2,4-$(CH_3)_2C_6H_3$), 27675-05-4; $ArTlF_2$ (Ar = 2,5-$(CH_3)_2C_6H_3$), 29396-64-3; $ArTlF_2$ (Ar = 2,4,6-$(CH_3)_3C_6H_2$), 27675-11-2; $ArTlF_2$ (Ar = 4-$C_6H_5C_6H_4$), 60705-29-5; ArF (Ar = 4-$CH_3C_6H_4$), 352-32-9; ArF (Ar = 4-$C_2H_5C_6H_4$), 459-47-2; ArF (Ar = 2,4-$(CH_3)_2C_6H_3$), 452-65-3; ArF (Ar = 2,5-$(CH_3)_2C_6H_3$), 696-01-5; ArF (Ar = 2,4,6-$(CH_3)_3C_6H_2$), 392-69-8; ArF (Ar = 4-$C_6H_5C_6H_4$), 324-74-3.

References and Notes

(1) (a) For the previous paper in this series, see E. C. Taylor, C.-S. Chiang, A. McKillop, and J. F. White, *J. Am. Chem. Soc.*, **98**, 6750 (1976). (b) We are indebted to the National Science Foundation (Grant MPS72-00427) and to Eli Lilly & Co. for support of this work. We also wish to express our gratitude to Dr. F. Scheidl and his staff at Hoffmann-La Roche, Inc., for the microanalysis of organothallium compounds.
(2) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", American Elsevier, New York, N.Y., 1965, pp 119–152.
(3) P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration, and Halogenation", Academic Press, New York, N.Y., 1959, pp 105–138.
(4) C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis", Wiley-Interscience, New York, N.Y., 1970, pp 392–407.
(5) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds", *Adv. Chem. Ser.*, **No. 155**, 1–9 (1962).
(6) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.
(7) M. Hudlicky, "Chemistry of Organic Fluorine Compounds", Macmillan, New York, N.Y., 1962, p 52.
(8) V. Grakauskas, *J. Org. Chem.*, **35**, 723 (1970).
(9) N. B. Kaz'mina, L. S. German, I. D. Rubin, and I. L. Knunyants, *Dokl. Chem.*, **194**, 757 (1970).
(10) J. F. Ellis and W. K. R. Musgrave, *J. Chem. Soc.*, 1063 (1953).
(11) D. H. R. Barton, A. K. Ganguly, S. N. Loo, M. M. Pechet, and R. H. Hesse, *Chem. Commun.*, 806 (1968).
(12) R. Stephens and J. C. Tatlow, *Q. Rev., Chem. Soc.*, **16**, 44 (1962).
(13) D. R. MacKenzie and J. Fajer, *J. Am. Chem. Soc.*, **92**, 4994 (1970).
(14) M. J. Shaw, R. Filler, and H. H. Hyman, *J. Am. Chem. Soc.*, **92**, 6498 (1970).
(15) I. N. Rozhnov, A. V. Bukhtiarov, N. D. Kuleshova, and I. L. Knunyants, *Dokl. Chem.*, **193**, 618 (1970).
(16) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956).
(17) French Patent 1 360 917 (1964).
(18) A. Roe, *Org. React.*, **5**, 193 (1949).
(19) H. Suschitsky, *Adv. Fluorine Chem.*, **4**, 1 (1965).
(20) E. Forsche in Houben-Weyl, "Methoden der Organischen Chemie", Vol. 5, Part 3, Georg Thieme Verlag, Stuttgart, 1955, pp 213–247.
(21) A. McKillop and E. C. Taylor, *Adv. Organomet. Chem.*, **11**, 147 (1973).
(22) S. Uemura, Y. Ikeda, and K. Ichikawa, *Tetrahedron*, **28**, 3025 (1972).
(23) E. C. Taylor, R. H. Danforth, and A. McKillop, *J. Org. Chem.*, **38**, 2088 (1973).
(24) E. C. Taylor, H. W. Altland, and A. McKillop, *J. Org. Chem.*, **40**, 3441 (1975).
(25) S. Uemura, Y. Ikeda, and K. Ichikawa, *Tetrahedron*, **28**, 5499 (1972).
(26) S. Uemura, K. Sohma, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **44**, 2490 (1971).
(27) A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Am. Chem. Soc.*, **93**, 4841 (1971).
(28) A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Organomet. Chem.*, **24**, 77 (1970).
(29) F. Challenger and O. V. Richards, *J. Chem. Soc.*, 405 (1934).
(30) E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray, and A. McKillop, *J. Am. Chem. Soc.*, **92**, 3520 (1970).
(31) E. C. Taylor, F. Kienzle, and A. McKillop, *Synthesis*, 38 (1972).
(32) E. C. Taylor, F. Kienzle, and A. McKillop, *J. Am. Chem. Soc.*, **92**, 6088 (1970).
(33) D. W. A. Sharp, *Adv. Fluorine Chem.*, **1**, 68 (1960).

Highly Strained Ring Systems. Hydrolysis of Tricyclo[4.1.0.0^{2,7}]hept-3-yl Derivatives. Evidence for Participation of Bicyclo[1.1.0]butane Ring

Kazuyuki Yano* and Kitaro Yoshida

Department of Chemistry, Saitama Medical School, 981 Kawakado, Moroyama, Iruma-gun, Saitama 350-04, Japan

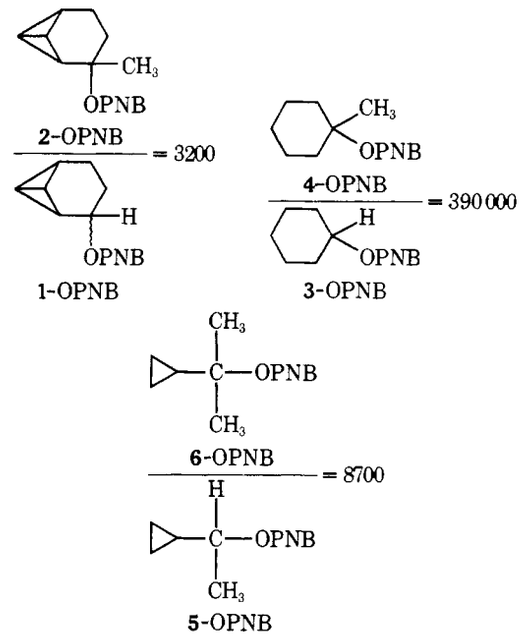
Received July 13, 1976

Preparation and studies of strained ring compounds have long intrigued organic chemists. Especially bicyclo[1.1.0]-butane, which has the highest strain energy in bicyclic ring systems, has provided many interesting aspects as regards relationships between strain energy and reactivity.[1] However, only a few solvolytic studies with bicyclo[1.1.0]butane derivatives have been reported.[2] Thus, we synthesized tricyclo[4.1.0.0^{2,7}]hept-3-yl and 3-methyltricyclo[4.1.0.0^{2,7}]-hept-3-yl *p*-nitrobenzoates (1-OPNB and 2-OPNB, respectively), and investigated their solvolytic reactivity in order to determine whether the tricyclo[4.1.0.0^{2,7}]hept-3-yl carbonium ion is a nonclassical ion by bicyclobutane ring participation or a classical ion associated with a relief of its ring strain.

Synthesis of the parent tricyclic ketone was carried out as described in the literature.[3] Treatment of this ketone with sodium borohydride or methyllithium gave alcohol 1-OH or 2-OH, wihch was converted to its corresponding *p*-nitrobenzoate 1-OPNB (mp 92.0–93.0 °C) or 2-OPNB (mp 79.5–80.5 °C) in the usual fashion.

The hydrolysis rates of 1-OPNB and 2-OPNB were measured in aqueous acetone mixtures by titrating the liberated *p*-nitrobenzoic acid displaying nice first-order behavior. The kinetic data are summarized in Table I with literature values for related compounds.

The *p*-nitrobenzoate (1-OPNB) undergoes hydrolysis at a rate 5×10^7 times faster than does cyclohexyl *p*-nitrobenzoate (3-OPNB), while the rate of 1-OPNB is essentially the same as that of methylcyclopropylcarbinyl *p*-nitrobenzoate (5-OPNB). It has been suggested that an α-CH_3/H rate ratio in solvolysis reaction of a charge-delocalized system would decrease when compared to that of a charge-localized system.[4] Thus a rate ratio of 2-OPNB/1-OPNB was compared to that of 4-OPNB/3-OPNB (a charge-localized system), as well as that of 6-OPNB/5-OPNB (a charge-delocalized system). As seen in Table I, the rate ratio of 2-OPNB/1-OPNB exhibits approximately the same as that of 6-OPNB/5-OPNB within



a factor of 3, whereas it is about 100 times less than that of 4-OPNB/3-OPNB. Consequently, these findings suggest that the importance factor underlying the solvolytic reactivity of 1-OPNB is stabilization of its transition state by assisting in charge delocalization rather than by a relief of angle strain.

Hydrolysis of 1-OPNB gives rise to *anti*-7-norbornenol (7-OH) as an only alcoholic product (89%, GLC analysis).

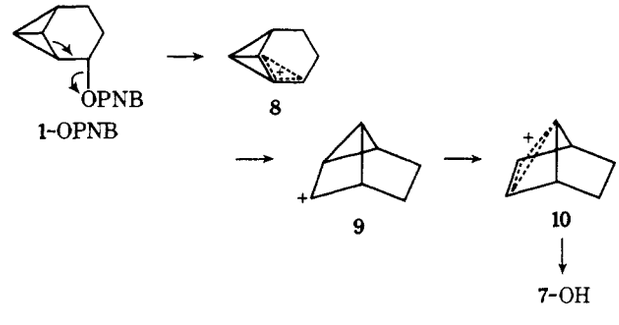


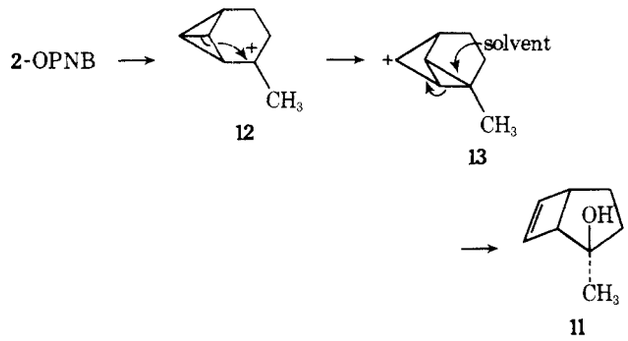
Table I. Kinetic Data for Hydrolysis of Tricyclo[4.1.0.0^{2,7}]hept-3-yl and 3-Methyltricyclo[4.1.0.0^{2,7}]hept-3-yl *p*-Nitrobenzoates (1-OPNB and 2-OPNB, Respectively) and Related Compounds

Registry no.	Substrate	Solvent,[a] %	Temp, °C	k_1, s^{-1}	k_{CH_3}/k_H
60595-06-4	1-OPNB	50	99.8	$(2.96 \pm 0.03) \times 10^{-5}$ [b]	
			80.1	$(4.93 \pm 0.11) \times 10^{-5}$ [b]	
		60	80.1	$(2.26 \pm 0.17) \times 10^{-5}$ [b]	
		80	25	7.03×10^{-9} [c]	
60595-07-5	2-OPNB	60	50.0	$(6.90 \pm 0.09) \times 10^{-4}$ [b]	
			25.0	$(6.05 \pm 0.01) \times 10^{-5}$ [b]	
		65	25.0	$(4.82 \pm 0.09) \times 10^{-5}$ [b]	
		80	25	2.22×10^{-5} [d]	3200
7511-32-2	3-OPNB	80	25	1.41×10^{-16} [e]	
31058-46-5	4-OPNB	80	25	5.48×10^{-11} [f]	390 000
18228-38-1	5-OPNB	80	25	4.28×10^{-9} [g]	
23437-99-2	6-OPNB	80	25	3.75×10^{-5} [h]	8700

[a] Aqueous acetone mixture (v/v). [b] The rates are average values for two independent runs. [c] Extracted from the data at high temperatures and estimated by Grunwald–Winstein equation ($m = 0.56$). [d] Estimated by Grunwald–Winstein equation ($m = 0.30$). [e] Extrapolated from literature data [H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956)] and converted with a factor of $(k_{OPNB,80\%}/k_{OTs,HOAc})_{25°C} = 3 \times 10^{-9}$ [H. C. Brown, M. Ravindrananthan, K. Takeuchi, and E. N. Peters, *ibid.*, **97**, 2899 (1975)]. [f] E. N. Peters and H. C. Brown, *ibid.*, **96**, 263 (1974). [g] Extrapolated from literature data [R. A. Sneen and A. L. Baron, *ibid.*, **83**, 614 (1961)] and converted to 80% acetone by a factor of 6.7 for the solvent change. [h] H. C. Brown and E. N. Peters, *ibid.*, **95**, 2400 (1973).

Although **1**-OH is found to be unstable under the solvolysis condition, it does not produce **7**-OH. Thus, the formation of **7**-OH can be explained as follows: the *p*-nitrobenzoate (**1**-OPNB) produces bicyclobutonium ion **8** first by an anchimeric assistance of the bicyclobutane ring, and this ion rearranges to tricyclocarbonium ion **9** which leads to **7**-OH through a stable bishomocyclopropenyl ion **10**.

On the other hand, hydrolysis of **2**-OPNB proceeds with stereospecific rearrangement to *exo*-2-methylbicyclo[3.2.0]-hept-6-en-2-ol (**11**)[5] (71%, GLC analysis) which is not a product from thermolysis of **2**-OH, since **2**-OH is stable under the solvolysis condition. A possible mechanism for the formation of **11** is that **2**-OPNB produces a classical carbenium ion **12** which rearranges to **13** by an interaction of the cationic center with the center bond of the bicyclobutane, and that this ion may give rise to **11** by a concerted process with the bond migration and solvent attack.[6]



Experimental Section[7]

Tricyclo[4.1.0.0^{2,7}]hept-3-yl *p*-Nitrobenzoate (1-OPNB). To a solution of tricyclo[4.1.0.0^{2,7}]hept-3-one[3] (323.9 mg) in 15 ml of methanol was added a solution of sodium borohydride (60.8 mg) in 5 ml of methanol at 0 °C. The resulting solution was allowed to stir at 0 °C for 1.5 h. Then water was added to the solution. After removal of the solvent, the product was extracted with ether three times. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated to give 234.3 mg (71%) of the crude alcohol (**1**-OH). Owing to unstability of **1**-OH, the NMR spectrum of **1**-OH was examined without purification: NMR (CCl_4) δ 3.52 (m, 1 H), 2.58–2.10 (m, 2 H), 1.65 (t, 2 H, J = 2.8 Hz), and 1.48–1.20 (5 H).

To a solution of **1**-OH (234.3 mg) in 7 ml of dry pyridine was added *p*-nitrobenzoyl chloride (438.0 mg) in one portion at 0 °C. The resulting solution was allowed to stand in a refrigerator for 2 days, and then poured onto ice–water. The product was extracted with chloroform to give 288.3 mg (52%) of **1**-OPNB: mp 92.0–93.0 °C; IR (Nujol) 1731 cm^{-1}; NMR (CCl_4) δ 8.19 (s, 4 H, aromatic), 4.96 (m, 1 H), 2.72 (m, 1 H), 2.43 (m, 1 H), and 1.94–1.02 (m, 6 H).

Anal. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05. Found: C, 64.57; H, 5.07.

3-Methyltricyclo[4.1.0.0^{2,7}]hept-3-yl *p*-Nitrobenzoate (2-OPNB). To freshly prepared methyllithium in ether (ca. 27 mmol) was added dropwise a solution of tricyclo[4.1.0.0^{2,7}]hept-3-one (848.7 mg, 7.86 mmol) in 5 ml of ether at room temperature under nitrogen. The resulting solution was stirred for 30 min. Then the excess methyllithium was destroyed with ammonium chloride. Ether extraction gave 3-methyltricyclo[4.1.0.0^{2,7}]hept-3-ol (**2**-OH) as a clear liquid (619.9 mg, 64%): bp 52–54 °C (6 mmHg); NMR (CCl_4) δ 2.38 (m, 2 H), 2.02 (s, 1 H, OH), 1.67 (t, 2 H, J = 2.4 Hz), 1.58–1.20 (4 H), and 1.10 (s, 3 H, CH_3–).

The alcohol **2**-OH (301.2 mg, 2.4 mmol) was converted to its corresponding *p*-nitrobenzoate **2**-OPNB as described above for **1**-OPNB to yield 104.9 mg (16%): mp 79.5–80.5 °C; IR (Nujol) 1727 cm^{-1} (>C=O); NMR (CCl_4) δ 8.20 (A_2B_2, 4 H, aromatic, J = 10 Hz), 3.10 (2 d, 1 H, J = 2.8, 7.0 Hz), 2.46 (m, 1 H), and 1.90–1.30 (9 H).

Anal. Calcd for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53. Found: C, 65.86; H, 5.90.

Kinetic Measurement. The *p*-nitrobenzoates were hydrolyzed in aqueous acetone mixtures (v/v), and the rates were measured as previously described.[8] The kinetic data are shown in Table I.

Solvolysis Product Study. *p*-Nitrobenzoate **1**-OPNB (32.2 mg) in 16 ml of 50% aqueous acetone containing 1.4 equiv of sodium bicarbonate was sealed in a test tube under nitrogen and heated for 8 h at 100 °C. The tube was cooled and opened. To the cooled solution was added 8.8 mg of cyclohexanol as an internal standard, and the product extracted with ether–chloroform was analyzed by GLC on a 15% FFAP column at 115 °C to indicate presence of *anti*-7-norbornenol **7**-OH (89%) which was identified by GLC and NMR comparisons.

p-Nitrobenzoate **2**-OPNB (18.3 mg) was solvolyzed as mentioned above except for being heated in 60% aqueous acetone for 3 h at 50 °C. The GLC analysis using the internal standard showed formation of *exo*-2-methylbicyclo[3.2.0]hept-6-en-2-ol (**11**, 71%), which was identified by GLC and NMR comparisons.

Stability of 1-OH and 2-OH under the Solvolysis Conditions. Alcohol **1**-OH (51 mg) in 13 ml of 50% aqueous acetone containing 1.3 equiv of sodium bicarbonate was sealed in a test tube under nitrogen and heated at 100 °C for 7 h. After workup, the crude product was examined by NMR and GLC analyses to indicate formation of bicyclo[3.2.0]hept-6-en-2-one but no observation of **7**-OH and **1**-OH. On the other hand, **2**-OH was found to be stable under the solvolysis condition (60% aqueous acetone, 50 °C, 3 h).

Acknowledgment. We thank Professor K. Kinoshita at S. M. S. for his discussion and encouragement. We are grateful for financial support from Moroyama-Kai and the Ministry of Education, Japan.

Registry No.—1-OH, 60595-08-6; 2-OH, 60595-09-7; 7-OH, 694-70-2; 11, 53585-67-4; tricyclo[4.1.0.0^{2,7}]hept-3-one, 37939-70-1; *p*-nitrobenzoyl chloride, 122-04-3.

References and Notes

(1) (a) For a review, see K. B. Wiberg, *Adv. Alicyclic Chem.*, **2**, 185 (1968); (b) L. A. Paquette, *Acc. Chem. Res.*, **4**, 280 (1971); (c) W. G. Dauben, A. J. Kielbania, Jr., and K. N. Raymond, *J. Am. Chem. Soc.*, **95**, 7166 (1973); (d) G. Zon and L. A. Paquette, *ibid.*, **96**, 5478 (1974); (e) M. Christl, U. Heinemann, and W. Kristof, *ibid.*, **97**, 2299 (1975).

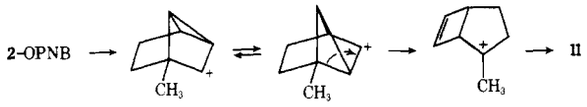
(2) (a) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *Tetrahedron Lett.*, 193 (1966); (b) R. Breslow, H. Bozimo, and P. Wolf, *ibid.*, 2395 (1970).

(3) J. Ipaktschi, *Chem. Ber.*, **105**, 1996 (1972).

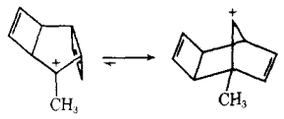
(4) For a recent review, see G. D. Sargent in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., pp 1175–1181.

(5) K. Yano, *J. Org. Chem.*, **40**, 414 (1975).

(6) A referee suggested the following alternate mechanism for the formation of **11.**



However, if this mechanism is involved in the hydrolysis of **2**-OPNB, methylnorbornenol would be expected to be a major product (but is not), since a great difference in the stability between the following carbonium ions has been reported.[9]



Thus, we prefer the above mechanism to this alternate one.

(7) Melting points were taken on a Yamato MP-21 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer and ultraviolet spectra were determined with a Shimadzu UV-200 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Hitachi R-24 instrument with chemical shift (δ) given in parts per million downfield from Me_4Si. Gas–liquid chromatography was performed on a Shimadzu GC-4B instrument. Microanalyses were determined in the microanalytical laboratory of the Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan.

(8) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970).

(9) R. M. Coates and K. Yano, *J. Am. Chem. Soc.*, **95**, 2203 (1973).

The Role of the Generalized Anomeric Effect in the Conformational Analysis of 1,3-Dioxacycloalkanes. Conformational Analysis of 3,5-Dioxabicyclo[5.1.0]octanes and 3,5,8-Trioxabicyclo[5.1.0]octanes

Michael H. Gianni,* Robert Cody, and Mohan Raj Asthana

Chemistry Department, St. Michael's College, Winooski Park, Vermont 05404

Karl Wursthorn, Patrick Patanode, and Henry G. Kuivila

Chemistry Department, New York State University at Albany, Albany, New York 12222

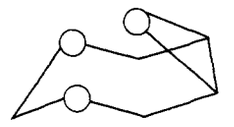
Received April 29, 1976

Conformational analysis of 1,3-dioxacycloalkanes has received considerable attention.[1-5] Equilibrium studies on substituted 1,3-dioxacyclopentanes and 1,3-dioxacycloheptanes indicate that numerous low-energy chair conformations, which are interconnected by pseudorotational pathways, are available to an equilibrating pair of diastereoisomers. In contrast 1,3-dioxacyclohexane has only one favorable low-energy chair conformation for each isomer of a cis–trans pair.

Examination of models of 1,3-dioxacycloheptanes reveals that when pseudorotation at C-5,6 is prohibited, only one chair conformation is possible. The pseudorotation pathway of the chair form may be excluded by introduction of a double bond at C-5,6 or by construction of a small ring containing C-5 and C-6. Studies of the conformations for compounds which contain a double bond at C-5,6 indicate that 2,2-dimethyl-1,3-dioxa-5,6-benzocycloheptene,[6] *cis*- and *trans*-4,7-dimethyl-1,3-dioxacycloheptene-5-ene, and *r*-2-*tert*-butyl-*c*-4,*t*-7-dimethyl-1,3-dioxacycloheptene-5-ene[5] exist in twist-boat conformations.

Our interest in twist-boat conformations in the 1,3-dioxacycloheptene-5-enes has led to an investigation of the effect that the construction of a small ring would have on the conformation of these compounds. Recent reports that cycloheptene oxide[7] exists in an equilibrium of two chair conformations and that cycloheptene is also in a chair conformation are of special interest. The conformation of 1,3-dioxacycloheptene-5-ene is unsettled.[8] Low-temperature proton magnetic resonance studies failed to indicate line broadening at −120 °C. However, carbon-13 magnetic resonance data strongly suggests that 2,2-dimethyl-1,3-dioxacycloheptene-5-ene is in a twist-boat conformation.[5]

It is evident that the epoxide ring does not impart sufficient strain to force cycloheptene oxide into a twist form nor does the double bond make the twist form the more stable conformer for cycloheptene. It seemed probable that 3,5,8-trioxabicyclo[5.1.0]octane (1,3-dioxacycloheptene-5-ene oxide) might be more stable in a twist-boat than in a chair conformation. In addition to the strain provided by the epoxide ring an unfavorable interaction due to an anomeric effect[9] could be anticipated for chair conformations **1** and **3** which is relieved in the twist-boat conformation **2.**



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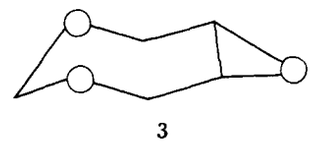

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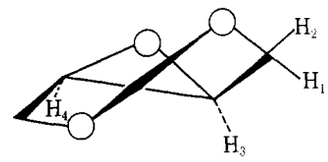

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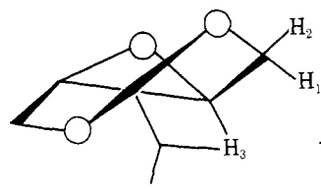

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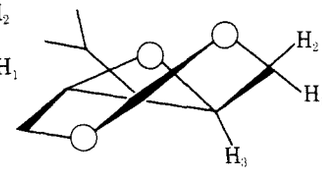

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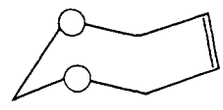

6

The 1,3-dioxacycloheptene-5-ene oxide was synthesized by epoxidation of 1,3-dioxacycloheptene-5-ene with *m*-chloroperbenzoic acid. The proton magnetic resonance spectrum of this compound remained unchanged in the temperature range 30 to −160 °C. This fact suggested that this molecule might indeed be in a twist-boat conformation. However, it is possible that the coalescence temperature is below −160 °C and that the compound exists as an equilibrium of conformations **1** and **3.**

Supporting evidence for a twist-boat conformation comes from coupling constants for *exo*- and *endo*-2-isopropyl-1,3-dioxacycloheptene-5-ene oxide, **4** and **5**, respectively. The endo isomer gave the following coupling constants: $J_{1,2}$ (−13.67),