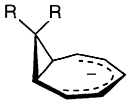
Rearrangements of Tricyclo[5.3.1.0]undecatrienyl Anion; Chemical Evidence Supporting Cyclopropane Ring Circumambulation of Anionic Species

Mitsunori Oda,* Yoshimi Masaki, Yoshimi Okazaki, Takanori Kajioka, Mayumi Izawa, Ryuta Miyatake,
Shigeyasu Kuroda,* and Lawrence T. Scott*†
Department of Materials Chemistry, Faculty of Engineering, Toyama University, Gofuku 3190, Toyama 930
†*Department of Chemistry, Boston College, Merkert Chemistry Center, Chestnut Hill MA 02167-3860, U.S.A.*

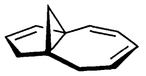
(Received March 10, 1997; CL-970166)

The tricyclic anion **5**, generated from the corresponding hydrocarbon **3** with n-BuLi, undergoes the circumambulatory rearrangement at -78 °C to afford the anion **6**, which stereoselectively reacts with deuterium oxide at low temperature and undergoes further rearrangements to the stable cyclopentadienyl anion derivative **9** at elevated temperature.

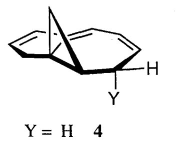
There are several reports on rearrangements in which a cyclopropane ring circumambulates on the periphery of a cyclic polyene or a polyenylium ion.[1,2,3] According to symmetry conservation considerations,[4] such a cyclopropyl migration can thermally proceed regardless of the number of total electrons concerned in the process. However, stereochemical behavior of the migrating group differs depending on the number; the migrating group should invert configuration in processes involving (4n+2) electrons and retain it in those involving 4n electrons. It has been recognized that in general circumambulation occurs much easier in the latter electron system, which displays antiaromatic character and is destabilized relatively to its transition state, than the former electron system.[5] Although many experimental and theoretical studies[3,5] on circumambulatory rearrangements of polyenyl and cationic species have been documented, neither thermal nor photochemical migration of a cyclopropane ring in anionic species has been disclosed yet.[6] For examlpe, two bicyclo[5.1.0]octadienyl anions, **1** and **2**, which are likely to be suitable for detecting a cyclopropyl migration, have appeared in the literature.[7,8] However, Kloosterziel *et al.* concluded that the degenerate circumambulation does not thermally occur in bicyco[5.1.0]octadienyl anion **1**, based on the result of its temperature-independent ^{1}H NMR spectra.[7] Additionally irradiation of solutions of **1** and **2** proved that disrotatory ring opening and closing are the only processes observed under the photochemical conditions.[8,9] Herein we report generation and thermal rearrangements of tricyclic undecatrienyl anions, derived from tricyclo[5.3.1.0]undeca-2,4,9-triene (**3**),[10,11] indicating chemical evidence supporting such cyclopropane ring circumambulation of anionic spieces.



R= H **1**
=CH_3 **2**

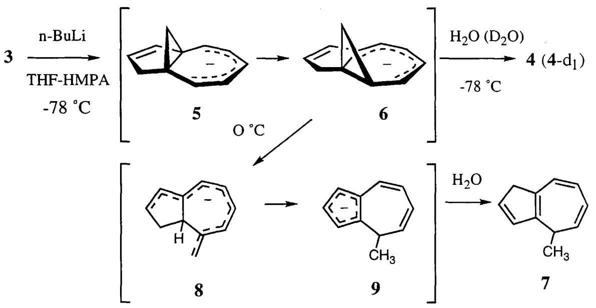


3



Y = H **4**
= D **4**-d$_1$

While treatment of **3** with n-BuLi in THF at -78 °C did not give any coloration of the solution, addition of HMPA as a co-solvent to this mixture resulted in a dark red solution to suggest generation of anionic spieces. Quenching of this reaction solution with water after 20 min at -78 °C gave the rearranged hydrocarbon as sole product in 49% yield. Though this product was an air-sensitive oil, its structure was confirmed as **4** through a combination of two-dimensional measurements and extensive NOE experiments in the ^{1}H and ^{13}C NMR spectroscopy.[12, 13] Quenching of the reaction solution with either D_2O or CH_3OD under the same reaction condition afforded the hydrocarbon containing one deuterium atom. The incorporation of deuterium atom was found to be site- and stereoselective by comparison of the ^{1}H NMR spectrum of the deuterated product with that of the undeuterated **4**, as shown partially in Figure 1. That is, the incorporation occurs selectively at the C-4 carbon of **4** with anti configuration against the cyclopropane ring. From these facts, it is evident that the rearrangement of **3** to **4** proceeds through an anionic intermediate. Therefore, the formation of **4** might best be explained by the mechanism depicted in the Scheme 1; deprotonation of **3** with n-BuLi gives the anion **5** which then undergoes the circumambulatory rearrangement to give the anion **6**,[14] followed by protonation to lead to **4** as a final product. Judging from the optimized structure of the anion **6** obtained by semiempirical molecular orbital calculations (PM3 method),[15] the anti face of **6** is sterically less crowded for an electrophilic attack. Therefore, the reason for the stereoselectivity observed in the deuteration reaction can be attributed to steric hindrance between deuteron and one of the methylene protons on the cyclopropane ring at least as one of it.[16] It is noteworthy that the rearrangement is quite a facile process, since quenching with deuterium oxide even after a short reaction period of 5 min at -78 °C gave **4**-d$_1$ and **3** without any detection of the dueterated **3** or its double bond position isomers. On the other hand, quenching of the solution with water after the reaction mixture was warmed to 0 °C gave a mixture of 4-methyldihydroazulenes, which included 4-methyl-1,4-dihydroazulene **7** as a major product, in 17% yield. This mixture of products was found to be entirely same as one obtained in the reaction of methyllithium and



Scheme 1.

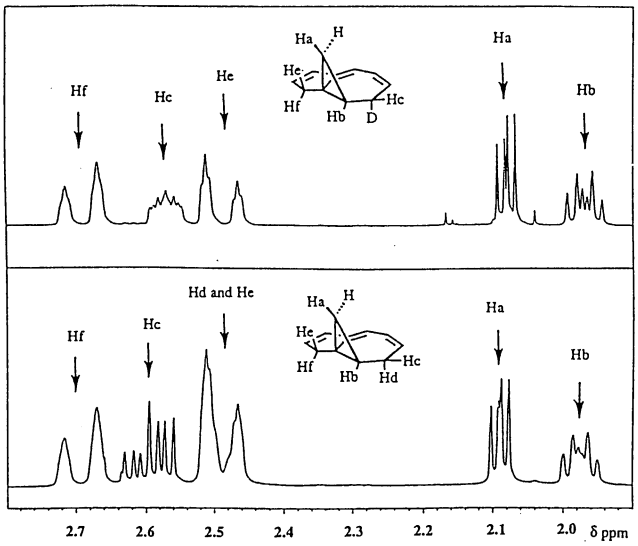


Figure 1. ^{1}H NMR Spectra (400 MHz) in $CDCl_3$ solution of **4**-d_1 (top) and **4** (bottom) (360 MHz sweep width).

azulene,[17] indicating the formation of 4-methyl-4*H*-azulenyl anion **9** as the latest intermediary carbanion for this second rearrangement. Since it has previously been reported that the anion **1** undergoes cleavage of the cyclopropane ring to the methylene cycloheptadienyl anion at above 0 °C [5] and the cycloheptadienyl anion in hexahydroazulene isomerizes to the more stable cyclopentadienyl anion by a stepwise protonation-deprotonation mechanism,[18] the formation of this mixture can be explained by the pathway shown in the Scheme 1.[19]

In summary, for the first time we have obtained chemical evidence that supports a cyclopropyl migration on the periphery of a cyclic polyenyl anion, though lacking direct detection of anionic species, **5** and **6**. Concurrently we revealed some chemical behavior of the intermediary anion, such as the selective incorporation of an electrophile at low temperature and the rearrangement to a stable anionic species at elevated temperature. Experiments designed to know whether in this rearrangement the migrating methylene group invert or retain its congfiguration are now in progress .

We thank Mr Y. Morita at Toyama National College of Technology for measurements of mass spectroscopy of **4**-d_1. This work was partially supported by a Grant-in-Aid Scientific Research (No. 08640677 to S. K.) from the Ministry of Education, Science, Sports and Culture, Japan. The financial support to one of authors (S.K.) by Yoshida Ikueikai Foundation is gratefully acknowledged.

References and Notes

1 J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2752 (1965) and **88**, 2494 (1966); F.-G. Klärner, *Angew. Chem.*, **84**, 892 (1972); M. B. Sohn, M. Jones, Jr., and B. Fairless, *J. Am. Chem. Soc.*, **94**, 4774 (1972).

2 D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1976); R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968); R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968); J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8908 (1972); R. F. Childs and C. V. Rogerson, *J. Am. Chem. Soc.*, **98**, 6391 (1976); R. F. Childs and C. V. Rogerson, *J. Am. Chem. Soc.*, **100**, 649 (1978); L. T. Scott and W. R. Brunsvold, *J. Am. Chem. Soc.*, **100**, 6535 (1978).

3 For a review on circumambulatory rearrngement, see:. R. F. Child, *Tetrahedron*, **38**, 567 (1982).

4 R. B. Woodward and R. Hoffmann, "*The Conservation of Orbital Symmetry*, " Academic Press, New York (1969).

5 W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 8908 (1972) and **96**, 5207 (1974).

6 For other circumambulatory rearrangements of anionic species, see: J. B. Grutzner and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2200 (1972); M. V. Moncur, J. B. Grutzner, and A. Eisenstadt, *J. Org. Chem.*, **39**, 1065 (1974).

7 H. Kloosterziel and E. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **88**, 1373 (1969)

8 S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 2731 (1973).

9 H. Kloosterziel and G. M. Gorter-LA Roy, *J. Chem. Soc., Chem. Commun.*, **1972**, 352.

10 L. T. Scott. W. R. Brunsvold, M. A. Kirms, and I. Erden, *J. Am. Chem. Soc.*, **103**, 5216 (1981).

11 For other reactions of **1**, see: L. T. Scott, I. Erden, W. R. Brunsvold, T. H. Shurtz, K. N. Houk, and M. N. Passon-Row, *J. Am. Chem. Soc.*, **104**, 3659 (1982).

12 All new compounds were characterized by the spectroscopic methods and by high resolution mass spectroscopy. *Selected data* for **4** : IR ν_{max} / cm^{-1} 2910s, 1590w, 1430m, 1065m, 1030m, 860m, 740m; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.56 (dd, J=8.4, 4.4Hz, 1H), 2.00 (dd, J=8.4, 6.0Hz, 1H), 2.10 (dd, J=6.0, 4.4Hz, 1H), 2.50 (dm, J=ca.18Hz, 2H), 2.60 (ddd, J=14.4, 8.8, 6.0Hz, 1H), 2.70 (dm, J=18.4Hz, 1H), 5.33 (ddd, J=11.2, 8.8, 4.2Hz, 1H), 5.64 (d, J=6.0Hz, 1H), 5.87 (ddd, J=11.2, 6.0, 3.2Hz, 1H), 6.07 (dt, J=5.6, 2.8Hz, 1H), 6.25 (dt, J=5.6, 2.0Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.3, 27.1, 27.5, 43.2, 46.0, 113.7, 126.2, 128.2 135.6, 136.2, 154.8; HRMS calcd. for $C_{11}H_{12}$ 144.0940, obsd. 144.0981; UV (MeOH) λ_{max} 302 (loge=3.86). For **4**-d_1: IR ν_{max} /cm^{-1} 2220w; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.56 (dd, J=8.7, 4.3Hz, 1H), 2.00 (dd, J=8.4, 5.6Hz, 1H), 2.09 (dd, J=5.9, 4.1Hz, 1H), 2.52 (dm, J=18.8Hz, 1H), 2.58 (m, 1H), 5.32 (t-like, J=9.8Hz, 1H), 5.64 (d, J=5.9Hz, 1H), 5.87 (dd, J=10.4, 5.6Hz, 1H), 6.07 (dt, J=5.6, 2.7Hz, 1H), 6.25 (dt, J=5.7, 2.1Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.2, 26.7 (t, $J_{C\text{-}D}$=0.19Hz), 27.5, 43.1, 46.0, 113.7, 126.1, 128.3, 135.6, 136.1, 154.7 ; MS *m/z* (70eV) 145 (M^+, 91%), 129 (100%); HRMS calcd. for $C_{11}H_{11}D$, 144.0993, obsd. 145.0974.

13 As seen in the ^{1}H NMR spectral data, it is a notable structural feature of **4** that the vicinal coupling between one of methylene protons at the C_4 position with anti configuration to the cyclopropane ring and the methine proton at the C_5 position is almost negligible. The computed structure of **4** by the MM2 method[20] revealed that the dihedral angle between these two hydrogen atoms through the C_4 - C_5 axis is 71.5 ° in fairly good agreement with the spectral observation. We thank Prof. K. Nakasuji and Mr. K. Tamaki at Osaka University for MM2 calculations of **4**.

14 A circumambulatory rearrangement of the intermediary anion **5** in the opposite direction which would lead to the different product via a less conjugated tricyclic anion was not observed. Therefore a major part of the driving force of the rearrangement seems to be the creation of the more conjugated anion.

15 J. J. Stewart, *J. Comput. Chem.*, **10**, 209, and 221 (1989).

16 For the similar site- and stereoselective incorporation of electrophiles by delocalized carbanions, see:K. Takahashi, K. Takase, and T. Kagawa, *J. Am. Chem. Soc.*, **103**, 1186 (1981); T. Kawase, M. Iyoda, and M. Oda, *Chem. Lett.*, **1985**, 489; C. E. Barry III, R. B. Bates, W. A. Beavers, F. A. Camon, B. Gordon III, H. F. -J. Hsu, N. S. Mills, C. A. Ogle, T. J. Siahaan, K. Suvannachut, S. R. Taylor, J. J. White, and K. M. Yager, *Synlett*, **1991**, 209.

17 K. Hafner and H. Weldes, *Chem. Ber.*, **606**, 90 (1957).

18 S. W. Staley and A. S. Hey, *J. Am. Chem. Soc.*, **97**, 3852 (1975).

19 As one of alternative pathways for conversion of **6** into **9**, the cleavage of a cyclopropane bond to generate a methylene anion and subsequent intra- or intermolecular proton transfer to give **9** is possible. However, such a process from **6** to the methylene anion is predicted to be endothermic (-77.7 kcal/mol) on the basis of PM3 calculations, while one from **6** to **8** to be exothermic (15.0 kcal/mol).

20 N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).