterosin family of natural products we observed a curious new rearrangement.<sup>1</sup> For when a chloroform solution of the tetralin **1** was stirred with zirconium tetrachloride at ambient temperature for 2 days the major product was found to be the tetralin **2** (67%) rather than the anticipated hexahydrophenalene **3** (10%).



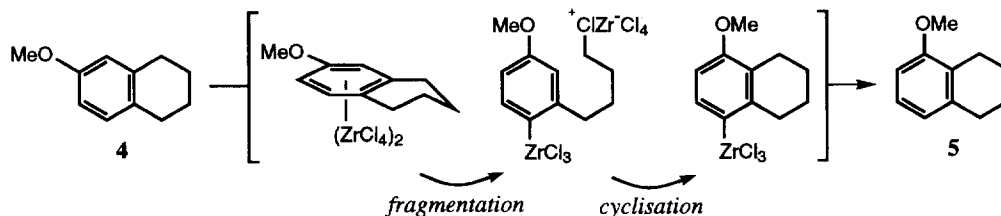
Scheme 1

Intrigued as to the scope and mechanism of this rearrangement we decided to explore the reaction further. The series of tetralins **4**, **6**, **8** and **10** were prepared and subjected to zirconium tetrachloride as before. Each was smoothly transformed into an isomeric tetralin, **5** (2d, 76%), **7** (8d, 71%), **9** (5d, 68%) and **11** (7d, 54%) respectively, with recovered starting material accounting for most of the remaining mass balance.<sup>2</sup>



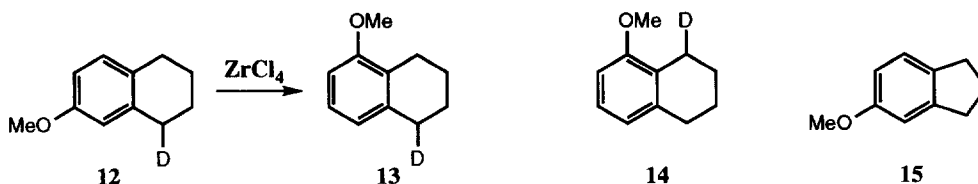


These results, when viewed in conjunction with the recent findings of Solari *et al.*, suggest that this reaction follows the course outlined in Scheme 2.<sup>3</sup> Further evidence in support of this mechanism was provided when the deuterated substrate **12** was converted into the tetralin **13** (59%, 2 days). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13** confirmed the absence from product mixture of the isomeric tetralin **14**.



**Scheme 2**

We have also examined the reaction of 6-methoxytetralin with several other Lewis acids.  $\text{HfCl}_4$  was found to be almost as effective as  $\text{ZrCl}_4$  at promoting this rearrangement while  $\text{TiCl}_4$  gave the reaction at a greatly diminished rate (<15% conversion of **1** to **2** after 7 days). The use of  $\text{FeCl}_3$ ,  $\text{SbF}_5$  and  $\text{AlCl}_3$  lead to decomposition products while  $\text{Sc}(\text{OTf})_3$ ,  $\text{LiCl}$ ,  $\text{YCl}_3$  and  $\text{BF}_3 \cdot \text{OEt}_2$  left the substrate unaltered. Attempts to effect rearrangement of the indane **15** also met with failure. We are presently investigating further aspects of this chemistry in an attempt to discover other reactions facilitated by the ambivalent, hard and soft Lewis acidic character of zirconium and hafnium tetrachloride.



**Acknowledgements** The authors wish to thank The University of Southampton for their financial support (to RFD), the EPSRC mass spectrometry service for their provision of HRMS data, Mrs. J. Street for some n.o.e. studies and Dr. W. Watkins for helpful discussions.

## References

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2. All new compounds gave satisfactory spectroscopic and analytical characteristics.
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(Received in UK 13 March 1996; accepted 3 April 1996)