

was obtained; nmr (DMSO-*d*₆) 1.41 (br d, *J* = 10 Hz, 2 H), 1.67 (s, 9 H), 2.11 (br s, 2 H), 2.31 (br d, *J* = 10 Hz, 2 H), 5.95 (br s, 1 H), 6.20 (br s, 1 H); ir (CH₂Cl₂) 3.26, 3.35, 7.09, 7.27, 9.48. *Anal.* Calcd for C₉H₁₇N₂BF₄: C, 45.03; H, 7.14; N, 11.71. Found: C, 45.01; H, 7.22; N, 11.79.

3-*tert*-Butyl-2,3-diaza-7,7-spirocyclopropyl-norborn-2-ene tetrafluoroborate (2) was prepared from the analogous azo compound^{20,28} by the method used for **1** in 68% yield: mp 164–167° dec; nmr (DMSO-*d*₆) 0.75 (br s, 4 H), 1.42 (m, 1 H), 1.59 (s, 9 H), 2.01 (br s, 1 H), 2.41 (m, 1 H), 3.22 (br s, 1 H), 5.72 (br s, 1 H), 5.82 (br s, 1 H). *Anal.* Calcd for C₁₁H₁₉N₂BF₄: C, 49.60; H, 7.20; N, 10.53. Found: C, 49.51; H, 7.09; N, 10.59.

8-*tert*-Butyl-8,9-diazadetracycl-2-ene tetrafluoroborate (3) was obtained from the azo compound^{21,27} in 54% yield: mp 181–183° dec; nmr (DMSO-*d*₆) 1.67 (s, 9 H), 2.12 (br s, 2 H), 2.42 (br s, 3 H), 3.12 (br s, 1 H), 5.88 (br s, 1 H), 6.04 (br s, 1 H). *Anal.* Calcd for C₁₁H₁₇N₂BF₄: C, 50.03; H, 6.49; N, 10.61. Found: C, 50.10; H, 6.34; N, 10.66.

3-*tert*-Butyl-2,3-diazabicyclo[2.2.2]oct-2-ene tetrafluoroborate (4) was prepared from the analogous azo compound^{21,28} by the method used for **1** in 62% yield: mp 243–245° dec; nmr (DMSO-*d*₆) 1.61 (br d, *J* = 8 Hz, 4 H), 1.77 (s, 9 H), 2.27 (br d, *J* = 8 Hz, 4 H), 5.99 (br s, 2 H). *Anal.* Calcd for C₁₀H₁₉N₂BF₄: C, 47.27; H, 7.54; N, 11.03. Found: C, 47.29; H, 7.45; N, 11.08.

4-*tert*-Butyl-3,4-diazatricyclo[4.2.1.0^{2,3}]nona-3,7-diene tetrafluoroborate (5) was obtained from the azo compound^{21,29} in impure form in 15% yield; mp 118–120° dec; partial nmr (DMSO-*d*₆) 1.72 (s, *t*-Bu), 5.78 (br s, 2 H?); several impurities were apparent, but we were unable to remove them. *Anal.* Calcd for C₁₁H₁₇N₂BF₄: C, 50.03; H, 6.49; N, 10.61. Found: C, 48.86; H, 6.30; N, 10.19.

3-Methyl-2,3-diazanorborn-2-ene tetrafluoroborate (6) was pre-

pared from the azo compound using methyl iodide: mp 181–183° dec. The sample was brown and not analytically pure, but the nmr indicated that **6** was the major component: nmr (DMSO-*d*₆) (br s, 1 H), 5.75 (br s, 1 H), 4.57 (s, 3 H), 1.3–2.6 (complex).

3-Ethyl-2,3-diazanorborn-2-ene tetrafluoroborate (7) was prepared from the azo compound using ethyl iodide: mp 66–67° dec; nmr (D₂O, vs. DSS) 5.82 (br s, 1 H), 5.63 (br s, 1 H), 4.72 (quant, *J* = 7 Hz, 2 H), 2.6–1.3 (complex, 6 H), 1.52 (t, *J* = 7 Hz, 3 H). *Anal.* Calcd for C₈H₁₃N₂BF₄: C, 39.66; H, 6.18; N, 13.21. Found: C, 39.86; H, 6.13; N, 13.22.

1-Allyl-1,2-di-*tert*-butyldiazanium Tetrafluoroborate (8). A mixture of 12.9 g (89.6 mmol) of freshly prepared 1,2-di-*tert*-butylhydrazine³⁰ and 18.1 g (89.6 mmol) of trimethylene dibromide was refluxed in 150 ml of ethanol containing 30 g of potassium carbonate for 19 hr, filtered, and distilled. A fraction boiling at 91–94° (110 mm), 4.6 g, proved to have the nmr spectrum expected for 1-allyl-1,2-di-*tert*-butylhydrazine: 1.01 and 1.02 (2 s, *t*-Bu), 3.3–3.55 (complex, CH₂), and 4.9–5.3 and 5.6–6.1 (complex, CH=CH₂). A solution of 0.66 g (3.59 mmol) of this material in 25 ml of methylene chloride was treated with 1.42 g (7.18 mmol) of silver fluoroborate causing rapid deposition of a silver mirror. After stirring for 15 min, filtration and washing with 10 ml of methylene chloride, the filtrate was diluted to 125 ml with ether, and cooled in Dry Ice. Filtration gave 200 mg (20%) of gray crude **8**, which was crystallized several times from chloroform-ether, to give 80 mg of white solid mp 100–104°; nmr (CDCl₃) 1.70 and 1.75 (2s, *t*-Bu), 5.52 (complex, 3 H), 6.0 (m, 1 H). *Anal.* Calcd for C₁₁H₂₃N₂BF₄: C, 48.19; H, 8.58; N, 10.37. Found: C, 48.55; H, 8.66; N, 10.36.

Acknowledgments. We thank the National Science Foundation for financial support of this work, both through a grant and the Major Instrument program, which provided funds used in purchase of the instruments employed. We thank Professor D. H. Evans for extensive discussions, and Mr. T. Rosanske for obtaining the cv spectrum of **1**⁺ in DMF.

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(26) W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, **730**, 82 (1969).

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Steric Effects at C-7 of Bicyclo[2.2.1]hept-2-enes. Thermodynamic and Kinetic Probes¹

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. Received May 29, 1973

Abstract: Thermodynamic and kinetic probes for the relative steric factors at C-7 of norbornenes, taken collectively, indicate that the etheno bridge is less hindering than the ethano bridge. The difference is relatively small. Among pairs of syn-anti isomers of 7,7-dialkoxynorbornenes that were equilibrated, the largest free energy difference (370 cal mol⁻¹ at 54°) was that separating the 7-methoxy-7-(2-pentoxy) pair.

Bicyclo[2.2.1]heptanes and -heptenes² have been studied very extensively and intensively because the comparative rigidity of those systems removes some of the uncertainties about geometry that are common to conformationally mobile systems. For example, norbornene systems have figured prominently in studies of homoallylic participation and skeletal rearrangements³ and of the stereochemistries of addition and elimination.^{4,5}

(1) Presented in part at 55th Annual Conference of the Chemical Institute of Canada, June 5, 1972.

(2) Referred to subsequently by their trivial names, norbornanes and norbornenes, respectively.

(3) P. D. Bartlett, "Nonclassical Ions, Reprints and Commentary," W. A. Benjamin, New York, N. Y., 1965.

In spite of the breadth and depth of investigations into the chemistry of norbornyl systems, one important aspect has received little attention. Steric effects at C-7 of norbornenes, arising from interactions of C-7 substituents with the ethano and etheno bridges, were not well understood when this work was undertaken. Two measurements, based on equilibrated systems, were recorded in the literature. Sauers⁶ reported that epimerization of 7-carbomethoxynorbornenes by methoxide in methanol at 65° gave a mixture in which the

(4) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

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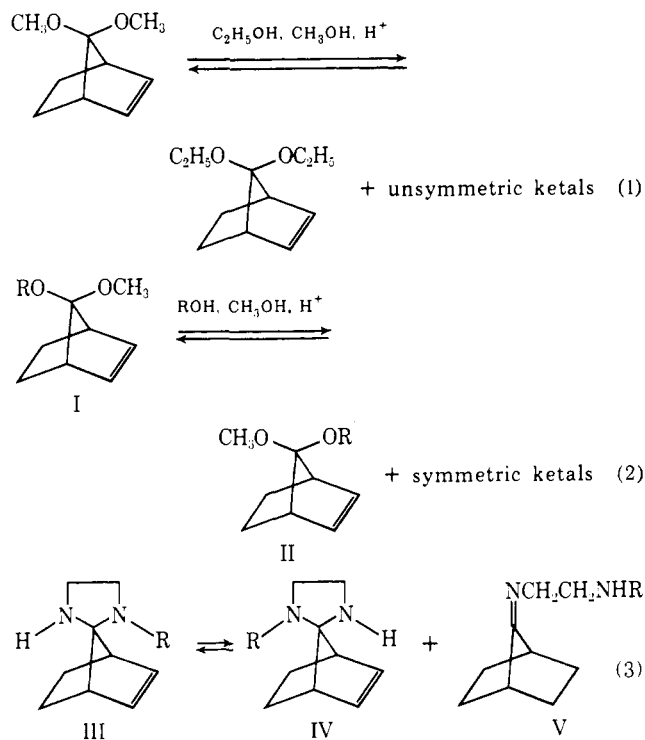
syn ester predominated slightly (55:45) over the anti ester. Gassman and coworkers⁷ equilibrated 7-methoxy-7-*p*-anisylnorbornenes in tetrahydrofuran-methanol at 130° and found the *syn*-anisyl-*anti*-methoxy compound favored over its isomer by the factor 94:6. Although these ratios surely reflect steric factors, it is not at all certain that those factors predominate over polar factors in systems having such widely different C-7 substituents. Although Sauers⁶ attributed the free energy difference in his system to a larger steric factor associated with the ethano bridge, Gassman and coworkers⁷ refrained from comment on the origin of the greater free energy difference between their isomers. Bly and coworkers^{8a,b} judged the etheno bridge to be less hindering in additions to norbornen-7-one while Brown and coworkers^{8c,d} assigned greater steric hindrance to etheno, rather than ethano, bridges of bicyclo[2.2.1] and bicyclo[2.2.2] systems. Thus, not only were the relative magnitudes of *syn* and *anti* hindrance unknown, but even the sense (which side is more hindered) was uncertain. This state of affairs was not very surprising, for many of the *syn*-*anti* rate factors that had been reported are so large that concern about the contribution of ground-state energy differences to those factors was minimal.⁹ However, in the interpretation of small *syn*-*anti* rate factors, such as those in addition of hydride^{8b} or organometallic reagents¹⁰ to norbornen-7-one, carbonation of 7-metallonorbornenes,¹¹ and abstraction from $DSnR_3$ by 7-norbornenyl radicals,¹² it is imperative that steric factors be considered.

The objective of this work was to gather unambiguous evidence for the sense of the steric factor at C-7 of norbornenes and to estimate the magnitude of ΔG° (steric) for a few 7-substituted, *syn*-*anti* isomers.

Methods

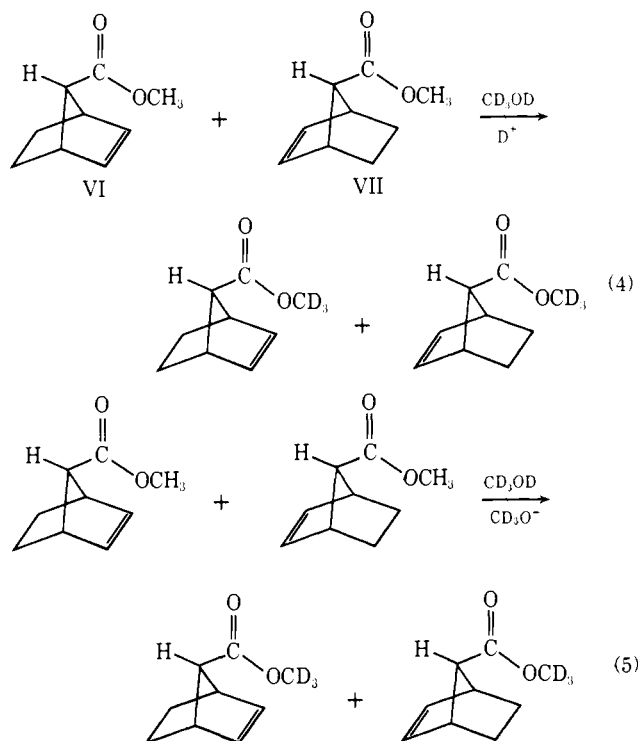
Thermodynamic methods were based on measurement of equilibrium constants for ketal formation (eq 1 and 2) and for imidazolidine isomerization (eq 3). Equilibrium compositions were determined by glpc, which separated symmetric ketals¹³ from each other as well as from unsymmetric ketals¹³ (eq 1), and by pmr spectroscopy on the combined unsymmetric ketals, separated from symmetric ketals but not from each other by glpc (eq 2). Identification of the isomers in the latter case is discussed in the next section.

Imidazolidine isomers (eq 3), although readily prepared from norbornen-7-one, have not yet been assigned or separated, but the magnitudes of the equi-



librium constants were readily determined by pmr of equilibrated systems.

Kinetic methods were based on relative rates of acid- and base-catalyzed transesterification of methyl esters with CD_3OD (eq 4 and 5). Epimerization did not



occur in those experiments but it was used, with other experimental conditions, to estimate the ground-state free energy difference between the isomeric methyl esters.

Results and Discussion

Equilibration of dimethyl ketals with diethyl ketals in the norbornene and norbornane systems (eq 1)

(7) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

(8) (a) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963); (b) R. S. Bly, F. B. Culp, Jr., and R. K. Bly, *ibid.*, **35**, 2235 (1970); (c) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966); (d) E. N. Peters and H. C. Brown, *ibid.*, **94**, 7920 (1972).

(9) The assumption that steric factors at C-7, such as steric acceleration of ionization, could be ignored seems to have been made implicitly by many authors working in this field.³

(10) (a) J. Warkentin, *Can. J. Chem.*, **48**, 1391 (1970); (b) F. R. S. Clark and J. Warkentin, *ibid.*, **49**, 2223 (1971).

(11) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).

(12) (a) E. C. Sanford and J. Warkentin, *J. Amer. Chem. Soc.*, **90**, 1667 (1968); (b) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969); (c) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3968 (1969).

(13) For convenience, the words symmetric and unsymmetric will be used to denote ketals with identical and different O-alkyl groups, respectively.

Table I. Proton Chemical Shifts of Ketals and Imidazolidines

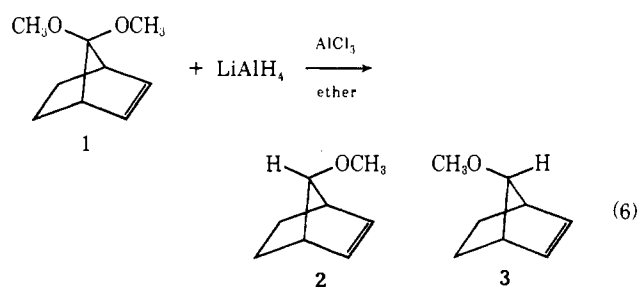
Compd	R	Chemical shifts (δ , CCl_4) ^a							
		H-2,3 ^b	H-1,4 ^b	H-5,6 ^b (exo)	H-5,6 ^b (endo)	O-CH _{α} Anti	O-CH _{α} Syn	O-C-CH _{β} Anti	O-C-CH _{β} Syn
	CH ₃	5.92	2.63	1.79	0.86	3.08 ^d	3.01 ^d		
	CH ₃ CH ₂	5.92	2.62	1.79	0.86	3.09 ^d	3.02 ^d		
	(CH ₃) ₂ CH	5.95	2.61	1.80	0.85	3.14 ^d	3.04 ^d		
	(CH ₃) ₃ CCH ₂	5.90	2.62	1.78	<i>e</i>	3.10 ^d	3.02 ^d		
	CH ₃ (CH ₂) ₂ CHCH ₃	5.92	2.64	1.80	<i>e</i>	3.14 ^d	3.04 ^d		
	CH ₃	5.92	2.63	1.79	0.86	3.08	3.01		
	CH ₃ CH ₂	5.90	2.61	1.80	0.86	3.37	3.27	1.10 ^f	1.02 ^f
	(CH ₃) ₂ CH	5.93	2.59	1.87	0.83	4.03	3.70	1.11 ^f	1.03 ^f
	(CH ₃) ₃ CCH ₂	5.93	2.69	1.82	<i>e</i>	3.00	2.88	0.91 ^{f,g}	0.86 ^{f,g}
	H	6.02	2.27	1.80	0.81	1.65 (NH)		2.82 (NCH ₂)	
	(R)HN-NR(H)								
	CH ₃	5.96 ^h	2.46 ^h	1.90	0.84	2.22 (NCH ₃)		2.82 (NCH ₂)	
		6.03 ^h	2.35 ^h	1.90	0.84	2.22 (NCH ₃)		2.82 (NCH ₂)	

^a Shifts measured from that of internal TMS with a Varian HA-100 instrument. Centers of multiplet signals are reported. ^b Peak shapes are those typical of norbornenes. ^c Mixtures of isomers. Proton signals from the norbornene skeleton of the isomers are not resolved by a 100-MHz instrument. ^d The OCH₃ signal. ^e Obscured by signals from R. ^f Assigned by analogy; assuming that the signal at lower field belongs to the *anti*-alkoxy group. ^g *t*-Butyl group. ^h Signals from a 50:50 mixture of the isomers; no assignment.

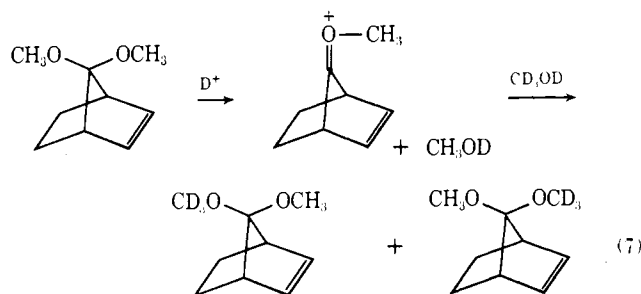
showed that the dimethyl ketal is favored in both, as expected. However, in identical, acidic, methanol-ethanol solutions, the equilibrium constant, $K = [\text{dimethyl ketal}][\text{EtOH}]^2/[\text{diethyl ketal}][\text{MeOH}]^2$, was 8.77 ± 0.33 in the "ane" system and 5.58 ± 0.24 in the "ene" system. It is unlikely that polar effects contribute measurably, for the dipole moments of the simple alcohols lie in the narrow range 1.66–1.71 D. The simplest explanation is that steric hindrance is greater in the norbornane system, leading to a larger fraction of dimethyl ketal at equilibrium than that in the norbornene system.

Assignment of the isomeric, unsymmetric ketals (eq 2) was based on pmr spectra and on analogy, as described below. The methoxy singlets in the pmr spectrum of 7,7-dimethoxynorbornene (1) are separated by about 7 Hz (Table I) but it was not known at the time of our work which signal belongs to which methoxy group. Assignment of those would permit identification of the unsymmetric ketals, for the chemical shifts of protons in the ring are so similar as to indicate that switching alkoxy groups does not alter ring geometry appreciably (Table I).

The methoxy signals of 1 were assigned on the basis of the following results and arguments. Capture of all 7-norbornenyl cations by external nucleophiles occurs preferentially from the anti face. Selectivity is total in capture of the 7-unsubstituted¹⁴ and 7-alkyl cations¹⁵ and can range from total to about 12:1 in capture of the 7-aryl-7-norbornenyl cations by methanol or water.^{7,16} Still lower selectivity (1.8:1), in the same sense, was observed in the reductive ring opening, by HAlCl_2 , of the ketal from norbornen-7-one and ethylene glycol.¹⁷ We found that reduction of 1 by $\text{LiAlH}_4\text{-AlCl}_3$ (eq 6) gave 2 and 3 in the ratio 2/3 = 5.6.¹⁸ This result shows that the 7-methoxynorbornenyl



cation is like the others in its preference for anti capture. With the reasonable assumption that the sense of this selectivity is the same in the transketalization reaction (eq 7), one can assign the more rapidly disappearing



methoxy signal (pmr) in that process to the *anti*-methoxy group. It was found that the low-field signal decays faster (twofold, 35°) and it was therefore assigned to the *anti*-methoxy group of 1. The same assignment has been made by Lamaty and coworkers¹⁹ although the basis for it was not discussed.

Once the methoxy signals of 1 were assigned, the pmr spectra of mixtures of unsymmetric ketals (eq 2) could be untangled. The methoxy signal at lower field was assigned to the *anti*-methoxy isomer and integration gave the isomer ratios of Table II.

It can be seen from Table II that the equilibrium constants corresponding to eq 2 agree qualitatively with those corresponding to eq 1. The differences between the free energies of isomers are small, and in the direction of greater stability of those isomers with the larger alkoxy group on the syn side. Again, as in

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(15) J. A. Berson, D. S. Donald, and W. J. Libbey, *J. Amer. Chem. Soc.*, **91**, 5580 (1969).

(16) P. G. Gassman and A. F. Fentiman, *J. Amer. Chem. Soc.*, **92**, 2549 (1970).

(17) H. A. Davis and R. K. Brown, *Can. J. Chem.*, **51**, 361 (1973).

(18) Ethers 2 and 3 were readily assigned on the basis of "w-coupling" between C₇-H and C_{2,3}-H of 2.

Table II. Ketal Equilibria (54°)

ROH	ROH/ CH ₃ OH ^a	Solvent	II	I
CH ₃ CH ₂ OH	2	None	52 ^b	48 ^b
(CH ₃) ₃ CCH ₂ OH	3	None	57	43
(CH ₃) ₂ CHOH	10	None	62	38
(CH ₃) ₂ CHOH	10	Ether ^c	62	38
(CH ₃) ₂ CHOH OH	10	CCl ₄ ^c	62	38
CH ₃ CHCH ₂ CH ₂ CH ₃	100	None	64	36

^a The initial mole ratio of alcohols fed. Ratios had to be different for different ROH in order to get reasonable fractions of unsymmetric ketals at equilibrium. ^b Numbers in these columns are percentages of the total unsymmetric ketals present at equilibrium. ^c Approximately 5 volumes of solvent per volume of alcohol solution.

the case of symmetric ketals, it is difficult to accommodate a polar contribution to these equilibrium constants and we attribute stability differences primarily to steric effects. Support for this assignment is found in the observation that the equilibrium constants are insensitive to changes of medium (Table II) and in the fact that isomeric ketals are not separable on either nonpolar or polar glpc columns of ordinary length.²⁰ Their heats of solution in polar solvents must therefore be very similar, a result incompatible with an appreciable difference in polarity.

Although the steric requirement of the ethano bridge is not much larger than that of the etheno bridge, both provide substantial steric hindrance to C-7 substituents. The large absolute magnitude of the steric hindrance is indicated by the large feed ratios (ROH/CH₃OH) required to get appreciable fractions of mixed ketals at equilibrium in those cases where ROH is a branched alcohol (Table II). It is not surprising that both the difference between the free energies of isomers and the overall steric factor, indicated qualitatively by the numbers in the last column, are greatest in cases of α -branched R. Such substituents have the largest steric requirements close in to C-7, meaning that nonbonded interaction with the appropriate 2-carbon bridge and with the other C-7 substituent cannot be avoided. The low sensitivity of the syn-anti ratio to β -branched R groups presumably means that such groups extend largely beyond the steric influence of the 2-carbon bridges.

Equilibrium constants among aminoimines and imidazolidines (eq 3) are listed in Table III. Those unstable compounds were not separated and assignment of gross structure rests on the method of synthesis (see

Table III. Imidazolidine and Imine Equilibria^a

R	III	IV	V
CH ₃	50	50	0
CH ₃ CH ₂	52	48	0
(CH ₃) ₂ CCH ₂	34	26	40
(CH ₃) ₂ CH	21	12	67
(CH ₃) ₂ C	<i>b</i>	<i>b</i>	96

^a The numbers are equilibrium percentages of the isomers indicated, in dimethyl sulfoxide at 37°. ^b Not measurable individually because of low concentration and because of signal overlap.

(20) Separation was just achievable with a 200-ft Apiezon L capillary column.

Experimental Section), the ready hydrolysis of the mixtures to norbornen-7-one, and on pmr and ir spectra (below). Assignment of the imidazolidine isomers was based on the isomer ratios at equilibrium, with the assumption that the equilibrium relationships among ketals (eq 1 and 2) carry over qualitatively to the nitrogen analogs. Although the results in Table III do not provide independent evidence concerning the identity of the more hindered face, they provide another measure of the magnitude of the difference if the basis of assignment is accepted.

As in the ketal systems, the large steric hindrance at either C-7 face is made manifest also in the imidazolidines, this time in the fraction of aminoimine at equilibrium (eq 3, Table III). Identification of the imino isomer rests on three observations. First, increasing the temperature of the sample increased the fraction of the third component at the expense of the imidazolidines and lowering the temperature caused rapid return to the original composition. Therefore, the third component in some of the equilibrium mixtures (Table III) is one that is rapidly equilibrated with the imidazolidines. Second, infrared spectra of mixtures containing an extra component (last three entries, Table III) had a strong band near 1710 cm⁻¹, consistent with the presence of a strained imine. Third, the pmr spectra of such mixtures showed not only the expected vinyl triplets of the imidazolidines but also an additional 16-line signal in the vinyl region. The chemical shift and the appearance of this multiplet was very similar to that in the spectrum of the semicarbazone of norbornen-7-one, the complexity of these spectra being a consequence of the asymmetry introduced by the 7 substituent, which makes the pairs of vinyl, bridgehead, and C_{5,6} protons nonequivalent.

Relative transesterification rates of the isomeric 7-carbomethoxynorbornenes, for both acid and base catalysis (eq 4 and 5), are given in Table IV. In the

Table IV. Relative Rates of Transesterification and Transketalization in CD₃OD at 35°

Compound	Catalyst	<i>k</i> _{rel}
VI	H ⁺	1 ^a
	CD ₃ O ⁻	1 ^a
VII	H ⁺	1.0
	CD ₃ O ⁻	1.8
1	H ⁺	2.0 ^b

^a The syn ester is taken as the reference for both acid- and base-catalyzed transesterification. ^b *k*_{anti}/*k*_{syn}.

acid-catalyzed reaction the esters react at the same rate while the anti isomer is 1.8-fold more reactive in the base-catalyzed process at 35°. Before these numbers could be interpreted it was necessary to determine the ground-state free energy difference between the isomers in the same solvent at 35°. At that temperature epimerization is very slow and it was necessary to estimate *K*_{eq} (syn-anti) by extrapolation from higher temperatures. When this was done using Sauers' value⁶ of 1.22 (65°) and newly measured values, *K* = 1.17 (80°), and *K* = 1.14 (95°), the value calculated was *K*_{eq} = 1.32 (35°). This corresponds to *G*^o_{anti} - *G*^o_{syn} = 162 cal mol⁻¹, which must also be the amount by which the transition state for reaction of the anti

isomer lies above that for the syn isomer in the acid-catalyzed process. Although the sense of this difference is in keeping with a less-hindered syn face, it is surprising that the difference between the free energies of the transition states is not larger than that separating the ground states. One must remember, of course, that the basis of ester hydrolysis as a kinetic criterion for steric effects is the fact that acid-catalyzed ester hydrolysis rates are *in general* insensitive to polar substituents in the ester. Presumably polar effects are not negligible in the present case.

The lower rate of the syn ester in base-catalyzed transesterification is probably the result of electrostatic repulsion, at the transition state, between the C-2,3 π electrons and the developing negatively charged substituent. Such a polar effect was proposed by Bly and Bly^{8a} to account for the preference of norbornen-7-one to add dimethylsulfoxonium methylide from the syn face. The lower acidity of norbornene-*syn*-7-carboxylic acid, relative to that of the anti isomer,²¹ can be attributed, in part, to a similar interaction. What is needed to accommodate the base-catalyzed transesterification data is that the polar factor be larger than the opposing steric factor.

Although the transesterification rate data can be rationalized, doubt is cast on the reliability of such kinetic criteria of steric effects, at least in cases like the one at hand where the rate factors are small. The thermodynamic criterion, with substituents so chosen as to minimize or eliminate differences in polarity of equilibrated isomers, seems preferable whenever the system of interest is adaptable to that approach.

In summary, the results of this work, taken together, are in keeping only with lesser steric hindrance at the syn, C-7 face than at the anti face of norbornenes. The differences are small; the differential effects of steric acceleration of ionization of anti-syn isomers for example, must be negligible compared to the observed rate factors in typical solvolyses. On the other hand, steric factors are probably important or even dominant in some other reactions of norbornene systems,²² some of which will be discussed in subsequent papers.

Experimental Section

7,7-Dimethoxybicyclo[2.2.1]hept-2-ene (1). 7,7-Dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene²³ (32 g, 0.11 mol), reduced according to Gassman's method B,²⁴ gave 8.7 g (52%) of **1**, bp 68–71° (26 mm).

Bicyclo[2.2.1]hept-2-en-7-one (4). Stirring of **1** (8.5 g) with 5% H₂SO₄ (1 l.) for 2 hr, followed by extraction with petroleum ether, drying of the extract with anhydrous magnesium sulfate, removal of solvent, and vacuum distillation gave **4** (5.5 g, 90%) as a colorless liquid, bp 70–74° (40 mm).²⁴

7,7-Dimethoxybicyclo[2.2.1]heptane. A solution of **1** (5.0 g, 0.032 mol) in methanol (10 ml) was stirred under hydrogen (1 atm) with palladium/carbon catalyst (200 mg, 5% Pd) until the pmr spectrum of an aliquot was free of vinyl signals. Filtration and evaporation of the methanol left 4.4 g (87%) of the saturated ketal containing a trace of methanol.

Equilibration of Ketals. To a solution of methanol, another alcohol (see Table II for structures and compositions), and **1** was added a trace amount of fuming sulfuric acid. The resulting solution, in a stoppered flask, was shaken and placed in a water bath at 54.0 ± 0.2°. Aliquots were withdrawn from time to time and

reaction in these was stopped by addition of excess 10 *N* sodium hydroxide which was also at the bath temperature. Extraction with ether, drying over anhydrous magnesium sulfate, and gas chromatography (10% SE-30, 10 ft × 3/8 in., 150°) led to separation of the unsymmetric ketals (together) from the two symmetric ketals and from traces of norbornen-7-one. Relative retention times of the ketals (7 substituents, followed by relative time) were: (O-CH₃)₂, 1.00; OCH₃, OCH₂CH₃, 1.20; -(OCH₂CH₃)₂, 1.35; OCH₃, OCH(CH₃)₂, 1.56; OCH₃, OCH₂C(CH₃)₃, 2.18; (OCH(CH₃)₂)₂, 2.43; OCH₃, OCH(CH₃)CH₂CH₂CH₃, 2.61; (OCH₂C(CH₃)₃)₂, 4.36. Collection of the unsymmetric ketals and integration of the pmr spectrum of the mixture gave their ratio.

Product ratios at equilibrium, from two or more experiments with a given pair of alcohols, were averaged. In each experiment, attainment of equilibrium was verified by showing that the ketal ratio data, from analysis of the older aliquots, were not time dependent. In a typical experiment, aliquots taken after 4, 10, 60, and 120 min gave the same ketal ratios.

Equilibration of dimethyl with diethyl ketals, in both the norbornene and the norbornane system, was done with **1** and 7,7-dimethoxynorbornane, using portions of a stock solution of acidified ethanol in methanol. Quenching, extraction, and gas chromatography as described above gave the ratios of dimethyl to diethyl ketals in the two systems. Injection of a nonequilibrium mixture of dimethyl and diethyl ketals into the column did not change the ratio and unsymmetric ketals were not produced during the separation.

Hydrogenolysis of 1 by LiAlH₄-AlCl₃. The procedure was similar to that of Eliel and coworkers.²⁵ To aluminum chloride (1.3 g, 0.010 mol) in 25 ml of dry ether, in a flask equipped with magnetic stirrer, condenser, and drying tube, was added, from a pressure-equalizing dropping funnel, a slurry of lithium aluminum hydride (1.0 g, 0.025 mol) in 5 ml of ether. When addition was complete the mixture was kept for 30 min before **1** (612 mg, 4.0 mmol) was dropped in during 15 min. The mixture was stirred at ambient temperature for 1.5 hr before addition of 10% H₂SO₄ (50 ml). Extraction with ether (3 × 50 ml), drying of the extract with anhydrous magnesium sulfate, and distillation of the ether left 324 mg of a liquid mixture. Gas chromatography (20% DEGS, 5 ft × 0.25 in., 110°) showed two major components (relative retention times 1:2, ratio 1:3.6) and a few per cent of a third component. Collection of the material corresponding to the smaller of the major peaks showed (pmr) that it consisted of *anti*-7-methoxybicyclo[2.2.1]hept-2-ene: pmr (CCl₄) δ 5.88 (t, 2, vinyl), 3.19 (s, 3, OCH₃), 3.00 (m, 1, C₇-H), 2.58 (m, 2, C_{1,4}-H), 1.66 (m, 2, C_{3,6}-H_{exo}), 0.86 (m, 2, C_{3,6}-H_{endo}). A weak singlet at δ 3.20 as well as small signals at higher field were attributed to a minor, unidentified contaminant. The major product of the hydrogenolysis was identified as *syn*-7-methoxybicyclo[2.2.1]hept-2-ene: pmr (CCl₄) δ 5.98 (m, 2, vinyl), 3.40 (m, 1, C₇-H), 3.21 (s, 3, OCH₃), 2.96 (m, 2, C_{1,4}-H), 1.69 (m, 2, C_{3,6}-H_{exo}), 1.00 (m, 2, C_{3,6}-H_{endo}). Irradiation of the multiplet at δ 3.40 caused the vinyl multiplet to collapse to a triplet.²⁶

Transketalization of 1 in Methanol-*d*₄. A tube containing methanol-*d*₄ (0.35 ml) and **1** (30 mg) was warmed in the probe of a Varian T-60 instrument for 20 min. *p*-Toluenesulfonic acid (0.3 mg), dissolved in 0.05 ml of methanol-*d*₄, was injected into the tube which was shaken and reinserted into the probe. The range through δ 3.0–3.3 was scanned at about 1-min intervals for 50–60 min. Signal heights from the ketal methoxy signals at δ 3.0 and 3.1 and from the methoxy signal of methanol were added and the former were expressed as fractions of the total. These fractions correspond to the familiar (*a* - *x*) terms of first-order kinetics, with *a* = 0.5 in this case. Plots of log (*a* - *x*) against time for the two ketal signals were straight lines to about 50% reaction, the ratio of slopes being 2.00 ± 0.12, with the downfield signal (δ 3.18) disappearing more rapidly. Corrections from equilibration²⁷ that would be required if individual rate constants, rather than their ratio, were of interest, were not applied.

Spiro[bicyclo[2.2.1]hept-2-ene-7,2'-imidazolidines]. The synthesis of the *N*-methyl compound, described below, is typical of the pro-

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(21) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

(22) See introductory paragraphs.

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cedure used to prepare the title compounds containing, where indicated in Table III, the corresponding isomeric imines.

To a solution of **4** (1.08 g, 0.010 mol) in benzene (25 ml) was added *N*-methylethylenediamine (0.89 g, 0.012 mol). Fast, exothermic reaction occurred and the water formed was removed by azeotropic distillation with benzene. Vacuum distillation (0.1 mm) of the dark residual oil gave *N*-methylspiro[bicyclo[2.2.1]hept-2-ene-7,2'-imidazolidine] (1.2 g, 73%) as a colorless liquid. Both isomers were produced (Table I), the ratio being 1.4:1. Attempts to separate those isomers or any of the other isomeric mixtures of Table III were unsuccessful.

Approximate yields of mixtures of other imidazolidines and imines (Table III) by analogous treatment of **4** with *N*-alkylethylenediamines were: *N*-ethyl, 60%; *N*-isopropyl, 60%, *N*-*tert*-butyl, 20%; *N*-neopentyl, 10%. All mixtures showed the expected vinyl absorption in the pmr spectra (see Discussion). However, those spectra of all but the simplest systems were very complex in the high-field region. The *N*-isopropyl and *N*-*tert*-butyl systems (neat) absorbed strongly in the infrared, at 1720 and 1718 cm^{-1} , respectively. All of the samples were unstable in CCl_4 , except for short periods, and all regenerated norbornen-7-one on treatment with water.

Equilibration of the imidazolidines (and imines) at 37°, in DMSO containing a trace of *p*-toluenesulfonic acid, was followed by pmr. Isomer ratios were determined by integration of the signals in the vinyl region.

Base-Catalyzed Transesterification of 7-Carbomethoxynorbornenes. A mixture of the isomeric esters (anti:syn = 1.38:1) was prepared by esterification of a mixture of the acids with diazomethane.²⁸ To 44 mg of the mixture in 0.4 ml of methanol- d_4 in an nmr tube at $35 \pm 0.5^\circ$ (probe temperature) was added sodium methoxide in methanol- d_4 (10 μl) from a solution containing 100 mg of NaOCH_3/ml . Anisole (10 mg) was also injected into the tube, which was shaken and returned to the probe. The spectrum covering the range δ 3.5–3.8 was scanned at 2–3-min intervals for 80 min. Peak heights for *anti*- and *syn*-methoxyl groups, at δ 3.6 and 3.5, respectively, were expressed as fractions of the heights of the methoxy signal of anisole (δ 3.8). Logarithms of these fractions, plotted against time, were linear, first-order, plots over the fractions of reaction (anti, 43%; syn, 27%) that were followed. The slopes of these lines were in the ratio 1.8:1, the anti ester reacting more rapidly.

Acid-Catalyzed Transesterification. The above procedure was followed, except for the addition of fuming sulfuric acid (98 mg) instead of methoxide. Pseudo-first-order plots were straight, parallel lines for transesterification of the two esters. Reactions were followed to 31% of completion.

Acknowledgment. This work was supported by the National Research Council of Canada.

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Conformational Analysis. XXIX. 2-Substituted and 2,2-Disubstituted 1,3-Dioxanes. The Generalized and Reverse Anomeric Effects¹

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Abstract: In solvent carbon tetrachloride, the axial isomers of 2-ethynyl-*cis*-4,6-dimethyl-1,3-dioxane and 2-phenylethynyl-*cis*-4,6-dimethyl-1,3-dioxane predominate at equilibrium over their equatorial epimers. The preference is attenuated in the more polar solvent ether and reversed in the still more polar acetonitrile. 2-Phenyl- and 2-*p*-trifluoromethylphenyl-*cis*-4,6-dimethyl-1,3-dioxanes show a lesser solvent sensitivity in their axial–equatorial preference and, despite the very much larger dipole differences in the *p*-trifluoromethyl as compared with the unsubstituted phenyl compound, have very similar ΔG° values in any given solvent. These results show that the anomeric effect evident in the ethynyl and, to a much lesser extent, in the phenyl compounds is not entirely caused by dipole interaction but, at least in part, by double bond–no bond resonance or the quantum mechanical equivalent thereof, as originally proposed by Altona. The 2,4-dimethyl-2-chloromethyl- and -2-bromomethyl-1,3-dioxanes show little equatorial–axial preference and only a small and rather unusual solvent dependence in that the epimer of higher dipole moment is less favored in more polar solvents. The same solvent dependence is found in the equilibrium of the 2-carbomethoxy-2,4-dimethyl-1,3-dioxanes which strongly favors the axial carbomethoxy isomer. These results provide only tenuous evidence for the reverse anomeric effect of a C–X group postulated by Coxon.

The preference for the *gauche* conformation exhibited by gem-dihetero moieties of the type R–X–C–Y (X = O, N, S; Y = an atom having unshared electron pairs) has recently been termed the generalized anomeric effect.^{3–5} This effect, observable in acyclic

compounds (such as dimethoxymethane⁶), as well as within rings (as in *N,N*-dialkyl-1,3-diazanes⁶), is a generalized manifestation of the preference of axial over equatorial C-1 alkoxy groups (aglycones) in pyranose sugars which has long been known as the anomeric

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