

Thermal transformation of 1 α - and 1 β -endo and exo-dicyclopentadienyl vinyl ethers (competitive Claisen and Cope systems)

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Dedicated to Professor T. R. Govindachari on the occasion of his 85th birthday
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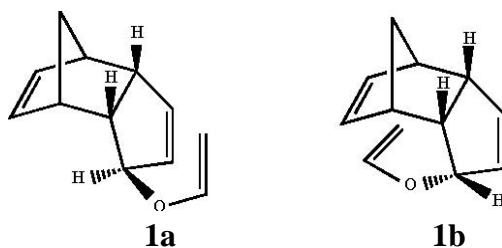
Abstract

1 α -endo-Dicyclopentadienyl vinyl ether undergoes Claisen rearrangement at 110°C, whereas at higher temperatures it suffered a tandem Claisen and Cope rearrangement. In contrast, the epimeric 1 β -vinylether undergoes only Cope, and no Claisen rearrangement. In exo-dicyclopentadienyl series where there is no possibility of Cope rearrangement, only the α -vinylether underwent a smooth Claisen rearrangement.

Keywords: Dicyclopentadienyl vinyl ethers, Claisen rearrangement, Cope rearrangement

Introduction

The stereochemical and regiochemical control of carbon - carbon bond formation offered by the Claisen rearrangement has made this named reaction a powerful synthetic tool. Many variants of this fundamental reaction have been developed to include hetero atoms, lower temperature conditions and better stereo control in the bond forming step. We wanted to exploit the Claisen rearrangement methodology for the stereospecific generation of new chiral centres in the synthesis of linear triquinanes. Linear triquinanes are an important class of sesquiterpene natural products possessing the fused *cis-anti-cis* [6.3.0.0^{2,6}]-undecane carbon skeleton. Some of these compounds have antitumour and antibiotic properties and hence there are many reports on their synthesis¹. As one of the approaches for the synthesis of linear triquinanes, *cis-anti-cis* and *cis-syn-cis*, we sought to investigate the Claisen rearrangement of vinylethers **1a** and **1b**.

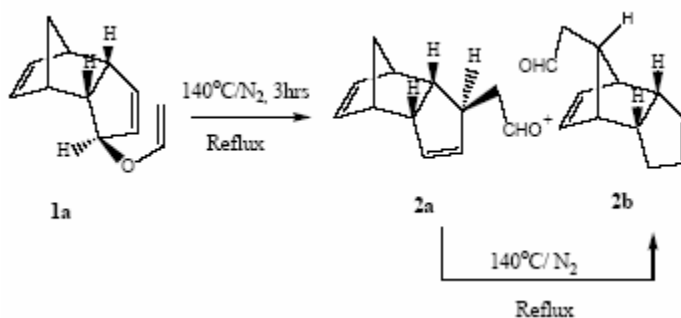


The activation energy for Claisen rearrangement is lower than that for Cope rearrangement². In the light of this fact, one could expect that Claisen rearrangement should occur preferentially in systems where competition between Claisen and Cope rearrangement exists. Indeed this has been observed by Cookson *et.al*³ in acyclic systems. We have encountered an unusual reverse preference *viz.*, a facile Cope migration in preference to Claisen rearrangement, which we describe herein.

While many examples can be found for tandem Claisen - Cope or sequential Claisen rearrangements, only a few examples are known where Claisen and Cope rearrangement mutually compete^{2, 3}. Hence, it was of interest to investigate the thermal rearrangement of the vinyl ethers **1a** and **1b**. The vinyl ethers were prepared from the respective alcohols⁴ by mercuric acetate catalyzed *trans* etherification using *n*-butyl vinyl ether.

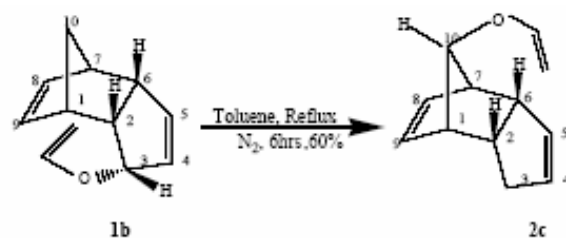
Results and Discussions

Thermolysis of 1α - vinyl ether **1a**⁵ in refluxing xylene for 3 h furnished a mixture of two aldehydic products **2a** and **2b** in 2:1 ratio in 70% yield, which are closely resolved in tlc. When **1a** was refluxed in toluene for 6 h, it gave exclusively only the aldehyde **2a**⁵ in 70% yield (based on recovery of starting material). Attempts to force this reaction to completion by prolonged heating led to the formation of **2b** *viz.*, product of sequential Claisen -Cope rearrangement demonstrating that Claisen rearrangement is preferred over Cope rearrangement in this system, which parallels literature reports³. When pure **2a** was refluxed in xylene for 3 h, it furnished a mixture of **2a** and **2b** in a ratio of 2:1. It is evident from the above experiment that the aldehyde **2b** formed in the thermolysis of vinyl ether **1a** at 140 °C, is due to the sequential Claisen and Cope rearrangement Scheme 1.



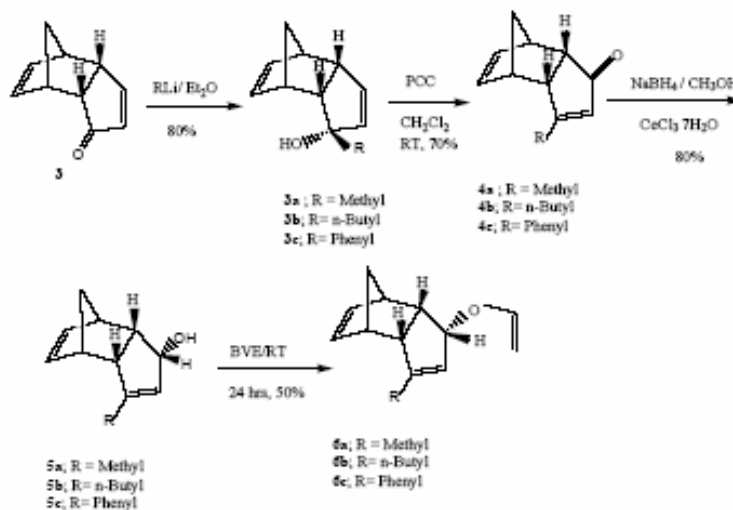
Scheme 1

In remarkable contrast to the behavior of **1a**, the epimeric vinyl ether **1b**⁵ under identical conditions exhibited an exclusive preference for the Cope pathway furnishing the anti ether **2c**⁵. No Claisen product could be observed Scheme 2. The structure of the anti ether **2c** was confirmed by synthesizing it from the literature⁴. The structure of **2c** can be easily distinguished from the starting 1 β -vinyl ether **1b**. The upfield shift 0.8 ppm in the case of H10 (δ 3.8) *viz.*, CH-O-CH=CH₂ in **2c** is due to the shielding of this proton by the norbornene double bond and in **1b** the signal due to the corresponding proton *viz.* H3 appears at δ 4.7. The signals due to H10 and H10' protons of the methylene bridge in **1b**, which resonated at δ 1.4 and 1.2 are absent in **2c**. The signals due to allylic methylene (H3 and H3') protons of **2c** resonated at δ 1.6 and 2.2 (Scheme 2).



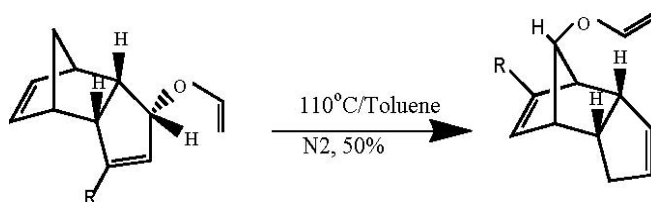
Scheme 2

While all the reported examples in the literature bring forth the propensity of the *endo*-dicyclopentadienyl derivatives to undergo Cope rearrangement, none of these is a Claisen system and hence there is no possibility for a competition between Claisen and Cope rearrangement⁶. In this context, the 1 β -vinyl ether **1b** is a unique system wherein competition between Claisen and Cope rearrangement is possible. In order to test the generality of this reverse preference exhibited by 1 β -vinyl ether **1b**, various γ -substituted vinyl ethers **6a-6c** were prepared as shown in Scheme 3^{7,8}



Scheme 3

When these vinyl ethers were subjected to thermolysis in refluxing toluene, they underwent exclusively Cope rearrangement and furnished the respective anti ethers **7a** – **7c** (Scheme 4 and Table).



6a; R=Methyl

6b; R=n-Butyl

7b; R=Phenyl

7a; R=Methyl

7b; R=n-Butyl

6c; R=Phenyl

Scheme 4

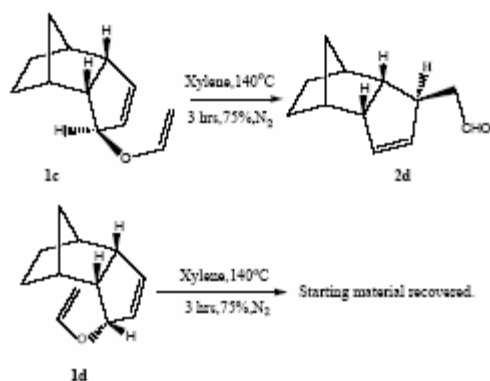
Table 1. Cope rearrangement of 1 β -Dicyclopentadienyl vinyl ethers at 110 °C

S.No	Vinylether	Product(s)	(s)	Yield % *
1	1b	2c		60
2	6a	7a		70
3	6b	7b		60
4	6c	7c		50

*The corresponding amount of starting material was recovered after 6 h.

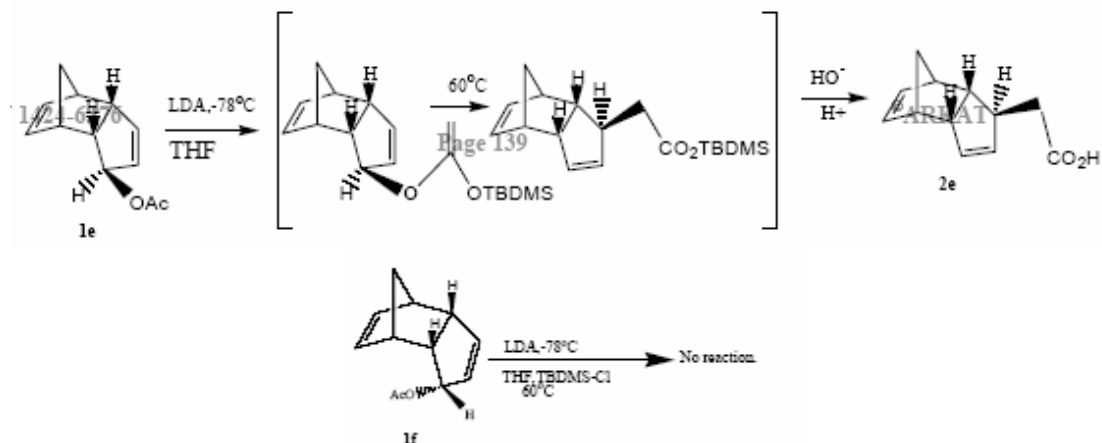
*Represents the isolated yields.

No Claisen products were observed in any of these cases. Inspection of the molecular model of these vinyl ethers show that there is a severe interaction between the norbornene double bond and the vinyl ether double bond, when the vinyl ether moiety is brought into the necessary geometry for the Claisen rearrangement. As a result the vinyl ether takes up other conformations, while no such unfavorable steric interactions exist for the formation of Cope geometry. Because of this the Cope rearrangement is favored over Claisen rearrangement. It is interesting to note that in the case of 8,9 dihydro derivatives **1c** and **1d** which are no longer Cope systems, only **1c**⁵ underwent a smooth Claisen rearrangement furnishing the aldehyde **2d**⁵ where as the epimeric β -vinyl ether **1d**⁵ did not undergo any rearrangement even after refluxing for longer time. In the later case the attainment of transition state for Claisen rearrangement is not possible due to steric reasons (Scheme-5).



Scheme 5

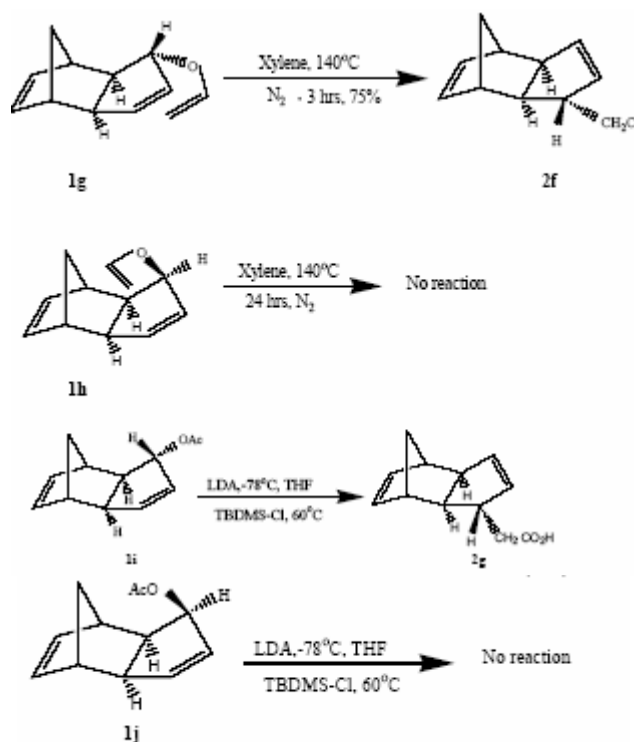
Since the ester enolate Claisen rearrangement occurs under relatively milder conditions compared to thermal Claisen rearrangement, it is of interest to find out whether the Claisen rearrangement of the acetate **1e** under Ireland conditions would stop at the Claisen rearrangement stage. Indeed the α -acetate **1e**, when subjected to Ireland ester enolate Claisen rearrangement⁹, was smoothly transformed to the carboxylic acid **2e** in 60% yield (Scheme 6). The epimeric β -acetate **1f**¹⁰ did not undergo the rearrangement and only starting material was recovered.



Scheme 6

In the case of *exo*-dicyclopentadiene series two allyl moieties are far away from each other. As a result of this, attainment of a six membered cyclic transition state is geometrically impossible in this system and hence there is no possibility of Cope rearrangement¹¹. We observed that the 1α -*exo*-dicyclopentadienyl vinyl ether **1g** underwent a clean Claisen rearrangement and furnished the aldehydic product **2f** in 75% yield⁵. Under identical conditions the epimeric 1β -vinyl ether **1h** remained inert and only the starting material was recovered while under drastic conditions i.e., refluxing in high boiling solvents like *p*-cymene, *o*-dichlorobenzene

no clean transformation was observed. The same trend was also observed in the ester enolate rearrangement of two acetates **1i** and **1j** and only the α acetate **1i** underwent the Claisen rearrangement to give the acid **2g** in 70 % yield whereas the epimeric β - acetate **1j** did not undergo rearrangement Scheme 7.



Scheme 7

Experimental Section

General Procedures. ^1H NMR spectra were recorded at 400 MHz except where indicated at 300 MHz. The ^{13}C NMR were recorded at 100.5 MHz except where indicated otherwise. The chemical shifts of all the NMR spectra are reported in parts per million relative to tetramethyl silane.

General procedure for Cope and Claisen rearrangements

The respective vinyl ether 1 m mole was dissolved in 5 ml of toluene and were refluxed under nitrogen atmosphere for 6 hrs. Solvent evaporated under reduced pressure and the products were purified over neutral alumina using hexane as an eluant. For Claisen rearrangements the vinyl ethers were refluxed with xylene for 3 hrs, solvent evaporated under reduced pressure and the products were purified by flash column chromatography on 230-400 mesh silicagel using 3%

Ethylacetate / Hexane as a eluant.

exo-Tricyclo [5.2.1.0^{2,6}]deca-4,8-dien-*exo*-3-yl-acetate (1i). ¹H NMR (400MHz;CDCl₃; Me₄Si): δ6.15 dd, *J* = 6.0,3.4 Hz (1H); 6.10 dd, *J* = 6.0,3.4 Hz (1H); 5.98 dt, *J* = 5.24,1.74 Hz (1H); 5.83 dt, *J* =5.24, 1.74 Hz (1H); 5.26 m (1H); 2.82 m (2H); 2.57 br s (1H); 2.05 m (4H); 1.35 dt, *J* = 8.55,1.42 Hz (1H); 1.25 d, *J* = 8.55 Hz (1H). ¹³C NMR (100.5 MHz;CDCl₃; Me₄Si) δ171.11 s; 140.17 d; 137.82 d; 137.41 d; 131.93 d; 82.87 d; 53.56 d; 50.75 d; 45.14 d; 43.76 d; 41.97 t; 21.34 q. HRMS:Calc. 190.09938 for C₁₂H₁₄O₂ Found 190.09609.

exo-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-*endo*-3-yl-acetate (1j): ¹H (400MHz;CDCl₃ ; Me₄Si): δ 6.15 dd, *J* = 6.0,3.4 Hz (1H); 6.1 dd, *J* = 6.0, 3.4 Hz (1H); 5.98 dt, *J* = 5.22, 1.74 Hz (1H); 5.83 dt, *J* =5.22, 1.74 Hz (1H); 5.2 m (1H);2.82 m (2H);2.57 br s (1H); 2.05 m (4H); 1.35 dt, *J* =8.53, 1.42 Hz (1H); 1.25 d, *J* = 8.55 Hz (1H). ¹³C (100.5 MHz; CDCl₃; Me₄Si) : δ171.11 s; 140.18 d ; 137.83 d; 137.42 d; 131.94 d; 82.88 d; 53.57 d; 50.76 d; 45.14 d; 43.76 d; 41.97 t; 21.34 q.

endo-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dienyl-*exo*-3-acetic acid. (2e): ¹H (400MHz;CDCl₃; Me₄Si) δ 11.5 br. S. (1H) ; 5.97 d, *J* = 6.28 (1H) ; 5.88 d, *J* =6.28 Hz (1H) ; 5.52 d, *J* =5.8 Hz (1H) ; 5.4 d, *J* =5.8 Hz (1H) ; 3.25 br.s. (1H) ; 2.58 br.s. (1H) ; 2.7 br.s.(1H) ; 2.4-2.4 m (4H) ; 1.5 m (1H) ; 1.2 m (1H) . ¹³C (100.5 MHz;CDCl₃; Me₄Si) 179.17 s ; 135.45 d ; 134.70 d ; 133.00 d ; 132.68 d ; 54.55 d ; 50.09 t; 48.93 d ; 45.81 d ; 44.75 d ; 43.73 d ; 40.74 t. HRMS: Calc. 190.09938 for C₁₂H₁₄O₂ Found 190.10141.

exo-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dienyl-*exo*-3-acetic acid (2g). ¹H (400MHz;CDCl₃; Me₄Si) δ11.5 br. S. (1H) ; 6.05 dd, *J* = 5.8,2.7 Hz (1H) ; 5.95dd, *J* = 5.8,2.7 Hz (1H) ; 5.62 dt, *J* =5.7,2.3 Hz (1H) ; 5.55 dt, *J* =5.7,2.3 Hz (1H) ; 2.2 – 2.6 m (6H); 1.8 m (1H) ; 1.7 d, *J* = 8.3 Hz (1H) ; 1.5 dt, *J* = 8.3,1.4 Hz (1H) . ¹³C (100.5 MHz;CDCl₃; Me₄Si) δ179.42 s ; 137.69 d ; 137.26d ; 135.82 d ; 133.71 d ; 54.05 d ; 49.54 t; 47.48 d ; 45.65 d ; 45.15 d ; 41.88 d ; 41.17 t . HRMS:Calc. 190.09938 for C₁₂H₁₄O₂ Found 190.0928.

5-n-Butyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-*endo*-3-one (4b). ¹H (400MHz;CDCl₃ ; Me₄Si) δ5.9 dd *J* =6.0, 2.5 Hz (1H) ; 5.75 dd, *J* = 6.0, 2.5 Hz (1H) ; 5.69 br. S. (1H) ; 3.26 t, *J* =5.0 Hz (1H) ; 3.18 br. S. (1H) ; 3.0 br. s. (1H) ; 2.8 t, *J* =5.0 Hz (1H) ; 2.2-2.3 m (2H) ; 1.7 dt, *J* =8,10 Hz (1H) ; 1.56-1.52 m (3H) ; 1.3-1.4 m (2H) ; 0.9 t, *J* =7 Hz (3H); ¹³C (100.5 MHz;CDCl₃; Me₄Si) δ 209.82 s ; 182.45 s ; 133.39 d ; 131.63 d ; 131.56 d ; 52.28 t ; 51.28 d ; 49.98 d ; 44.14 d ; 43.56 d ; 32.02 t ; 28.90 t ; 22.43 t ; 13.74 q . HRMS: Calc.202.13576 for C₁₄H₁₈O Found 202.1364.

5-Phenyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (4c) . ¹H (400MHz;CDCl₃ ; Me₄Si) δ7.7 m (2H) ;7.5 m (3H) ; 6.35 br s (1H); 6.0 dd, *J* =5.4, 3.0 Hz (1H) ; 5.65 dd, *J* =5.4, 3 Hz (1H) ; 3.9 t, *J* =4.32 (1H) ; 3.3 br. s (1H) ;3.25 br. s.(1H) ; 3.05 t, *J* =4.4 Hz (1H) ; 1.8 dt, *J* =8.4 Hz (1H) ; 1.7 d, *J* =8.4 Hz (1H). ¹³C (100.5 MHz;CDCl₃; Me₄Si) δ 209.56 s ; 173.94 s ;133.76 s ; 133.52 d; 132.03 d ; 131.03 d ; 129.77 d ; 128.92 d ; 127.09 d; 52.14 d ; 52.03 t ; 47.50 d ; 44.79 d ; 44.31 d HRMS: Calc. 222.10446 for C₁₆H₁₄O Found 222.10482.

5-Methyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-*endo*-3-ol (5a) . ¹H (400MHz;CDCl₃; Me₄Si) δ6.21 dd, *J* =5.66, 2.96 Hz (1H) ; 5.88 dd, *J* =5.66, 2.96 Hz (1H) ; 5.2 dd, *J* =2.6, 1.22 Hz (1H) ;4.6 br s (1H) ; 3.49 m (1H) ; 2.8 -2.98 m (3H); 1.6 s merging with a multiplet (4H) ; 1.4 d, *J*

=8.0 Hz (1H); 1.2 d $J=8.0$ Hz (1H) ^{13}C (100.5 MHz; CDCl_3 ; Me_4Si) 144.78 s; 134.25 d; 133.28 d; 129.78 d; 75.82 d; 68.79 d; 52.27 t; 47.82 d; 45.99 d; 44.53 d; 15.34 q. HRMS: Calc 162.10446 for $\text{C}_{11}\text{H}_{14}\text{O}$ Found: 162.09106.

5-n-Butyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-endo-3-ol (5b). ^1H (400MHz; CDCl_3 ; Me_4Si) δ 6.2 dd, $J=6.0$, 2.5 Hz (1H); 5.82 dd, $J=6.0$, 2.5 Hz (1H); 5.2 t, $J=0.8$ Hz, (1H); 4.65 dd, $J=8$, 1.0 Hz (1H); 3.15 m (1H); 2.9-3.0 m (3H); 1.9 m (2H); 1.3-1.7 m (7H); 0.9 t, $J=7$ Hz (3H). ^{13}C (100.5 MHz; CDCl_3 ; Me_4Si) δ 148.78 s; 134.09 d; 133.08 d; 128.26 d; 75.36 d; 55.38 d; 51.96 t; 47.29 d; 46.06 d; 44.31 d; 29.49 t; 29.43 t; 22.48 t; 13.77 q; HRMS: Calc. 204.151415 for $\text{C}_{14}\text{H}_{20}\text{O}$; Found: 204.151415.

5-Phenyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-endo-3-ol (5c). ^1H (400MHz; CDCl_3 ; Me_4Si) 7.4 m (2H); 7.3 m (2H); 7.25 m (1H); 6.2 dd, $J=5.64$, 3.1 Hz (1H); 5.95 br. s (1H); 5.67 dd, $J=5.54$, 3.1 Hz (1H); 4.8 dd, $J=8.8$, 1.76 Hz (1H); 3.7 ddt, $J=8.4$ Hz (1H); 3-3.2 m (3H); 1.8 d, $J=8.3$ Hz (1H); 1.5 m (2H). ^{13}C (100.5 MHz; CDCl_3 ; Me_4Si) δ 145.7 s; 135.29 s; 134.01 d; 133.89 d; 129.80 d; 128.37 d; 126.77 d; 126.28 d; 75.31 d; 53.56 d; 51.92 t; 47.63 d; 47.13 d; 44.50 d. HRMS: Calc.: 224.1201 for $\text{C}_{16}\text{H}_{16}\text{O}$, Found: 224.11889.

5-Methyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-endo-3-yl vinyl ether (6a). ^1H (400MHz; C_6D_6 ; Me_4Si) δ 6.4 dd, $J=14.64$, 6.83 Hz (1H); 6.3 dd, $J=5.38$, 2.93 Hz (1H); 5.77 dd, $J=5.37$, 2.93 Hz (1H); 5.2 d, $J=1.46$ Hz (1H); 4.6 d, $J=7.8$ Hz (1H) 4.33 dd, $J=14.16$, 1.46 Hz (1H) 4.04 dd, $J=6.84$, 1.46 Hz (1H); 3.0 br.s. (1H); 2.6-2.8 m (3 H); 1.6 d, $J=8.0$ Hz (1H); 1.5 s merging with a multiplet (4H). ^{13}C (100.5 MHz; C_6D_6 ; Me_4Si) δ 151.89 d; 145.14 s; 135.95 d; 130.97 d; 126.76 d; 86.93 t; 81.72 d; 56.48 d; 51.01 t; 46.50 d; 45.64 d; 44.73 d; 15.37 q. HRMS: Calc 188.120115 for $\text{C}_{13}\text{H}_{16}\text{O}$ Found: 188.11967.

5-n-Butyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-endo-3-yl vinyl ether (6b). ^1H (400MHz; C_6D_6 ; Me_4Si) δ 6.4 dd, $J=14.63$, 6.83 Hz (1H); 6.3 dd, $J=5.37$, 2.93 Hz (1H); 5.8 dd, $J=5.37$, 2.93 Hz (1H); 5.35 s (1H); 4.65 d, $J=8.3$ Hz (1H); 4.3 dd, $J=14.7$, 1.46 Hz (1H); 4.0 dd, $J=6.83$, 1.46 Hz (1H); 3.09 br. s (1H); 2.86 m (1H); 2.79 m (1H); 2.7 m (1H); 0.8-1.9 m (11H). ^{13}C (100.5 MHz; C_6D_6 ; Me_4Si) δ 151.89 s; 149.20 s; 135.79 d; 130.98 d; 125.31 d; 86.65 t; 81.57 d; 55.23 d; 51.04 t; 46.08 d; 45.84 d; 44.62 d; 29.91 t; 29.72 t; 22.84 t; 14.0 q.

5-Phenyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-endo-3-yl vinyl ether (6c). ^1H (400MHz; C_6D_6 ; Me_4Si) 7.2-7.5 m (5H); 6.5 dd, $J=14.6$, 6.5 Hz (1H); 6.4 dd, $J=6.3$ Hz (1H); 6.05 m (1H); 5.8 dd, $J=6.3$ Hz (1H); 4.8 d, $J=8$ Hz (1H); 4.4 dd, $J=14$, 1.5 Hz (1H); 4.1 dd, $J=6.5$, 1.5 Hz (1H); 3.45 m (1H); 3.05 m (2H); 2.85 m (1H); 1.62 ddd=dt, $J=8$, 1.5 Hz (1H); 1.3 d, $J=8$ Hz (1H). ^{13}C (100.5 MHz; C_6D_6 ; Me_4Si) δ 151.66 d; 146.43 s; 135.57 s; 135.35 d; 131.36 d; 128.41 d; 127.79 d; 126.44 d; 126.37 d; 86.94 t; 80.99 d; 53.19 d; 50.58 t; 46.67 d; 46.13 d; 44.57 d.

8-Methyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-anti-10-yl vinyl ether (7a). ^1H (400MHz; C_6D_6 ; Me_4Si) δ 6.2 dd, $J=14.16$, 6.35 Hz (1H); 5.5 m (2H); 5.35 m (1H); 4.4 dd, $J=14.65$, 1.49 Hz (1H); 4.03 dd, $J=6.35$, 1.49 Hz (1H); 3.87 ddt, $J=1.46$ (1H); 3.57 m (1H); 3.0 m (1H); 2.8 br. s (1H); 2.54 brs (1H); 2.2 m (1H); 1.8 m (1H); 1.6 s (3H). ^{13}C (100.5 MHz; C_6D_6 ; Me_4Si) δ 150.33 d; 144.04 s; 132.40 d; 130.73 d; 123.37 d; 89.79 d; 88.37 t; 52.41 d; 52.09 d; 48.13 d 38.82 d; 34.15 t; 18.09 q.

8-n-Butyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-anti-10-yl vinyl ether (7b). ¹H (400MHz; C₆D₆; Me₄Si) δ 6.3 dd, *J* = 14.16, 6.84 Hz (1H); 5.55 m (1H); 5.4 s (2H); 4.4 dd, *J* = 14.16, 1.46 Hz (1H); 4.05 dd *J* = 6.85, 1.46 (1H); 3.88 ddt, *J* = 1.95 Hz (1H); 3.6 m (1H); ; 3.08 m (1H); 2.8 br. s. (1H); 2.6 m (1H); 2.2 m (1H); 1.9 m (3H); 1.4 m (4H); 0.97, t *J* = 7 Hz (3H). ¹³C (100.5 MHz; C₆D₆; Me₄Si) δ 150.36 d; 148.83 s; 132.4 d; 130.55 d; 121.83 d; 89.82 d; 88.32 t; 52.44 d; 58.78 d; 47.84 d; 38.53 d; 34.13 t; 31.90 t; 29.31 t; 22.87 t; 14.14 q.

8-Phenyl-endo-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-anti-10-yl vinyl ether (7c). ¹H (400MHz; C₆D₆; Me₄Si) δ 7-7.26 m (5H); 6.2 dd, *J* = 14, 16, 6.35 Hz (1H); 5.98 dd, *J* = 5.71, 3.1 Hz (1H); 5.4 m (1H); 5.33 m (1H); 4.4 dd, 14.16, 1.46 Hz (1H); 4.05 dd, *J* = 6.35, 1.46 Hz (1H); 3.94 ddt, *J* = 1.95 Hz (1H); 3.68 m (1H); 3.3 m (1H); 3.15 m (1H); 2.91 m (1H); 2.2 m (1H); 1.8 m (1H). ¹³C (100.5 MHz; C₆D₆; Me₄Si) δ 150.42 d; 146.64 s; 136.57 s; 132.54 d; 132.61 d; 125.74 d; 123.72 d; 90.06 d; 88.86 t; 52.55 d; 49.25 d; 49.16 d; 39.72 d; 34.22 t.

Conclusions

Our study has been shown that 1β-vinyl ether **1b** undergoes Cope rearrangement in preference to Claisen rearrangement, furnishing the anti ether **2c**⁵. This preference for Cope rearrangement has also been observed with a few other γ-substituted vinyl ethers. In none of these cases, any Claisen rearrangement was observed. In the dihydro series where there is no possibility of Cope rearrangement, the 1α-vinylether **1c** underwent Claisen rearrangement, whereas the 1β-vinylether **1d** remained unchanged even after refluxing for a long time. In exo-dicyclopentadiene series, only the 1α-vinyl ether **1g** underwent a smooth Claisen rearrangement.

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References

1. Metha, G.; Srikrishna, A. *Chem. Rev.* **1997**, *97*, 671.
2. Ziegler, F.E. *Comprehensive Organic Synthesis* Trost, B. M.; Fleming, I.; Paquette, L. A., Ed.; Pergamon press, Oxford, 1991; Vol. 5, 875, and references cited therein.

3. Cookson, R. C.; Rogers, N. R. *J. Chem. Soc. Perkin Trans. I.* **1973**, 2741.
4. Woodward, R. B.; Thomas, J. K. *Tetrahedron* **1959**, 5, 70.
5. Palani, N.; Chadha, A.; Balasubramanian, K. K. *J. Org. Chem.* **1998**, 63, 5318.
6. (a) Antonius, J. Z.; Klunder, S. H.; Zwanenburg, B. *Tetrahedron Lett* **1994**, 35, 2787. (b) Suri, S. C.; Rogers, S. L. *Tetrahedron Lett* **1988**, 29, 4031. (c) Chavan, S. P.; Ethiraj, K. S.; Kamat, S. K. *Tetrahedron Lett* **1996**, 37, 7827. and also see ref 3. d. Mal, D.; Hazra, N. K. *Chem. Commun.* **1996**, 1181.
7. (a) Dols, P. P. M. A.; Verstappen, M. M. H.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1993**, 49, 11353. (b) Dauben, W. G.; Michno, J. *J. Org. Chem.* **1977**, 42, 682. (c) Gemal, A. L.; Luche, J. A. *J. Am. Chem. Soc.* **1981**, 103, 5454.
8. Takano, S.; Inomata, A.; Ogasawara, K. *J. Chem. Soc. Chem Commun* **1989**, 271.
9. (a) Wipf, P. In *"Comprehensive Organic Synthesis"*, Trost, B. M.; Fleming, I.; Paquette, L. A., Ed; Pergamon Press: Oxford, 1991; Vol 5, 827. (b) Pereira, S.; Srebnik, M. *Aldrichim Acta.* **1993**, 26, 17. (c) Ireland, R. E.; Wipf, P.; Xiang, J.N. *J. Org. Chem.* **1991**, 56, 3572.
10. Farina, V. *Tetrahedron Lett* **1989**, 30, 6645.
11. Cookson, R. C.; Issac, N. S.; Szelke, M. *Tetrahedron* **1964**, 20, 714.