bornane molecule is known to be less crowded than the *endo* toward attack by external reagents; therefore, according to Brown,[12] 3,2 shifts should occur preferentially *exo*. Examination of models of the two presumed transition states, XII and XIII, fails to give much support for this steric suggestion. During a 3,2-*exo,exo* shift (XII) the migrating group must pass by the *syn*-7-hydrogen.[6] In the transition state for a 3,2-*endo,endo* shift (XIII) the migrating group is favorably situated *between* the two normally hindering *endo* protons on C_5 and C_6 In addition, when the migrating group is only a small hydrogen atom, the nonbonded distances would appear to be sufficiently large (>2.2 A) so that no crowding should be present. Furthermore, the R group in XIII is *quasi-exo*, which should be favorable, while in XII the R group is *quasi-endo*, a more strained situation. Not only is it not clear which transition state, XII or XIII, should be of lower energy due to nonbonded steric effects, but even more seriously it would not appear possible that the energy differences between XII and XIII could be very large. There appears to be at least a 100-fold preference for *exo,exo* over *endo,endo* 3,2 shifts.[6] One cannot explain such a 3-kcal/mole phenomenon by an effect likely to be of much smaller magnitude.

Torsional effects have been overlooked as a cause of the anomalous behavior often observed in the norbornane series[1,2,12,13] and in other polycyclic systems.[14] The significance of torsional strain to the problem under consideration is easily demonstrated. Molecular models of the presumed 3,2-shift transition states XII and XIII (approximated by the *endo* and *exo* isomers of tricyclo[3.2.1.0^{2,4}]octane or of norbornene epoxide) reveal that the arrangements around bonds C_1–C_2 and C_3–C_4 of the *exo* isomer XII are nearly ideally *skewed*. By contrast, in the *endo* conformation XIII the arrangements around the same bonds are almost exactly eclipsed, an energetically unfavorable situation. Since a three-membered ring has little effect in reducing the usual 3-kcal/mole C–C rotation barrier,[15] this means that *endo* transition state XIII (as well as *endo*-bicyclo[3.2.1.0^{2,4}]octane and *endo*-norbornene epoxide) should be less stable than the *exo* arrangement XII by up to 6 kcal/mole! This magnitude is more than sufficient to account for the experimentally observed degree of stereospecificity of 3,2 shifts without recourse either to bridging or to nonbonded steric effect arguments. The diverse cations—secondary; methyl-, phenyl-, and anisyl-substituted tertiary—all of which rearrange by stereospecific 3,2-hydride or -methyl shifts, have but one unifying feature: the contrasting torsional arrangements in the isomeric transition states, as XII and XIII. A torsional strain explanation for the stereospecificity of norbornyl 3,2 shifts appears to me to be preferable to both of the alternative current rationalizations.

Acknowledgments. This work was supported by grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society. Stimulating discussions with Professor H. C. Brown are gratefully acknowledged. Professor J. A. Berson kindly provided copies of his manuscripts[6] prior to publication.

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(14) Accompanying communication: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(15) Propylene oxide, 2.56 kcal/mole: D. R. Herschbach and J. D. Swalen, *J. Chem. Phys.*, **29**, 761 (1958); propylene sulfide, 3.25 kcal mole: W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963).

Torsional Effects in Polycyclic Systems. II. The Stereochemistry of Attack and Departure in Norbornane Derivatives

Sir:

It has not been possible to understand fully the behavior of norbornane derivatives in terms of ideas presently employed.[1-8] Norbornyl cations have long been regarded as being bridged; the formation of such nonclassical species and their reactions with nucleophiles are believed to occur preferentially *exo*.[1-7] The stereochemistry of reactions not involving bridged transition states is believed to be governed by nonbonded steric effects: the *exo* side of the norbornane molecule is more accessible unless 7,7-dimethyl or similar hindering substituents are present, then the *endo* side is less crowded.[1-8] Although these two basic concepts can account for a large number of reactions involving bicyclo[2.2.1]heptane derivatives, significant exceptions are known, and many of these have been cataloged by Brown.[8] Brown has shown that something is wrong with current theory, but he has not yet supplied a convincing alternative explanation.

I believe that an evaluation of the influence of torsional effects provides a simple solution to many of these problems,[9] and an appreciation of torsional factors will introduce a new dimension of understanding into often complex norbornane chemistry. Such torsional effects should exert an important influence favoring *exo* over *endo* additions and processes involving *exo* bond ruptures. Table I summarizes the predicted

Table I. Favored Transition-State Orientations due to Various Effects

Effect	In norbornane derivatives	In 7,7-dimethyl-norbornane derivatives
Bridged ion	*exo*	*exo*
Steric hindrance	*exo*	*endo*
Torsional strain	*exo*[a]	*exo*[a]

[a] Probably unimportant for processes involving the generation or destruction of exocyclic double bonds. See text.

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(1) P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956.

(2) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(3) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(4) G. E. Greame, *Rev. Pure Appl. Chem.*, **16**, 25 (1966).

(5) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(6) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms-1965," Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 1.

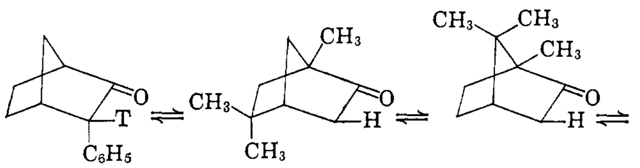
(7) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(8) H. C. Brown, *Chem. Brit.*, 199 (1966), and references therein summarized.

(9) See accompanying communication: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699 (1967).

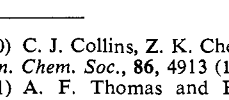
influences of bridging, nonbonded, and torsional effects.

Enolization of 2-norbornanones is unexpectedly stereospecific.[8,10–12] 3-*endo*-Phenyl-2-norbornanone-3-*t* (I) exchanges hydrogen for tritium in base much more rapidly than it undergoes epimerization to the 3-*exo*-phenyl ketone.[10] 2-Norbornanone,[11,12] isofenchone (II),[11] and camphor (III)[11] exchange the 3-*exo*-hydrogens for deuterium much more rapidly than the 3-*endo*-hydrogens. Since the reaction site, the 3 position, is hindered by methyls from the *endo* side in II and from the *exo* side in III, a steric explanation[12] hardly seems likely. Electronic theory does not help either;[11] carbanions stand the least chance of being bridged.[12a]

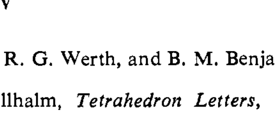


I II III

Torsional theory supplies an attractive explanation. IV shows a 2-norbornanone enolate ion seen from the side, a view which emphasizes the approximately 20° dihedral angle between the bonds to the 4 and to the 3 substituents. (A similar dihedral angle is found between the C_1 and C_2 exocyclic substituent bonds.) Such a 20° angle represents a partially eclipsed and unfavorable orientation, since in propene and in similar multiply bonded molecules the minimum energy conformation is that with the adjacent single bonds in a 60° relationship.[13] Deuteration from the *exo* side should be favorable, since in the transition state (V) the 3 substituent is bent toward the *endo* side, the dihedral angle is *increased*, and torsional strain is relieved. In the transition state for *endo*-deuteration (VI), the 3 substituent is bent toward the *exo* side, the dihedral angle is *decreased*, and torsional strain increases. *Torsional effects thus favor exo over endo attack, and, by microscopic reversibility, exo over endo departure.* This effect would obviously be operative whatever the disposition of methyl substituents, as in II and III.



VI



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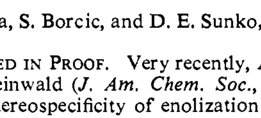
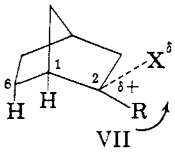


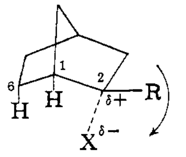
V

Such torsional effects should be quite general in bicyclo[2.2.1]heptane chemistry. Additions to norbornenes—hydroboration (*exo*/*endo* = 200),[8] oxymercuration, epoxidation, cyclopropanation, azide formation, etc.[14]—should be strongly influenced by torsional factors especially when multicentered transition states are involved since the effect should be simultaneously operative at *two* centers, C_2 and C_3. Free radicals, which have a planar or near-planar conformation,[15] and *carbonium ions even in the absence of bridging*, should also be attacked preferentially from the *exo* side.[1–8]

Brown's high *exo*/*endo* rate ratios in tertiary norbornyl systems[8] have been hard to explain. No other evidence for bridging in such cations has been detected,[8,16] and they appear to be classical. There are no important differences in the ground-state energies of the *exo* and *endo* isomers.[17] Brown has proposed that the *endo* isomers react slowly because of steric retardation.[8] While this suggestion cannot be summarily dismissed,[18] it would seem that the observed tertiary *exo*/*endo* ratios are too large to be rationalized in this way.



VII



VIII

Torsional effects provide at least a partial solution to this dilemma. In the transition state for *exo* solvolysis, VII, the $C_2\cdots X_{exo}$ bond is partially broken, a favorable situation since it was originally nearly eclipsed with the C_1–H bridgehead bond. In VII, the bulky R group has moved away from the C_6 *endo* hydrogen, and the nonbonded repulsion between these two groups is relieved. Movement of the C_2–R bond toward the *exo* side of the molecule is also favorable, since in the ground state it was partially eclipsed with the C_6–C_1 bond. In the *exo* transition state, then, both torsional and nonbonded strains are minimized. The opposite situation pertains in the *endo* transition state, VIII. The 2-*exo*-R group moves toward the *endo* side, but this group was sterically unencumbered and no appreciable nonbonded strain is relieved. However, as in VI, this movement causes eclipsing of the C_2–R and C_1–H bonds. In addition, to the extent that the departing X group is forced to move inward,[16] nonbonded interactions with the *endo* C_6 hydrogen might be increased or at least not relieved. The torsional and nonbonded energy differences in the two transition states VII and VIII are likely to be sufficiently great to account for the observed *exo*/*endo* $\sim$ 500 ratios in tertiary norbornyl solvolyses.[8] It follows also, by microscopic reversibility, that attack on a classical 2-norbornyl cation should be strongly favored from the *exo* direction.

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(10) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964).

(11) A. F. Thomas and B. Willhalm, *Tetrahedron Letters*, 1309 (1965); *cf.* the stereoselective monomethylation of 2-norbornanone: E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Am. Chem., Soc.*, **84**, 2611 (1962).

(12) J. M. Jerkunica, S. Borcic, and D. E. Sunko, *Tetrahedron Letters*, 4465 (1965).

(12) (a) Note Added in Proof. Very recently, A. F. Thomas, R. A. Schneider, and J. Meinwald (*J. Am. Chem. Soc.*, **89**, 68 (1967)) have fully confirmed the stereospecificity of enolization of II and III. Particular attention is called to the last paragraph of the general section of this paper.

(13) See the summary by J. Dale, *Tetrahedron*, **22**, 3373 (1966).

(14) See the summary of references given by Sargent,[3] pp 334–345.

(15) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.* **1**, 283 (1966).

(16) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **88**, 5336 (1966).

(17) M.-H. Rei and H. C. Brown, *ibid.*, **88**, 5335 (1966).

(18) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

Ketones and exocyclic methylene groups are functional groups differing in type from those already considered. Double bonds prefer 0° and not 60° torsional angles to adjacent single bonds.[13] During *exo* attack on 2-norbornanones and 2-methylenenorbornanes, the dihedral angle between the C_2 exocyclic double bond and the C_1 bridgehead bond increases, which would be unfavorable except for the fact that during this process the double bond is becoming single. In this kind of situation torsional effects are in opposite directions and would tend to cancel. Processes involving the formation of exocyclic double bonds or the reverse should therefore be controlled stereochemically by nonbonded steric effects (Table I). It is probably for this reason that *exo/endo* ratios in reactions of this type in norbornane derivatives typically are low: ketal exchange (16);[19] ketone reductions by $NaBH_4$ (6.2,[20] 5)[21] and $LiAlH_4$(10)[21]; chromic acid alcohol oxidations (*exo*-H/*endo*-H = 2.5,[22] 6.5[23]). Reactions such as these should *not* be good models for the behavior of classical carbonium ions because of the expected difference in response toward torsional effects.

Still needed is quantitative evaluation of the importance of torsional, steric, and bridging effects in the various reactions involving norbornyl derivatives. However, it already seems likely that torsional effects are of appreciable magnitude.[24] The extent to which torsional effects (in conjunction with nonbonded interactions)[18] are involved in 2-norbornyl carbonium ion reactions reduces the need to ascribe observed behavior, such as high *exo/endo* rate ratios or the propensity toward *exo* attack, to bridging.[8,12a,18]

Acknowledgments. Exchanges of information and stimulating conversations with Professor H. C. Brown are gratefully acknowledged. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

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

(20) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

(21) R. Howe, E. C. Friedrich, and S. Winsten, *ibid.*, **87**, 379 (1965).

(22) H. Kwart and P. S. Francis, *ibid.*, **81**, 2116 (1959).

(23) I. Rothberg and R. V. Russo, unpublished observations.

(24) Recent oxymercuration results of Professor H. C. Brown, soon to be published, provide dramatic confirmation.

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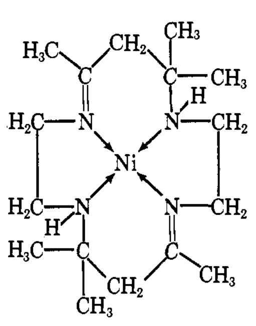
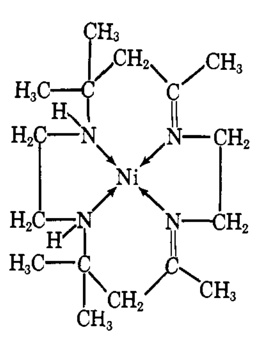
Received January 3, 1967

Stereochemistry of a Macrocyclic Complex. Chelate Ring Conformations and Unusual Isomers[1]

Sir:



I
Ni (1,7-CT)$^{2+}$

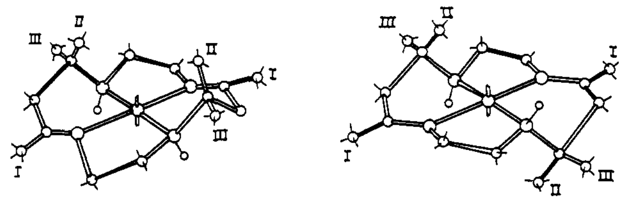


II
Ni (1,4-CT)$^{2+}$

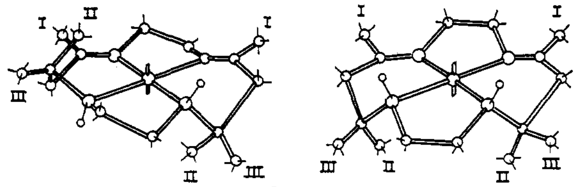
In addition to the obvious position isomers (structures I and II) of the ligand in the planar nickel(II) complexes,[2] hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II), Ni(CT)$^{2+}$, more subtle forms of isomerism are possible. We report here two additional kinds of isomerism, one arising from the asymmetry of coordinated secondary amines, and the other exemplifying the rare phenomenon of "coordination-number" isomerism. Studies on the pmr and visible spectra and other physical properties of these compounds have yielded detailed information on chelate ring conformations and conformational stability.

Curtis, Curtis, and Powell[3] have claimed that unpublished X-ray studies show that the Ni(1,4-CT)$^{2+}$ forms the least soluble isomer perchlorate. Our pmr studies confirm this conclusion. Further, Curtis reports that the Ni(1,7-CT)$^{2+}$ is separable into isomers of unspecified structures. Working with the fluoroborate and thiocyanate derivatives of Ni(CT)$^{2+}$, we had independently discovered the isomers[4] of Ni(1,7-CT)$^{2+}$ and can assign complete structures to them.

Figure 1 represents the structures of the four expected isomers of planar complexes containing either 1,4- or 1,7-CT. The optical activity of the two amine groups should yield a racemic isomer and a *meso* isomer in each case. Two distinct materials are readily obtained from Ni(1,7-CT)(NCS)$_2$, these being diamagnetic and appearing orange and yellow in color. The orange isomer can be resolved into enantiomers (Table I), thereby establishing it as the racemate. Best resolutions were obtained chromatographically using Fisher potato starch. All attempts to resolve the *meso* complex failed. In addition to serving as a structure



(a) Ni(racemic-1,7-CT)$^{2+}$ (b) Ni(meso-1,7-CT)$^{2+}$



(c) Ni(racemic-1,4-CT)$^{2+}$ (d) Ni(meso-1,4-CT)$^{2+}$

Figure 1. Idealized structures of the stereoisomers of Ni(CT)$^{2+}$.

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(1) Supported in part by U. S. Public Health Services Grant GM 10040 from the National Institute of General Medical Sciences.

(2) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **86**, 1331 (1964), and references therein.

(3) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.*, *Sect. A*, 1015 (1966).

(4) L. G. Warner, N. J. Rose, and D. H. Busch, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966.