Tetrahedron Letters, Vol.31, No.28, pp 3973-3974, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

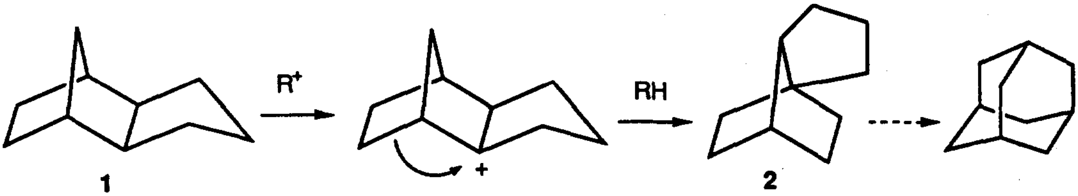
A NOVEL ISOMERIZATION REACTION OF TRICYCLO[5.2.1.0^{2,6}]DECANE[1]

Pavel A. Krasutsky,[†] Igor R. Likhotvorik,[+†] Andrey L. Litvyn,[†] Alexander G. Yurchenko,[†] and Donna Van Engen[+]

[†]Department of Chemical Engineering, Kiev Polytechnic Institute, 252056, Kiev, USSR
[+]Department of Chemistry, Princeton University, Princeton, New Jersey 08544-1009, USA

Abstract: HNO_3-catalyzed isomerization of tricyclo[5.2.1.0^{2,6}]decane affords tricyclo[4.2.2.0^{1,5}]decane - the "bottle neck" in the adamantane rearrangement.

Discovery of the isomerization of tricyclo[5.2.1.0^{2,6}]decane **1** to adamantane by Paul Schleyer more than 30 years ago[2] stimulated a great interest in the chemistry of adamantanoid compounds. Since 1957 the mechanism of "one of the most fascinating intramolecular rearrangements known in carbocation chemistry"[4] has received considerable attention.[3-8] Two of the most likely rearrangement pathways suggested by Whitlock and Siefken[5] and Schleyer and his coworkers[6] were proved by series of interesting experiments.[7,8]



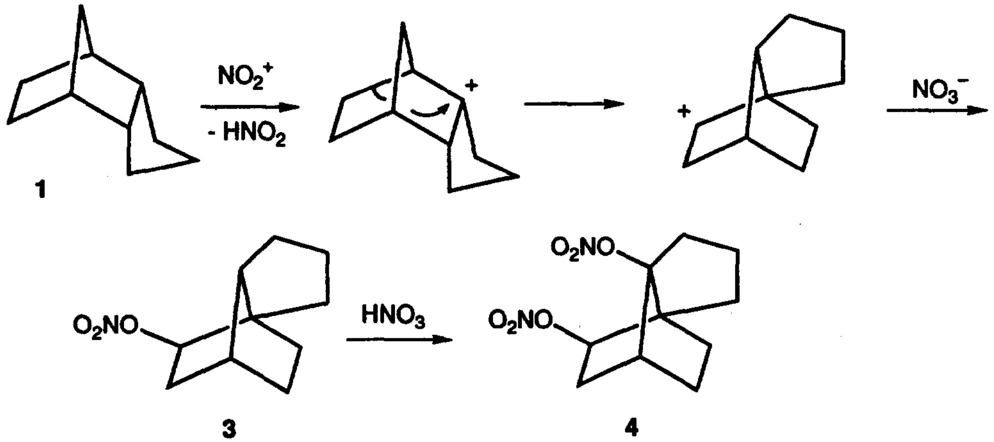
1 2

However, no direct synthetic evidence for the first stage - isomerization of **1** to tricyclo[4.2.2.0^{1,5}]decane **2**, named the "energetic bottle neck,"[8] in the proposed pathways to adamantane has been found as the rearrangement inevitably stopped far short of **2**, falling into the "bottomless pit" of the thermodynamically most stable adamantane structure.

We wish to report that the use of nitric acid as good catalyst for carbocation generation, and as a trap for intermediate structures, helped us to prove the first stage of the adamantane rearrangement and find a new useful synthetic method for the preparation of the tricyclo[4.2.2.0^{1,5}]decane cage structure.

When **1** was treated with 98-100% nitric acid, a rapid exothermic reaction occurred leading to a complicated mixture of oxidized products in which 1-hydroxytricyclo[5.2.1.0^{2,6}]decane and bicyclo[5.2.1]decane-2,6-dione could be positively identified. In order to reduce oxidative activity we used a HNO_3 - Ac_2O - CH_2Cl_2 mixture. Indeed, we have found that when a solution of endo-**1** (1.36 g, 10 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of 100% nitric acid (12.5 mL, 0.3 M), CH_2Cl_2 (12.0 mL, 0.19 M) and Ac_2O (9.8 mL, 0.1 M) at 0-5 °C, stirred for 4 hr at 10 °C, poured onto ice, and extracted with CH_2Cl_2, the desired rearranged compound **4** could be obtained as a major product in 65% yield after recrystallization from ethanol.[9] The structure of **4** was determined by X-ray analysis[10] and NMR spectroscopy. A single crystal measuring 0.32 mm x 0.40 mm x 0.42 mm was used for X-ray measurements. Crystal data: $C_{10}H_{15}N_2O_6$; monoclinic, space group P 2_1/n; a = 6.946(2) Å, b = 25.889(8) Å, c = 6.974(2) Å,

$V = 1162.2(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.48$ g/cm^3. Intensity measurements were made with $3° \leq 2\theta \leq 114°$ by using Cu Kα radiation ($\lambda = 1.5418$ Å) at 296K on a Nicolet R3m diffractometer. Systematically absent reflections were eliminated and equivalent reflections were averaged ($R_{int} = 0.026$) to give 1569 unique reflections of which 1510 were considered to be observed [$|Fo| \leq 3\sigma(Fo)$]. The structure was solved by direct methods using the SHELXTL software. Refinement converged (shift/error ≤ 0.015) of $R = 0.052$, $Rw = 0.069$. The ^{13}C NMR spectrum showed the presence of 10 carbons (2 quaternary, 2 tertiary and 6 secondary; δ 21.56, 24.84, 25.21, 27.12, 30.29, 38.48, 42.66, 45.77, 63.59, 81.41, 108.53).



The stereoselectivity of the reaction indicated that the most probable mechanism for this transformation should include rearrangement of the starting *endo*-tricyclo[5.2.1.0^{2,6}]decane 1 to 8-*exo*-nitroxy-*exo*-tricyclo[4.2.2.0^{1,5}]decane 3. Subsequent rearrangement of 3 followed by fast attack of nitric acid yielded the corresponding dinitrate 4.

References and Notes

1. We warmly thank Professor Maitland Jones, Jr., for his hospitality and support of this work. An IREX Fellowship to I.R.L. is gratefully acknowledged. Work at Princeton was supported by a National Science Foundation grant to Maitland Jones, Jr., CHE-8800448.
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9. Satisfactory elemental analysis, MS, ^{1}H NMR and IR spectra were obtained for the dinitrate 4.
10. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Date Centre.

(Received in USA 27 June 1989; accepted 24 May 1990)