The uv spectrum, thermal stability, and nmr spectrum of **4** all seem most consistent with *trans*-2-tetrazene groups; in the absence of *cis*-tetraalkyl-2-tetrazenes as models, however, this point remains possibly ambiguous. Further attempts at synthesis of *cis*-tetraalkyl-2-tetrazenes are continuing in these laboratories.

Acknowledgment. We thank the Wisconsin Alumnae Research Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this work. We thank Professor P. D. Bartlett for making the data from N. A. Porter's thesis available

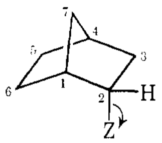
M. Iwamura, P. J. Hintz, S. F. Nelsen
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received March 5, 1970

Ring Contraction in Solvolysis of a Norbornyl System[1]

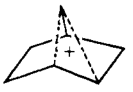
Sir:

A characteristic of Wagner–Meerwein rearrangements in 2-substituted bicyclo[2.2.1]heptyl (norbornyl) systems is that they involve migration of the C_1–C_6 bond whether the departing group at C-2 is initially *exo* or *endo*.[2] For *exo* groups the shift of C-6 is understandable on geometric grounds whether the first intermediate is viewed as a (nonclassical) bridged cation or as a classical cation shielded on the *exo* side by the departing species. Failure to observe migration of C-7 (**1** → **2** → **3**) in ionization of *endo* groups might be rationalized in terms of a distorted initial geometry for backside participation and/or of an increase in skeletal strain that would presumably accompany a ring contraction.[2,3] Conceivably these unfavorable features might be mitigated if the stability of the rearranged ion were substantially enhanced by appropriate substitution and if C-7 became involved before the ionization site lost its *endo* identity.[4] We now report that solvolysis of 1-methoxy-2-*endo*-norbornyl brosylate (**6b**) produces a product with a bicyclo[3.1.1]heptyl skeleton and thus provides the first example of a ring contraction in solvolysis of a norbornyl system.[5]

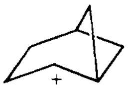
In our synthetic work, 1-methoxynorbornan-2-one (**4**)[6] was reduced with $LiAlH_4$ to a mixture of C-2 epimeric liquid alcohols, which were separated by preparative glpc. The *exo* alcohol (**5a**, $C_8H_{14}O_2$)[7] and its *endo* epimer (**6a**, $C_8H_{14}O_2$) were individually converted to the corresponding *p*-bromobenzenesulfonates and acetates by treatment, in pyridine, with brosyl chloride and with acetic anhydride, respectively. The 1-methoxy-*exo*-2-norbornyl brosylate (**5b**, $C_{14}H_{17}O_4BrS$; mp 69–69.5° from ether–hexane) showed four groups of proton signals (CCl_4) at δ 7.75 (q, 4, aromatic), 4.58 (m, 1, C-2), 3.14 (s, 3, OCH_3), and 2.3–0.8 (m, 9). The corresponding 2-*exo*-acetate (**5c**, $C_{10}H_{16}O_3$; ir 2838, 1740 cm^{-1}) also showed four groups of nmr signals: δ 4.86 (d, J = 7 Hz, C-2), 3.21 (s, 3, OCH_3), 1.97 (s, 3, $COCH_3$), 2.4–0.7 (m, 9). The 1-methoxy-*endo*-2-norbornyl brosylate (**6b**, $C_{14}H_{17}O_4BrS$) had mp 65–67° (ether–hexane); δ 7.75 (q, 4, aromatic), 4.82 (d, J = 9 Hz, 1, C-2), 3.11 (s, 3, OCH_3), 2.5–1.0 (m, 9). The 2-*endo*-acetate **6c** ($C_{10}H_{16}O_3$, ν 2833, 1740 cm^{-1}) had δ 5.07 (d, J = 10 Hz, 1, C-2), 3.26 (s, 3, OCH_3), 2.00 (s, 3, $COCH_3$), 2.7–0.8 (m, 9).[8]



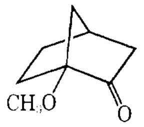
1



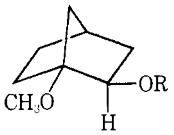
2



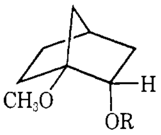
3



4

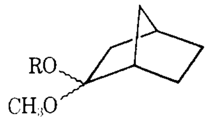


5

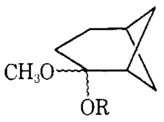


6

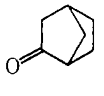
a, R = H
b, R = Bs
c, C = Ac



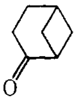
7



8



9



10

Acetolysis of the *exo*-brosylate **5b** at 50° (HOAc–KOAc) followed by aqueous work-up gave only one product, norbornan-2-one (**9**, >99.9% by glpc) identified by infrared comparison with an authentic sample. With nortricyclanone[9] as an internal glpc standard the conversion appeared virtually quantitative. In contrast, acetolysis of *endo*-brosylate **6b** gave norbornan-2-one (**9**), 1-methoxy-2-*exo*-norbornyl acetate (**5c**), and bicyclo[3.1.1]heptan-2-one (**10**), whose glpc ratios are summarized in Table I. The ring-contracted ketone **10** was also formed when the solvolysis was conducted in trifluoroacetic acid and in 60% aqueous acetone. The products were separated by preparative glpc[10] and

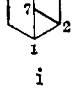
---

(1) This work was supported by the National Science Foundation.

(2) For recent reviews see: (a) G. D. Sargent, *Quart. Rev. Chem. Soc.*, **20**, 301 (1966); (b) G. E. Greame, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); *Chem. Eng. News*, **45** (7), 86 (1967); (d) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3; (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms-1955," Interscience, New York, N. Y., 1966, Chapter 1.

(3) F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5688 (1969).

(4) The isolation of products containing the tricyclic system i in solvolysis of *anti*-7-norbornenyl substrates shows that the geometry for bonding of C-7 simultaneously to C-1 and C-2 is attainable: H Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).



i

(5) For an authentic example in a diazoketone rearrangement see P. Yates and R. J. Crawford, *ibid.*, **88**, 1561 (1966), and in a deamination see C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967). For recent work and leading references on solvolytic rearrangements in reverse direction ([3.1.1] → [2.2.1]) see: W. Kirmse and R. Siegfried, *ibid.*, **90**, 6564 (1968); P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964); E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2721 (1964).

(6) (a) A. Nickon, T. Nishida, and Y-i Lin, *ibid.*, **91**, 6860 (1969); (b) A. Nickon and Y-i Lin, *ibid.*, **91**, 6861 (1969).

(7) Satisfactory carbon and hydrogen analyses were obtained for all new compounds whose empirical formulas are given.

(8) The nmr characteristics of the C-2 proton in **5** and **6** (*e.g.*, doublets are broadened) are consistant with our stereochemical assignments. For extensive literature references see: P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(9) W. G. Dauben, Ed., *Org. Syn.*, **45**, 77 (1965).

(10) The *exo*- and *endo*-acetates **5c** and **6c** were not resolved under our glpc conditions whereas the alcohols **5a** and **6a** were. We showed

Table I. Solvolysis of 1-Methoxy-*endo*-2-norbornyl Brosylate (**6b**)

Solvent	[ROBs] × 10^2 *M*	[Salt] × 10^2 *M*	Temp, °C	Time, hr	Products, rel %[a] **9**	**10**	**5**
HOAc	5.10	9.20[b]	105	22	88.4	7.4	4.2[c]
CF_3CO_2H	2.71	58.0[d]	115	13	95.0	5.0	
60% aq acetone	1.66	6.20[e]	125	3	82.4	8.8	8.8[f]

[a] No elimination products (<0.1%) were detected. [b] Potassium acetate. [c] *exo*-Acetate **5c**. [d] Sodium trifluoroacetate. [e] Sodium bicarbonate. [f] *exo*-Alcohol **5a**.

each was identified by direct spectroscopic comparison with authentic samples.[11]

Formation of norbornan-2-one (**9**) from the *exo*-brosylate (**5b**) is understandable since rearrangement of the C_1–C_6 bond produces a 2-methoxy-2-norbornyl cation, which, from earlier work, is expected to be favored.[6,12] The rearranged system (**7**) would provide ketone **9** on hydrolytic work-up.

In acetolysis of *endo*-brosylate **6b** the 1-methoxy-*exo*-2-norbornyl acetate **5c** is presumably derivable by direct nucleophilic attack on the covalent substrate or on an intermediate C-2 cation. Importantly, the formation of both norbornan-2-one (**9**) and bicyclo[3.1.1]heptan-2-one (**10**) indicates a competition between C-6 and C-7 migration at some stage. That no ring-contracted product is formed in solvolysis of the *exo*-brosylate **5b** (or in solvolysis of the parent *endo*-2-norbornyl brosylate[2]) suggests that at least for a fraction of molecules of **6b** the C-7 bridge migrates before the *endo* group has fully departed.[13]

Solvolysis rates for **5b** and **6b** in HOAc–excess KOAc were measured spectrophotometrically[14] and are summarized in Table II along with data for the parent norbornyl analogs determined under the same conditions. The last column in Table II lists relative *ionization* rates, which were obtained by correction for known internal return (k_α/k_t = 4.6[15]) in *exo*-2-norbornyl brosylate. No such corrections are made for the 1-methoxynorbornyl substrates because internal return after Wagner–Meerwein rearrangement would produce α-methoxy brosylates (**7** and **8**), which would be expected to ionize exceedingly more rapidly than the starting brosylates.

Table II. Rates of Solvolysis of Substituted Norbornyl Brosylates in HOAc–KOAc

Norbornyl brosylate	Temp, °C	$k \times 10^6$, $\sec^{-1}$ [a]	Rel rates at 25° Solvolysis	Ionization
exo-2	(25.0)[b]	9.02	348	1600
exo-2	28.0	13.2 ± 0.2[c]		
exo-2	49.9	172 ± 1		
1-Methoxy-*exo*-2	(25.0)[b]	7.24	279	279
1-Methoxy-*exo*-2	28.0	10.8 ± 0.2[d]		
1-Methoxy-*exo*-2	49.9	160 ± 2		
endo-2	(25.0)[b]	0.0259	1.00	1.00
endo-2	80.0	27.5 ± 0.3[e]		
1-Methoxy-*endo*-2	(25.0)[b]	0.000737	0.0285	0.0285
1-Methoxy-*endo*-2	80.0	1.24 ± 0.01[f]		
1-Methoxy-*endo*-2	100.0	10.8 ± 0.2		

[a] Mean value from two or three runs. [b] Calculated. [c] $\Delta H^{\ddagger}$ = 22.1 kcal/mol; $\Delta S^{\ddagger}$ = −3.1 eu, in agreement with reported values (see ref 15b). [d] $\Delta H^{\ddagger}$ = 23.2 kcal/mol; $\Delta S^{\ddagger}$ = +0.25 eu. [e] Reported $\Delta H^{\ddagger}$ = 26.0 kcal/mol; $\Delta S^{\ddagger}$ = −1.5 eu for unbuffered acetic acid (ref 15b). [f] $\Delta H^{\ddagger}$ = 27.6 kcal/mol; $\Delta S^{\ddagger}$ = −3.1 eu.

Interpretation of the rate data is not attempted here, however it is noteworthy that the 1-methoxy retards ionization of an *exo*-2-brosylate by a factor of 5.7 and of an *endo*-2-brosylate by a factor of 35. This retardation on the *exo*-2 system is less than the retardations that have been observed when a methoxy is located more remotely on the norbornane skeleton.[16] Evidently some factor is partially compensating for inductive withdrawal[17] by a 1-methoxy for an *exo* departing group.[18]

---

that the acetate product was entirely *exo* by reduction with $LiAlH_4$ to give *exo*-alcohol **5a** exclusively (<0.1% **6a**).

(11) We are grateful to Drs. W. Kirmse, H. Musso, and K. Grychtol for authentic bicyclo[3.1.1]heptan-2-one, whose ir and nmr were identical with those of our **10**.

(12) T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, 88, 4934 (1966).

(13) In terms of bridged ions facile leakage from a C-7 σ-bridged ion to a C-6 σ-bridged ion would account for both skeletons. Reverse leakage is excluded by the results with the *exo*-brosylate **5b**.

(14) G. C. Swain and C. R. Morgan, *J. Org. Chem.*, 29, 2097 (1964).

(15) (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, 87, 376 (1965); (b) E. Clippinger, Ph.D. Thesis, University of California, Los Angeles, Calif., 1955.

(16) (a) P. J. Stang and P. von R. Schleyer, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts P 192; (b) the results of Professor Schleyer's kinetic studies are being separately submitted for publication.

(17) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 113; (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(18) Contrast the effects of a 1-cyano group in 2-apobornyl and 2-apoisobornyl systems. R. Muneyuki and T. Yano, *J. Amer. Chem. Soc.*, 92, 747 (1970).

Yang-i Lin, Alex Nickon
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received February 24, 1970

Mechanisms of Photochemical Reactions in Solution. LXIII.[1] A 1,2- and 1,3-Benzyl Group Migration in Compounds Containing Phenyl and Conjugated Dienyl Chromophores

Sir:

As a continuation of our interest in the photochemistry of compounds containing two nonconjugated chromophoric units,[2] we wish to report the novel photochemical behavior of some 7-phenyl-2,4-heptadienes (**1**).

The dienes **1a–c** (Chart I) were synthesized by adding the Wittig reagent prepared from (2-methyl-2-butenyl)-triphenylphosphonium chloride to the appropriate aldehyde or ketone. Irradiation of *cis–trans* mixtures of the hydrocarbons in hexane solution with a low-pressure mercury lamp resulted in smooth conversion to a mixture containing 36–44% **2a–c** and 56–64% *cis*- and *trans*-**3a–c**.[3a] The 1,4-dienes, **2**, could be readily separated from the substituted vinylcyclopropanes **3** by preparative vapor chromatography.[3b] The structures of the 1,4-dienes are apparent from their spectra. Each contains a phenyl group and two olefinic units (nmr) which are not conjugated either to each other or to the phenyl group (ultraviolet). The 2-methyl-

---

(1) Part LXII: R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2739 (1970).

(2) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967).

(3) (a) Satisfactory elemental analysis was obtained for all new compounds. (b) The column used was a 10 ft × $^3/_8$ in. Carbowax 20 M (15%) on 60–80 mesh Chromosorb W, at 150°.