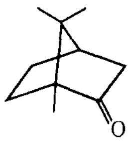
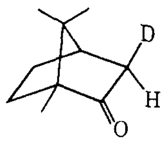
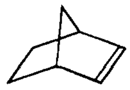


1

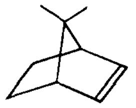


2

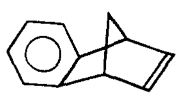
Reactions, however, that proceed through a cyclic transition state are postulated[1] to be influenced by the size of the substituent located at the *syn*-7 position. Norbornene (**3**), for example, forms a very stable complex with silver ion (presumably *exo*)[4] whereas apobornene (**4**) does not.[1]



3



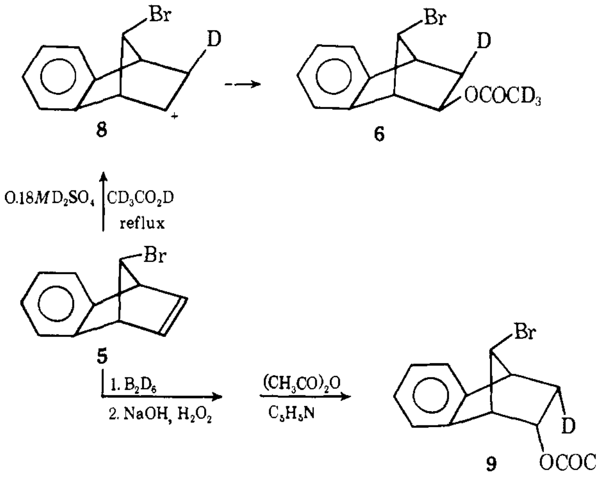
4



7

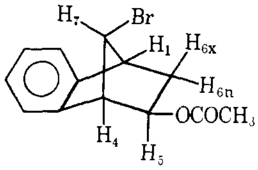
The proposal was postulated to be capable of being tested for addition reactions by utilizing mechanisms which were clearly either single-stage or two-stage additions. The acid-catalyzed addition of acetic acid has been shown previously to occur in a stepwise manner[5,6] and the hydroboration reaction is known to proceed in a concerted fashion to yield the *cis* addition product resulting from attack on the least-hindered side of the olefin.[7] These two reactions seem, therefore, well suited for testing the above hypothesis on a *syn*-7 substituted norbornene system.

The sulfuric acid-d_2 catalyzed addition of acetic acid-d_4 to *anti*-7-bromobenzonorbornadiene (**5**) produced the unrearranged *cis-exo* addition product **6** as the first and only observable (nmr) product. Addition of the same reagent to benzonorbornadiene (**7**) produced extensive rearrangement.[5] The analogous rearrangement is precluded in the addition to **5** by the apparent need to keep the bulky groups, bromine and acetate, as far apart as possible in product formation. The acid-catalyzed addition of acetic acid-d_4 to **5** provides, then, an example of a stepwise *cis-exo* addition where conceivably some factor is accounting for both the preference for *exo* electrophilic attack and for the *exo* nucleophilic attack on the intermediate benzonorbornenyl cation **8**.

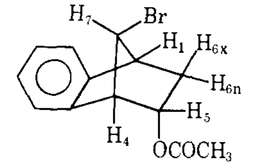


Whereas the stepwise electrophilic addition of acetic acid-d_4 is *cis-exo*, the deuterioboration of **5** occurred exclusively *cis-endo* to produce, after acetylation, the acetate **9**. The concerted nature of this reaction, according to the above argument,[1] prevents attack at the corners of **5** and hence interaction with bromine, which is located *syn* to the double bond, is inevitable with *exo* approach. This makes *endo* approach more favorable on steric grounds, as expected.

The configurations of the acetates **6** and **9** were established by comparison (nmr) with the corresponding undeuterated acetates, **10** and **11**.[8-10] In *anti*-7-bromo-*exo*-5-benzonorbornenyl acetate (**10**), the signal for H_5 occurs at δ 4.70 with $J_{5,6n} = 7.5$ Hz, $J_{5,6x} = 3.5$ Hz, and $J_{5,7} = 1.2$ Hz. In the corresponding *cis*-deuterio acetate **6**, this signal collapses to a quartet with $J_{5,6n} = 7.5$ Hz and $J_{5,7} = 1.2$ Hz. In *anti*-7-bromo-*endo*-5-benzonorbornenyl acetate (**11**), the signal for H_5 occurs at δ 5.71 with $J_{5,6x} = 8.7$ Hz, $J_{5,6n} = 3.1$ Hz, and $J_{5,4} = 4.0$ Hz. In the corresponding *cis*-deuterio acetate **9** this multiplet collapses to a quartet with $J_{5,6x} = 8.7$ Hz and $J_{5,4} = 4.0$ Hz.



10



11

Acknowledgment. We are indebted to the donors of The Petroleum Research Fund, administered by he American Chemical Society, for partial support of this research.

---

(2) A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1309 (1965).

(3) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

(4) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

(5) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

(6) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719 (1966).

(7) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962).

(8) Correct microanalyses were obtained for the acetates.

(9) Chemical shifts are relative to tetramethylsilane (60 MHz).

(10) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967), and references cited therein.

(11) National Science Foundation Undergraduate Research Participant, 1967–1969.

Ronald Caple, Casmir S. Ilenda[11]
Department of Chemistry, University of Minnesota, Duluth
Duluth, Minnesota 55812

Received March 20, 1970

On the Relative Importance of Through-Space *vs.* Through-Bond Interaction between the Lone Pairs in 1,4-Diazabicyclo[2.2.2]octane[1,2]

Sir:

Some time ago Hoffmann, Imamura, and Hehre[3] discussed the electronic mechanism for the interaction of electron lone pairs in diazabicycloalkanes (I). They showed that the relative sequence of the orbitals $a_1'(n_+)$, $a_2''(n_-)$ associated with the linear combinations $n_+ = N_+(n_1 + n_2)$ (S) and $n_- = N_-(n_1 - n_2)$ (A)

---

(1) Part X of "Applications of Photoelectron Spectroscopy."

(2) Part IX: E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, in press.

(3) R. Hoffmann, A. Imamura, and J. W. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

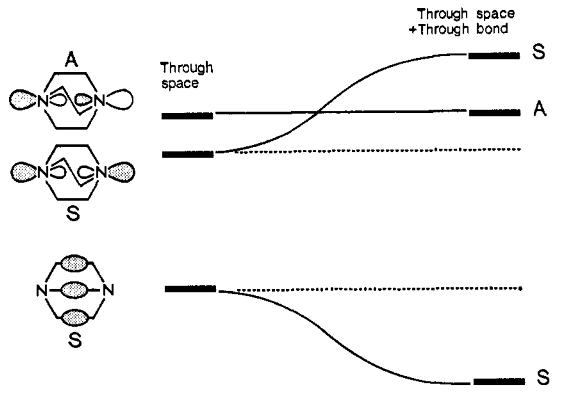


Figure 1. Schematic corrrelation diagram for the dependence of the relative orbital energies of the symmetric (S) and antisymmetric (A) lone-pair orbitals on through-space and through-bond interaction: left side, through-space interaction only. Through-bond interaction increases from left to right.

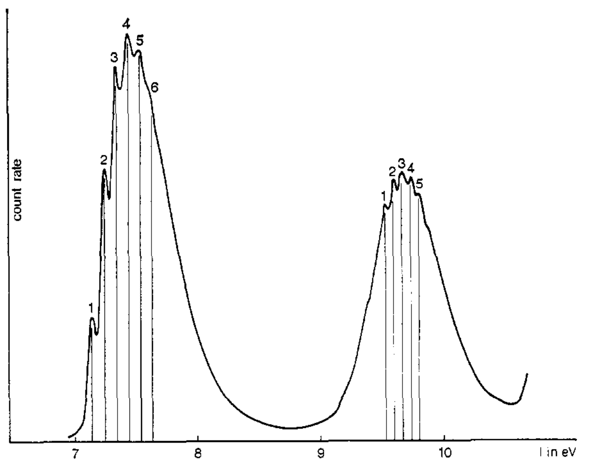
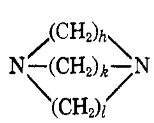
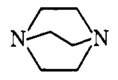


Figure 2. Photoelectron spectrum of 1,4-diazabicyclo[2.2.2]octane (II).

depends primarily on two factors: (1) a first-order through-space interaction between n_1 and n_2 which places $a_2''(n_-)$ above $a_1'(n_+)$ and (2) a second-order interaction with the energetically low-lying C–C and/or C–H σ orbitals which yields the sequence $a_1'(n_+)$ above $a_2''(n_-)$. Theory predicts that effect 1 dominates for $h = k = l = 1$ (see structure I), *i.e.*, for short N···N distances, while (2) should be responsible for the ordering of the lone-pair orbitals in molecules in which *h*, *k*, and *l* are all larger than 1. (This situation is summarized in Figure 1.)



I



II, $h = k = l = 2$

In a previous communication[4] of this series we have shown that the splitting between the n ionization bands in the photoelectron spectrum (PE spectrum) of 1,4-diazabicyclo[2.2.2]octane (dabco, II) amounts to 2.13 eV, in reasonable agreement with the predicted value of 1.57 eV[3] obtained from an extended Hückel model.[5] However, we left open the question of the ordering of the orbitals $a_1'(n_+)$ and a_2'' (n_-). In this note we wish to show that an analysis of the vibrational pattern of the two n bands in the PE spectrum of II strongly supports the prediction by Hoffmann, Imamura, and Hehre;[3] namely, that in the case of II, the through-bond interaction dominates the through-space interaction of the lone pairs n_1 and n_2. (The same result has recently been obtained by Dewar,[6] using the MINDO/2 method.[7])

Figure 2 shows the first two bands in the PE spectrum of II (maxima at 7.52 and 9.65 eV), which are associated with ionization processes in which an electron vacates one or the other of those molecular orbitals, to which n_+ or n_- is the major contributor. Both bands (labeled 1 and 2 in Figure 2) show vibrational fine structure, the maxima of which have been numbered by $x = 1, 2, \ldots$. These numbers x differ from the true vibrational quantum numbers $v = 0, 1, 2, \ldots$ by an unknown constant, *i.e.*, $v = x + k$, which in the case of band 1 could be $k = -1$ or 0 and for band 2 probably $k = 1$ or 2.

With reference to the arbitrary numbers x, the positions $I(x)$ of the fine structure maxima (in eV) satisfy the following linear regressions $I(x) = I_0 + bx$. For band 1

$$I(x) = 7.638 + 0.098x \text{ eV} \tag{1a}$$

and for band 2

$$I(x) = 10.047 + 0.069x \text{ eV} \tag{1b}$$

From a variance analysis one finds that the lower (l) and upper (u) 95% confidence limits of the slopes b are the following (ϕ = degree of freedom). For band 1

$$b_l = 0.095 \text{ eV} \qquad b_u = 0.101 \text{ eV} \qquad \phi = 4 \tag{2a}$$

and for band 2

$$b_l = 0.063 \text{ eV} \qquad b_u = 0.075 \text{ eV} \qquad \phi = 3 \tag{2b}$$

As a control, independent PE spectra with a spread of 0.25 eV/in. have been recorded. They yield mean fine structure spacings of 0.095 eV (band 1) and 0.066 eV (band 2), in good agreement with the above results.[8]

From these values of the slopes, the following 95% confidence limits of the vibrational frequencies (in wave numbers) are obtained. For band 1

$$765 \leqslant \tilde{\nu}_1 \leqslant 815 \text{ cm}^{-1} \tag{3a}$$

and for band 2

$$510 \leqslant \tilde{\nu}_2 \leqslant 555 \text{ cm}^{-1} \tag{3b}$$

In the following we shall assume that the radical cation II^+, like the neutral molecule II itself,[9] has D_{3h} symmetry. The two highest occupied orbitals of II belong to the nondegenerate irreducible representations A_1' (orbital $a_1'(n_+)$ containing n_+) and A_2'' (orbital $a_2''(n_-)$ containg n_-). The removal

---

(4) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969).

(5) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2745, 2474, 2480 (1964); *Tetrahedron*, **22**, 521, 539 (1966).

(6) M. J. S. Dewar and J. S. Wasson, private communication.

(7) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(8) In a previous communication[4] the slope for band 2 is incorrectly given as 0.82 eV.

(9) T. Wada, E. Kishida, Y. Tomiie, H. Suga, S. Seki, and I. Nitta, *Bull. Chem. Soc. Jap.*, **33**, 1317 (1960); see also O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969), and ref 11 and 13.

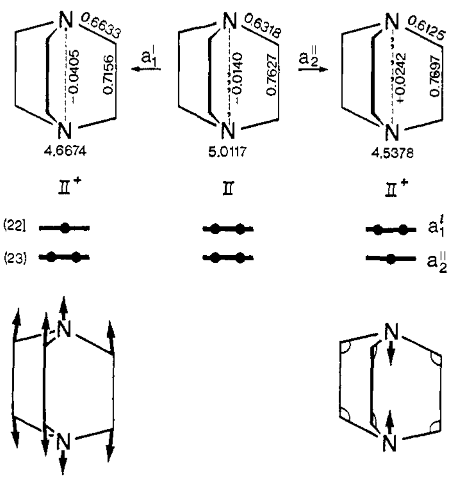


Figure 3. Bond populations for 1,4-diazabicyclo[2.2.2]octane (II) (center) and its radical cations obtained by removing an electron from orbitals a_1' (left) or a_2'' (right), respectively. The schematic drawings at the bottom of the figure indicate the type of totally symmetric distortion of the molecular frame associated with the corresponding ionization.

of an electron from $a_1'(n_+)$ or $a_2''(n_-)$ will affect all symmetry-equivalent bonds of II in the same way and thus lead to a distortion belonging to the irreducible representation A_1' of D_{3h}. The Franck–Condon transitions from II to II^+ must therefore excite totally symmetric vibrations (A_1') of the radical cation II^+.

We shall now predict which of the six totally symmetric modes is excited by the removal of an electron from either orbital $a_1'(n_+)$ or from $a_2''(n_-)$.

A normal coordinate analysis for the parent compound bicyclo[2.2.2]octane has first been carried out by Macfarlane and Ross,[10] and for II by Weiss, Parkes, Nixon, and Hughes[11] as well as by Marzocchi, Sbrana, and Zerbi.[12] For the sake of simplicity we shall use the results and the symbols of a recent publication on the same subject due to Brüesch and Günthard.[13] (The corresponding values and symbols will be marked "B and G".)

In the diagram of Figure 3 we give the results of an extended Hückel calculation[5] for those changes in overlap population $OP_{\mu\nu}$ (between centers μ and ν) which are associated with the removal of an electron from $a_1'(n_+)$ (EHT orbital 22) or from $a_2''(n_-)$ (EHT orbital 23). We shall assume, as a first approximation, the proportionality

$$\Delta R_{\mu\nu} \propto -\Delta OP_{\mu\nu} \qquad (4)$$

between the changes $\Delta OP_{\mu\nu}$ in overlap population and the corresponding changes $\Delta R_{\mu\nu}$ in interatomic distances $R_{\mu\nu}$. Depending on the nature of the vacated orbital, two different totally symmetric deformations of the molecular frame of II are predicted to accompany the transitions II → II^+.

A. Orbital Vacated, $a_1'(n_+)$. If the electron leaves $a_1'(n_+)$ (which is predicted by Hoffmann, Imamura, and Hehre to be the top occupied orbital, no. 22, in II), then we observe a decrease, $\Delta OP_{23} = \Delta OP_{56} = \Delta OP_{78} = -0.0471$, of the overlap populations for the three axial C–C bonds and an increase, $\Delta OP_{12} = \ldots = \Delta OP_{48} = +0.0315$, for the six C–N bonds. Furthermore, the negative OP_{14} between the two nitrogen lone-pair orbitals n_1 and n_2 (*i.e.*, along the threefold axis of the molecule) changes by an amount $\Delta OP_{14} = -0.0265$. As a consequence, we predict the totally symmetrical deformation of the molecular frame indicated in Figure 3, *i.e.*, one which is dominated by a synchronous stretching of the three C–C bonds such that the two halves ($N(CH_2)_3$–) of the molecule move apart with only minor changes in the bond angles. This is essentially the internal symmetry coordinate S_3 (B and G[13]).

B. Orbital Vacated, $a_2''(n_-)$. In this case there is only a small increase in the overlap population along the C–C bonds ($\Delta OP_{23} = \Delta OP_{56} = \Delta OP_{78} = +0.0070$), which is accompanied by a decrease $\Delta OP_{12} = \ldots = \Delta OP_{48} = -0.0193$ for the six C–N bonds. The main change is in the through-space interaction of the lone-pair orbitals n_1 and n_2 between which the overlap population changes by $\Delta OP_{14} = +0.0382$. The corresponding change in the interatomic distances is again shown in Figure 3. In this case the deformation affects mainly the six CCN bond angles, and is properly described by the symmetry coordinate S_7 (B and G[13]).

The normal coordinate (B and G[13])

$$\mathbf{Q}_k = \sum_s L_{ks}^{-1}\mathbf{S}_s \qquad (5)$$

excited in a photoionization process may be determined from the following considerations. The vertical Franck–Condon ionization process, II + $h\nu$ → II^+, is followed by a relaxation process in which the ion II^+ assumes its new energy minimum geometry. In our particular example, this change is described essentially by S_3 or by S_7 (B and G[13]). In each case, the normal coordinate $\mathbf{Q}_k$ primarily excited by this process will be the one in which S_3 (or S_7) is affected with the highest coefficient L_{k3}^{-1} (or L_{k7}^{-1}).

Brüesch and Günthard have compared the computed frequencies, $\tilde{\nu}$(comptd), of normal coordinates $\mathbf{Q}_k$ belonging to the irreducible representation A_1' with the observed frequencies, $\tilde{\nu}$(exptl), of the Raman-active, infrared-forbidden vibrations of II. They found that the two normal modes $\mathbf{Q}_k$ dominated by the symmetry coordinate S_3 (C–C stretch) and by S_7 (NCC bending) have the frequencies (cm^{-1}) given in Table I.

Table I

		II		II^+
	B and G	$\tilde{\nu}$(comptd)	$\tilde{\nu}$(exptl)	$\tilde{\nu}$(exptl)
ν_4	$Q_{C-C,\ stretch}$	1005	965	765–815
ν_6	$Q_{NCC,\ bending}$	550	600	510–555

The coefficients L_{ks}^{-1} (in 10^{-13} g$^{1/2}$) of the normal coordinates $\mathbf{Q}_4$ and $\mathbf{Q}_6$ are (B and G[13]) given in Table II. The symmetry coordinates S_2 and S_8 which, besides S_3, are also major contributors to $\mathbf{Q}_6$ correspond to C–N stretching and CNC bending, respectively.

From the last column of Table I we see that the vibrations induced in II^+ by removing an electron from

---

(10) J. J. Macfarlane and I. G. Ross, *J. Chem. Soc. London*, 4169 (1960).

(11) G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1964).

(12) M. P. Marzocchi, G. Sbrana, and G. Zerbi, *J. Amer. Chem. Soc.*, **87**, 1429 (1965).

(13) P. Brüesch, *Spectrochim. Acta*, **22**, 861, 867 (1966); P. Brüesch and Hs. H. Günthard, *ibid.*, **22**, 877 (1966).

Table II

S	1	2	3	4	5	6	7	8
Q_4	−1	7	**−28**	−2	+3	−8	+1	−2
Q_6	−1	−15	+19	−1	−3	−3	**+24**	−19

the orbital $a_1'(n_+)$ or $a_2''(n_-)$, *i.e.*, due to deformations corresponding to S_3 or S_7, have to be assigned as follows. For band 1

$$\nu_4 \text{ and } Q_{C-C,\text{stretch}} \longrightarrow a_1'(n_+) \qquad (6a)$$

and for band 2

$$\nu_6 \text{ and } Q_{NCC,\text{bending}} \longrightarrow a_2''(n_-) \qquad (6b)$$

This is in agreement with the interaction pattern shown in the correlation diagram of Figure 1 and thus proves the essential correctness of the prediction made by Hoffmann, Imamura, and Hehre;[3] namely, that through-bond interaction between n_1 and n_2 dominates the through-space interaction.

To conclude, we wish to compare our results with some of the conclusions reached by Halpern, Roebber, and Weiss[14] from a study of the electronic spectrum of II. This spectrum shows two strong absorption bands at 40,700 and 49,380 cm^{-1} (0-0 transition) with progressions of 700, 800, 875, and 1270 cm^{-1} (first band) and of 800 and 1320 cm^{-1} (second band). The fine-structure pattern is dominated by the 800- and 875-cm^{-1} (first band) and the 800-cm^{-1} (second band) progressions. This seems to correspond satisfactorily with the spacing of 765–815 cm^{-1} of the vibrational pattern obtained for the first ionization band at 7.52 eV in the PE spectrum of II (see Figure 2). However, in view of the complexity of the vibrational structure of the bands observed in the electronic spectrum of II, which, according to McKinney,[15] may be higher than suggested above, not too much significance should be attached to this correspondence.

Halpern, Roebber, and Weiss[14] have interpreted the two strong bands in the electronic spectrum of II as $3p \leftarrow 2sp^3$ and $4p \leftarrow 2sp^3$ Rydberg transitions. According to the results reported in this paper, their $2sp^3$ lone-pair orbital has to be identified with the top occupied orbital $a_1'(n)$. Hence, the promotion of an electron from $a_1'(n)$ to $3p_z$ or $4p_z$ would give rise to two Rydberg transitions, $A_2'' \leftarrow A_1'$, polarized parallel to the threefold z axis of the molecule. This is the same assignment as that obtained by the above authors from a comparison of their experimental results with the predictions derived from a simple theoretical model. Again the agreement may be in part accidental, as the model used by Halpern, Roebber, and Weiss assumes zero split between $a_1'(n)$ and $a_2''(n)$, because of neglect of through-bond interaction.

Acknowledgment. This contribution is part of Project No. 2,120,69 SR of the Schweizerischer Nationalfonds. K. A. M. expresses his gratitude to the Bank Julius Bär & Co., Zurich, and especially to Mr. Walter J. Bär, for the grant of a fellowship.

---

(14) A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49**, 1348 (1968).

(15) T. M. McKinney, *Spectrochim. Acta, Part A*, **25**, 501 (1969).

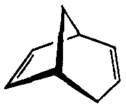
E. Heilbronner, K. A. Muszkat
Institute of Physical Chemistry
University of Basel, Basel, Switzerland

Received March 3, 1970

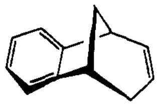
Stereoselectivity in the Acid Quenching of a Nonclassical Carbanion

Sir:

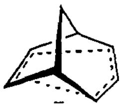
Following prior kinetic and spectroscopic studies on nonclassical behavior in carbanions[1–5] we carried out an examination of the stereochemistry of base-catalyzed exchange in I and II. The stereoselectivity observed in both systems[6] has encouraged us to attempt to separate out the stereochemical consequences of discrete steps in the overall exchange sequence and we therefore examined the protonation of III in detail. Solutions of III in tetrahydrofuran were prepared as before[3] and quenched by syringing under nitrogen into a substantial excess of (A) CD_3OD; (B) CD_3SOCD_3; or (C) 20% CD_3OD, 80% CD_3SOCD_3. The quench medium was in each case held in a constant temperature bath at 45° for compatibility with the kinetic results,[6] and in (B) D_2O was added within 15 sec of quenching to ensure that further exchange did not take place. Deuterated I was recovered by preparative glc and subjected to nmr analysis at 100 or 220 MHz in carbon tetrachloride solution. Spectra recorded at 100 MHz are shown in Figure 1. We feel that the assignment of 4-*exo* (low field) and 4-*endo* (high field) resonances is secure, being based on analogies in bicyclooctadiene systems[2] and supported by numerous observations on norbornanes and norbornenes.[7] It will be seen that the spectra from quenches (A) and (B) show a remarkable feature, amply confirmed by duplicate runs. *Whereas DMSO as quenching agent approaches almost exclusively from the exo face of the anion, a complete reversal of selectivity occurs in the methanol quenching and here approach is highly selective from the endo side.* Apparently a small amount of adventitious quench to produce undeuterated I has occurred during the reaction but this in no way affects our conclusions. Even at 220 MHz the 4-*endo* signal is partially obscured, and the effect is best evaluated by consideration of the 4-*exo* signal at τ 7.8 which in (A) has collapsed from its normal appearance of a doublet of multiplets ($J_{4\text{-}exo/4\text{-}endo} \sim 18$ cps) to a single multiplet, concomitant with loss of the 4-*endo*



I



II



III

---

(1) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc., B*, 411 (1968).

(2) S. W. Staley and D. J. Reichard, *J. Amer. Chem. Soc.*, **91**, 3998 (1969).

(3) J. M. Brown, *Chem. Commun.*, 638 (1967); S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

(4) J. B. Grutzner and S. Winstein, *ibid.*, **90**, 6562 (1968).

(5) W. A. Böll, *Tetrahedron Lett.*, 5531 (1968).

(6) J. M. Brown, E. N. Cain, and M. C. McIvor, *J. Chem. Soc., B*, in press. II exchanges eight times slower than I in KOBu-*t*/DMSO-d_6 at 45°, with 4-*exo* being replaced 6–8 times faster than 4-*endo* in both cases.

(7) *E.g.*, F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967).