*First International Electronic Conference on Synthetic Organic Chemistry (ECSOC-1), www.mdpi.org/ecsoc/, September 1-30, 1997*

[A0041]

# Stereospecific Synthesis of cis and trans 1-Oxabicyclo[4,4,0]decanes and 9-Methoxycarbonyl-1-oxabicyclo[4,3,0]nonanes

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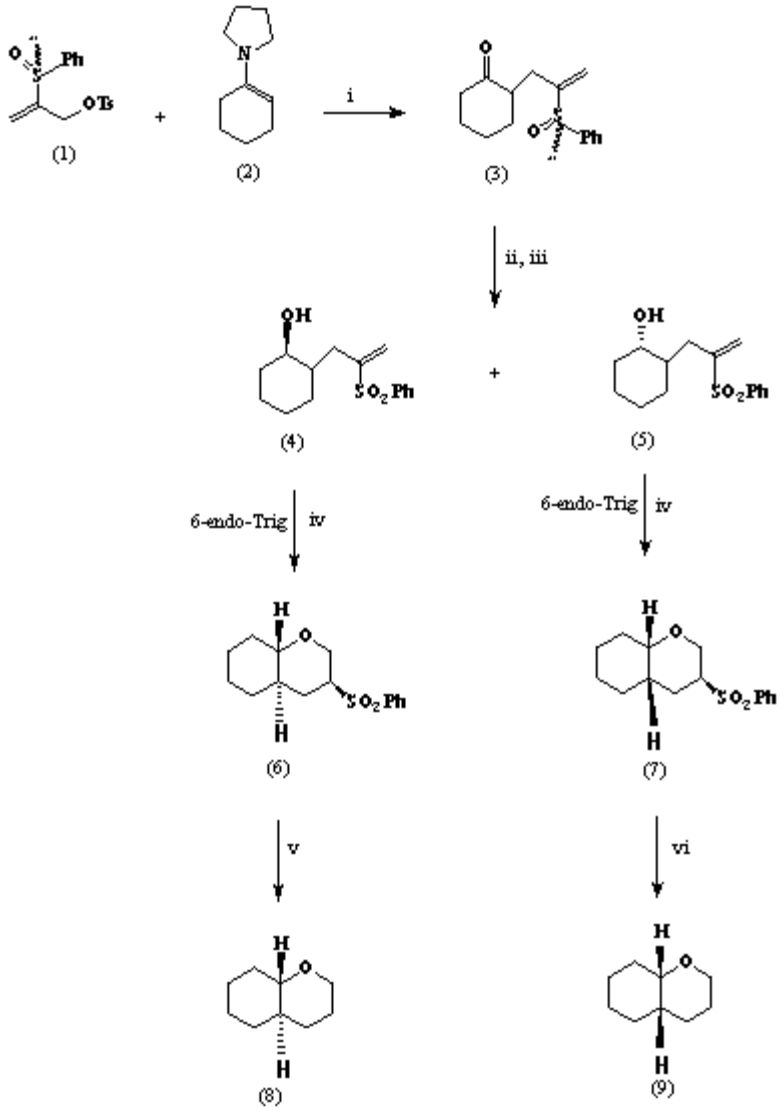
*Received: 14 August 1997 / Uploaded: 14 August 1997*

**Abstract:** 2-(2'-Phenylsulphinylprop-2'-enyl)cyclohexanone (3) and 2-ethoxycarbonyl-2-(2'-phenylsulphinylprop-2'-enyl) cyclopentanone(12) derived from 2-phenylsulphinyl-3--toluenesulphonyloxyprop-1-ene (1) and 2-phenylsulphinyl-3-methanesulphonyloxyprop-1-ene (10) by reaction with 1-pyrroridinylcyclohexene (2) and 2-ethoxycarbonyl cyclopentanone (11) respectively, were reduced with sodium borohydride to afford in each case a racemic mixture of four isomeric hydroxy alkenyl sulphoxides that on oxidation produced in each case two hydroxy alkenyl sulphones cis (4),(13) and trans (5),(14) which separated by column chromatography. Treatment of the hydroxy alkenyl sulphones (4),(5),(13) and (14) with a molar equivalent of base yielded the corresponding 3-phenylsulphonyl cyclic adducts (6),(7),(15) and (16) respectively that were reduced with Raney nickel to afford the requisite cis and trans 1-oxabicyclo4,4,0decanes (8) and (9) and 9-methoxycarbonyl-1-oxabicyclo4,3,0nonanes (17) and (18) in good yields.

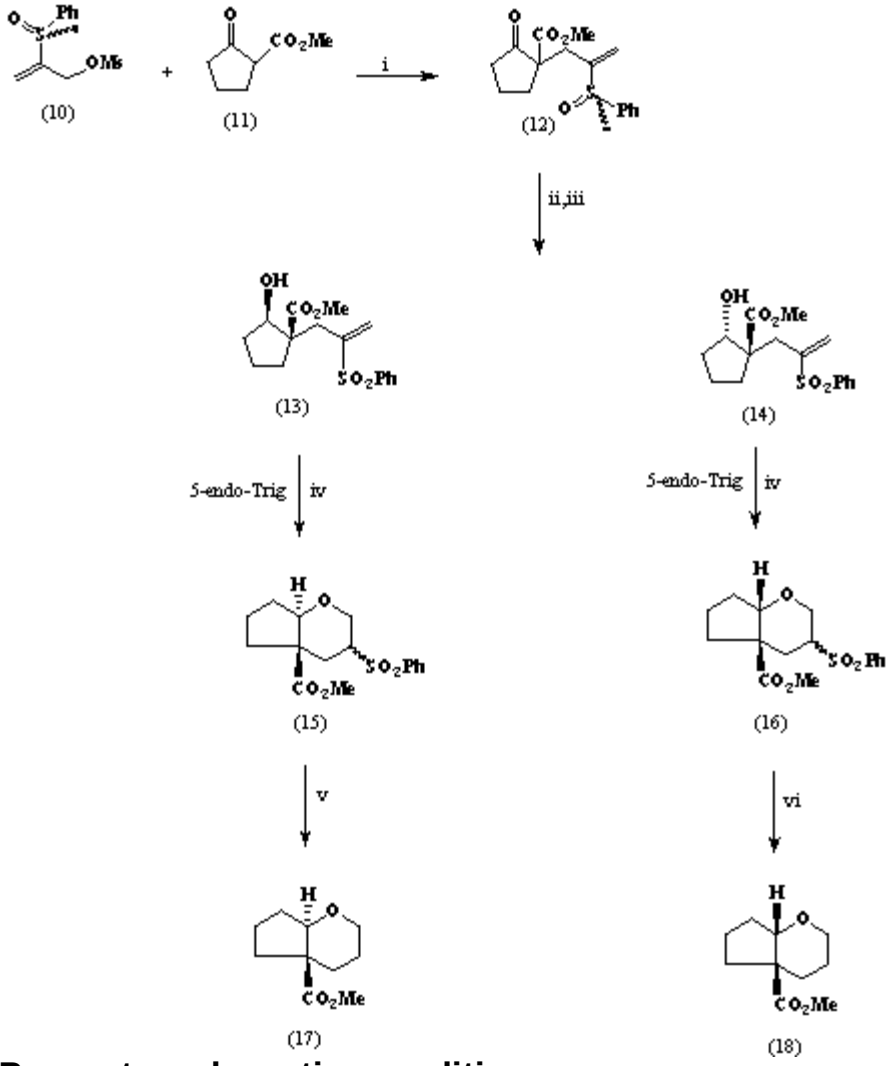
## Introduction

A survey of the literature reveals that although 1-oxadecalins have been synthesised by a variety of methods, they have invariably been obtained as mixtures of cis and trans isomers. As part of our research on the synthetic utility of alkenyl sulphoxides to construct some natural products5, we became interested in the stereospecific synthesis of cis and trans 1-oxadecalins and cis and trans 1-oxahydrindanes. To our knowledge the 1-oxahydridanes(170 and (18) have not been previously synthesised. Our approach makes use of readily obtainable starting alkenyl sulphoxides (1) and (10)[1] and involves cyclisation, oxidation and desulphurisation reactions. The outline of our synthesis is provided in the accompanying two schemes. All of the compounds (9),(10),(17) and (18) had charicteristic penetrating smells.

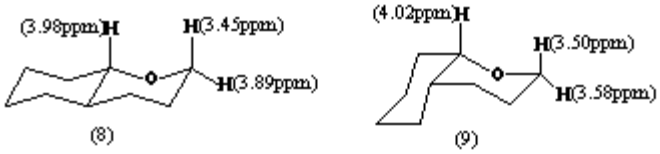


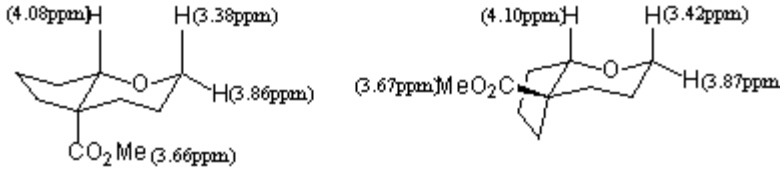

**Reagents and reaction conditions:**

i-DCM / , 2h, 80% ii-$NaBH_4$ / i-PrOH, 12h, quantitative yield iii- m-$ClC_6H_4CO_3H$ / DCM / 0C, 2h, 91-92% iv- K t-BuO / t-BuOH / $N_2$, 56C, 2.5h, 98% v- Raney Ni / EtOH / reflux, 9h, 60% by GLC analysis (6' Harflex), $t_R$ = 12min. vi-Raney Ni / EtOH / reflux, 10h, 65% by GLC analysis (6' Harflex), $t_R$ =12 min.




**Reagents and reaction conditions:**
i-$K_2CO_3$ / THF, RT, overnight, 87% ii-$NaBH_4$ / EtOH,0C, 2h, 66% iii- m-$ClC_6H_4CO_3H$ / DCM / OC, 1h, 99% iv- K t-BuO / t-BuOH /Ar / 50C, 2h, 95% v- Raney Ni / EtOH / / Ar, reflux, overnight, 73% by GLC analysis (7' OV17), $t_R$ = 7.4min. vi-Raney Ni / EtOH / Ar / reflux, overnight, 71% by GLC analysis (7' OV17, 150C), $t_R$ =9.5 min.




**References and Notes:**

1. For the preparation of the tosylate (1) and mesylate (10) see:- M.A.Khan and B.Al-Salaeh, *J. Chem. Research (S)*, 30, 1989; M.A.Khan and B.Al-Saleh, *J. Chem. Research (M)*, 320, 1989.

2. For the theoretical background to assignment of isomers by 1H-nmr spectroscopy see:-E.Eliel, N.L. Allinger, S.J. Angyal and E.A. Morrison, *Conformational Analysis*., Interscience, London, 1966,

3. For the endocyclic cyclisation reactions see:- J.E. Baldwin, *J. Chem. Soc. Chem. Commun.*, 736, 1976.

4. For a general reference on the addition of sulphenic acids to terminal alkynes to produce alkenyl sulphoxised see:- R. Bell, P.D. Cottam, J. Davies and D.N.Jones, J.Chem.Soc. PerkinTrans 1, 2106, 1981.

5. D.N. Jones, P. Brown, M.A. Khan and N. Meanwell, *Tetrahedron Letters*, 24, 405, 1983; D.N. Jones, P. Brown, M.A. Khan and N. Meanwell, J.C.S. Perkin Trans 1, 2049, 1984.

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## Biographical Background

M. Akram Khan was born (12/12/51) in the NWF province of Pakistan and at the age of ten came to England where he has lived ever since. He received his degrees of BSc(Hons)(chemistry)(1975), MSc(1976)(organoelectrochemistry, supervisor:R. Brettle), PhD(1979)(organosulphur chemistry, supervisor: D.N. Jones) from the University of Sheffield,U.K. After his doctorate he went to the University of Kuwait (1979-1990) where he taught for some eleven years before returning back to England (1990) to take up his present position of senior lecturer in organic chemistry at Sheffield Hallam University(1990- ). His current research interests are focussed on quinoline and indazole derived compounds of medicinal importance e.g. arthritis. He is married with three children(two sons Omar-4 and Haris-1 and daughter Alia-3). He is a member on the editorial board of *Molecules* and a member of the Royal society of chemistry,U.K.

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## Comments

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