# THE EQUILIBRIUM BETWEEN EXO- AND ENDO-9-CHLORO-CIS-BICYCLO[4.3.0]NONA-2,4,7-TRIENES[1]

Yujiro Nomura, Yoshito Takeuchi, and Shuji Tomoda*
Department of Chemistry, College of General Education
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

The title equilibrium constant has been found to be 9.0 with predominant exo-isomer at 25°C.

Despite numerous examples of isomerization accompanying solvolysis of allylic halides,[2] their rearrangements in the absence of external nucleophiles have been studied only for interconversions of primary $\rightleftharpoons$ tertiary[3] and primary $\rightleftharpoons$ secondary[4] pairs, with the primary member being always predominant at equilibrium. Tertiary allylic chlorides[3] and α-arylallylic chlorides[4a] isomerize via cationic intermediate at appreciable rates even at room temperature in the absence of proton sources or Lewis acids, whereas secondary allylic chlorides are usually quite stable at ordinary temperatures in the absence of acid catalysts. We now wish to report the title equilibrium as an example of a secondary $\rightleftharpoons$ secondary pair of allylic chlorides and reevaluate the degree of electron delocalization in potentially homoaromatic cis-bicyclo[4.3.0]nona-2,4,7-trien-9-yl cation.

The present study began with unanticipated generation of thermally labile endo-9-chloro-cis-bicyclo[4.3.0]nona-2,4,7-triene (1-endo) from syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl chlorosulfite (2) either by flash vacuum pyrolysis or by thermolysis in carbon tetrachloride thoroughly degassed at 10^{-6} Torr.[5,6] Although a high proportion of the endo-isomer(1-endo, 65%) relative to the exo-isomer(1-exo, 30%) was achieved by gas phase pyrolysis, concomitant formation of indene(5%) and hydrogen chloride, an excellent catalyst for the isomerization, could not be avoided.[5] By contrast, thermolysis of the chlorosulfite (2) in carbon tetrachloride at 45°C in a base-washed nmr tube sealed under 10^{-6} Torr provided a 60:40 mixture of endo- and exo-isomers (1), which upon standing at room temperature underwent clean conversion to a 10:90 mixture containing predominant exo-isomer within four days. Significantly, indene was not detected in this mixture throughout the process of thermal isomerization.[7]
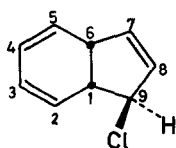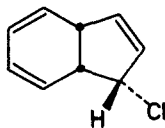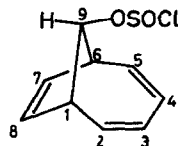

1-exo   1-endo   2

That the two isomers (1) were in equilibrium in the final mixtures was ascertained by an independent synthesis and subsequent epimerization of pure exo-isomer (1-exo) derived from anti-9-chloro-cis-bicyclo[6.1.0]nona-2,4,6-triene (3).[8] When pure 1-exo was heated in carbon tetrachloride at 70°C for 5 hr,[9] the colorless mixture containing 1-endo(10%) and 1-exo(90%) again was not contaminated by indene. The endo:exo ratio remained unchanged upon prolonged heating, indicating that the equilibrium could be reached from either isomer.
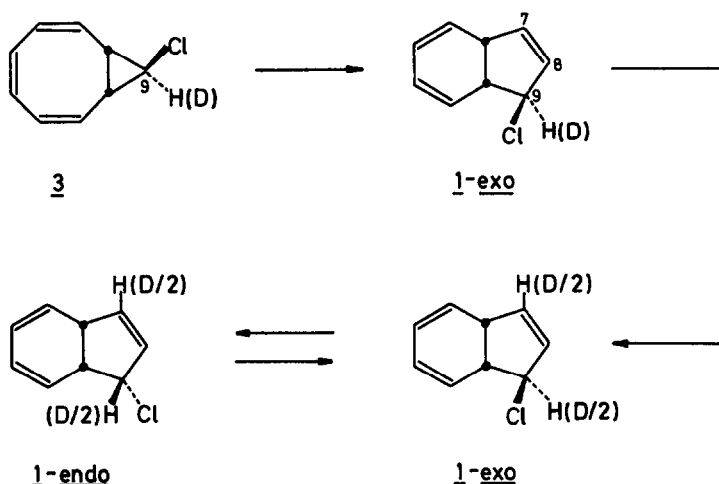
In order to delineate the mechanism of the rearrangement studies were continued using the corresponding deuterium labeled compounds. The equilibrium mixture from thermal decomposition of 2-9-d(100% isotopic purity) contained 1-exo-8-d(90%) and 1-endo-8-d(10%).[10] This suggested the existence of a symmetrical intermediate for the isomerization, but did not preclude the possibility of local epimerization at C-9 nor simple 1,5-vinyl migration of C(6)-C(7) bond.[11] Thus heating 1-exo-9-d, generated from 3-9-d[12], at 70°C for 5 hr resulted in relocation of the deuterium into C-9(0.53D ± 0.05) and C-7(0.48D ± 0.04) in virtually equal amounts within experimental error.[10] Since a thermally allowed antarafacial [1,3] sigmatropic shift seems highly unlikely in such cyclic systems,[13] the simplest key intermediate consistent with these deuterium labeling studies would be the cis-bicyclo[4.3.0]nona-2,4,7-trien-9-yl cation (4) as shown in the following kinetic scheme.
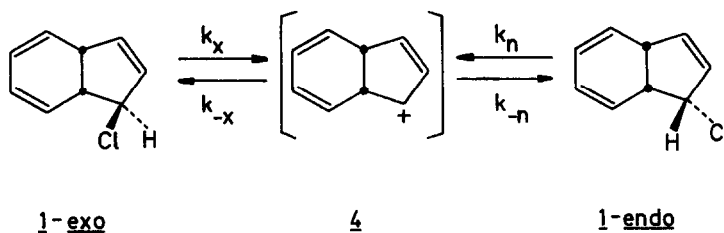
The present equilibrium data may be useful to discuss the long-standing controversy concerning π-electron delocalization in cation $\underline{4}$. Although direct observation of cation $\underline{4}$ in super acid media by NMR was suggested to be more consistent with the bishomotropylium structure $\underline{4a}$, rather than open allylic cation $\underline{4b}$,[14] subsequent solvolytic studies in aqueous acetone provided no definite evidence for the intermediacy of $\underline{4a}$.[15] In the latter investigation, it was briefly mentioned that less than 5% of endo-9-hydroxy-cis-bicyclo[4.3.0]nona-2,4,7-triene ($\underline{5\text{-endo}}$) was formed as indicated by ^{1}H-NMR. This result as well as kinetic measurements seemed to indicate the open allylic form ($\underline{4b}$) since the formation of endo-product certainly implies capture of an open allylic cation like $\underline{4b}$. More recently, Diaz and Fulcher reported that solvolytically generated cation $\underline{4}$ from bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate in methanol afforded only exo-9-methoxy-cis-bicyclo[4.3.0]nona-2,4,7-triene ($\underline{6\text{-exo}}$) with no trace amount of the other isomer ($\underline{6\text{-endo}}$).[16] By contrast, reexamination of Diaz's solvolysis by Kirmse and Voigt indicated the formation of 6% $\underline{6\text{-endo}}$ in addition to 94% $\underline{6\text{-exo}}$, but again the minor product was not characterized.[17] Since previous workers have not even shown that the $\underline{5\text{-endo}}$ and $\underline{6\text{-endo}}$ are kinetically controlled products, it may be of some significance to evaluate the relative rate of the attack of a nucleophile from the endo-face of the cation $\underline{4}$ utilizing our equilibrium data.
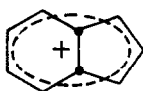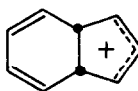
$\underline{4a}$ $\underline{4b}$

Based on the reasonable assumption that the exo/endo rate ratio, k_x/k_n, of these isomeric chlorides ($\underline{1}$) leading to cation $\underline{4}$ should closely resemble the solvolytic exo/endo rate ratio of the exo- and endo-cis-bicyclo[4.3.0]nona-2,4,7-trien-9-yl 3,5-dinitrobenzoates(k_x/k_n = 11.0/0.904 at 50°C in 60% aqueous acetone[15]) and using the equilibrium constant, K, between our isomeric chlorides ($\underline{1}$)(K = [$\underline{1\text{-exo}}$]/[$\underline{1\text{-endo}}$] = 9.0), k_{-x}/k_{-n} is estimated to be roughly 110. This implies that the formation of exo-chloride from cation $\underline{4}$ is kinetically overwhelmingly(99.1%) favored. The electronic structure of cation $\underline{4}$ may therefore be more reasonably represented by bishomoaromatic structure $\underline{4a}$ than the open allylic cation $\underline{4b}$.

It should be noted that $\underline{1}$ appears to be exceptionally susceptible to thermal isomerization as a secondary allylic chloride having no conjugative group at 1- or 3-position. This may also qualitatively account for the bishomoaromatic nature of cation $\underline{4}$.

References and Notes

1. Presented in part at the 26th IUPAC Congress, Tokyo, 1977.

2. (a) R.H. DeWolfe and W.G. Young, Chem. Rev., 56, 753(1956), (b) P.B.D. de la Mare, "Mo-
   lecular rearrangement", P. de Mayo Ed., Interscience, 27(1963). (c) R.H. DeWolfe and W.
   G. Young, "Chemistry of Alkenes" in "The Chemistry of Functional Groups", S. Patai Ed.,
   John Wiley & Sons, Chap. 10, 681(1964).

3. (a) A.J. Altee, J. Chem. Soc., 1948, 530, (b) L.F. Hatch and G.E. Journeay, J. Am. Chem.
   Soc., 66, 545(1953), (c) D. Barnard, L. Bateman, A. J. Harding, H.P. Koch, N. Sheppard and
   G.B.M. Sutherland, J. Chem. Soc., 1950, 915.

4. (a) G. Valkanas and E.S. Waight, J. Chem. Soc., 1959, 2720, (b) J.F. Lane, J. Fentress
   and L.T. Sherwood, J. Am. Chem. Soc., 66, 545(1944), (c) L.F. Hatch and S.S. Nesbitt,
   ibid, 72, 727(1950), (d) W.G. Young and J.F. Lane, ibid, 59, 2051(1937), (e) W.G. Young
   and K. Nozaki, ibid, 62, 311(1940), (f) W.G. Young, L. Richards and J. Azorlosa, ibid, 61,
   3070(1939), (g) L. Batemann and J.I. Cuneen, J. Chem. Soc., 1950, 941, (h) I.D. Webb and
   G.T. Borchert, J. Am. Chem. Soc., 73, 2654(1951).

5. Y. Nomura, Y. Takeuchi, S. Tomoda and M.J. Goldstein, J. Chem. Soc. Chem. Commun., 1977,
   545.

6. Y. Nomura, Y. Takeuchi and S. Tomoda, Tetrahedron Lett., 1978, 911.

7. Isomerization of 1 was followed by ^{1}H-NMR using a clean nmr tube rinsed with aqeous ammon-
   ia and then water.

8. (a) T.J. Katz and P.J. Garratt, J. Am. Chem. Soc., 86, 5194(1964), (b) E.A. LaLancette and
   R.E. Benson, ibid, 87, 1941(1965).

9. Appearance of 1-endo was followed by the characteristic doublet of doublet at δ=4.94 ppm
   (J=7 and 2 Hz). The ^{1}H-NMR spectrum of the equilibrium mixture obtained from 1-exo entire-
   ly coincided that of the equilibrium mixture obtained from 2.

10. The location of deuterium was determined by an ^{1}H-NMR analysis of the tetracyanoethylene
    adduct[8] of these isomeric chlorides separated by fractional crystallization.[5]

11. (a) M.F. Semmelhack, H.N. Weller and J. Clardy, J. Org. Chem., 43, 3791(1978), (b) M.F.
    Semmelhack, H.N. Weller and J.S. Foos, J. Am. Chem. Soc., 99, 292(1977).

12. J.C. Barborak, T.-M. Su, P. von R. Schleyer, G. Boche and G. Schneider, J. Am. Chem. Soc.,
    93, 279(1971).

13. R.B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 2512(1965).

14. P. Ahlberg, D.L. Harris and S. Winstein, J. Am. Chem. Soc., 92, 2146, 4454(1970).

15. D. Cook, A. Diaz, J.P. Dirlam, D.L. Harris, M. Sakai, S. Winstein, J.C. Barborak and P.
    von R. Schleyer, Tetrahedron Lett., 1971, 1405.

16. A. Diaz and J. Fulcher, J. Am. Chem. Soc., 98, 789(1976).

17. W. Kirmse and G. Voigt, J. Am. Chem. Soc., 96, 7598(1974).