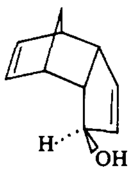
consistent also with the hydrogen migration occurring through a concerted, suprafacial pathway not requiring the intermediacy of I.

No evidence has been reported to date which allows a distinction to be made between the two mechanisms. We wish now to report the results of experiments designed to make this distinction.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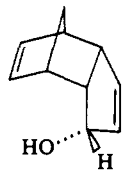
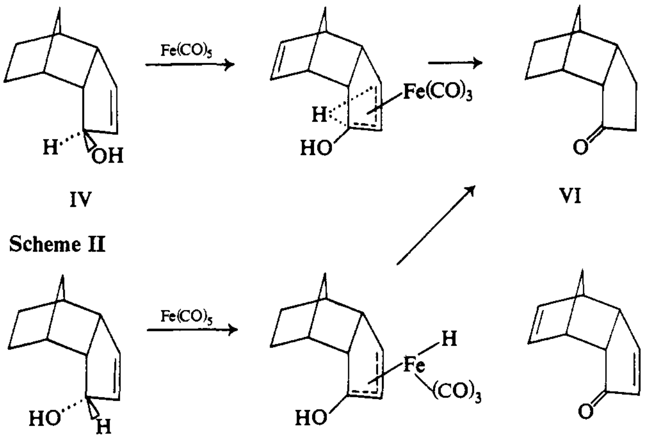

III

endo-α-1-Hydroxydicyclopentadiene (II) and *endo*-β-1-hydroxydicyclopentadiene (III) were prepared from *endo*-dicyclopentadiene by the method of Woodward and Katz.[9] These were converted to the corresponding *endo*-α-1-hydroxy-5,6-dihydrodicyclopentadiene (IV) and *endo*-β-1-hydroxy-5,6-dihydrodicyclopentadiene (V) by catalytic hydrogenation in the presence of a palladium on charcoal catalyst, a method known to selectively saturate the strained double bond in this tricyclic ring system.[10] Compounds IV and V were shown to be epimers by the fact that stirring an acetone solution of V with dilute HCl at room temperature produced a mixture consisting of only IV (*ca.* 60%) and V (*ca.* 40%).[11]

Scheme I



IV VI

Scheme II

V VII

Schemes I and II illustrate the essentials of the two possible mechanisms. In both schemes, only approach of Fe(CO)$_5$ from the least hindered *exo* side is reasonable. In fact, reduction of 5-6-dihydrodicyclopentadien-1-one (VII) with NaBH$_4$ gave a 9:1 ratio of V to IV.

As shown in Scheme I rearrangement of IV to tetrahydrodicyclopentadien-1-one (VI) would be expected to occur only if a 1,3-suprafacial hydrogen shift is operative. In this case, the migrating hydrogen is clearly not properly positioned to allow the formation of a π-allyl–hydroiron tricarbonyl complex. However, a concerted suprafacial 1,3-hydrogen shift would be expected to proceed without any obvious restraints.

Scheme II illustrates the isomerization of the β-alcohol V proceeding to VI *via* a π-allyl–hydroiron tricarbonyl complex. In V, the migrating hydrogen is in a favorable position to allow its facile transfer to the iron, and for any rearrangement to occur *some mechanism involving iron–hydrogen bonding is required.*

Compound V was found to isomerize to ketone VI in about 40% yield when heated at 130° for 16 hr with 10 mole% Fe(CO)$_5$ under a N$_2$ atmosphere. In contrast, however, under the same conditions and, even with prolonged heating at 160°, compound IV *exhibited no detectable change.*[11b]

Our findings definitely indicate that isomerizations of unsaturated alcohols, and quite likely other similar olefin transformations, brought about by reaction with Fe(CO)$_5$ require a definite stereochemical relationship between the migrating hydrogen and the iron atom. A mechanism involving a π-allyl–hydroiron tricarbonyl complex is compatible with these results, while a concerted, sigmatropic hydrogen shift of order [1,3] involving no hydrogen–iron bonding is not. However, a mechanism involving a suprafacial 1,3-hydrogen shift occurring on the same face as the metal atom is also possible. This need not involve a discrete Fe–H intermediate, but the transition state could resemble a cyclobutadiene–metal type interaction. Such a transition state would be isoconjugate with cyclobutadiene metal complexes according to Dewar's concepts of the energetics of the allowed Woodward–Hoffmann processes.[12]

Acknowledgment. The authors are grateful to the National Science Foundation for financial support of this work.

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(8) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(9) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(10) K. Alder and G. Stein, *Ann. Chem.*, **485**, 223 (1931); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).

(11) (a) This analysis and subsequent product analyses were determined by gas–liquid partition chromatography. (b) The lower limit of detectability of VI by this method was found to be less than 0.1%.

(12) Professor M. J. S. Dewar, personal communication; M. J. S. Dewar, "Aromaticity," Special Publication No. 21, The Chemical Society, London.

Frank G. Cowherd, J. L. von Rosenberg
Department of Chemistry, Clemson University
Clemson, South Carolina 29631

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A Double Consecutive Inversion at Two Nitrogens in a Heterocyclic Diamine. The Conformational Isomerization of N,N′-Di-*t*-butylpiperazinium Dichloride

Sir:

The ring inversion, I$_R$, of an N,N′-dialkylpiperazine[1] causes the methylenic protons and the N substituents R to exchange their axial and equatorial positions (E$_C$ and E$_N$ exchanges, respectively), while a nitrogen inversion, I$_N$, without ring distorsion, brings about E$_N$ only (Figure 1, eq 1 and 2). An alternative (likely to account also for

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(1) L. W. Reeves and K. O. Stromme, *J. Chem. Phys.*, **34**, 1711 (1961); R. K. Harris and R. A. Spragg, *Chem. Commun.*, 314 (1966); *J. Chem. Soc., B*, 684 (1968).

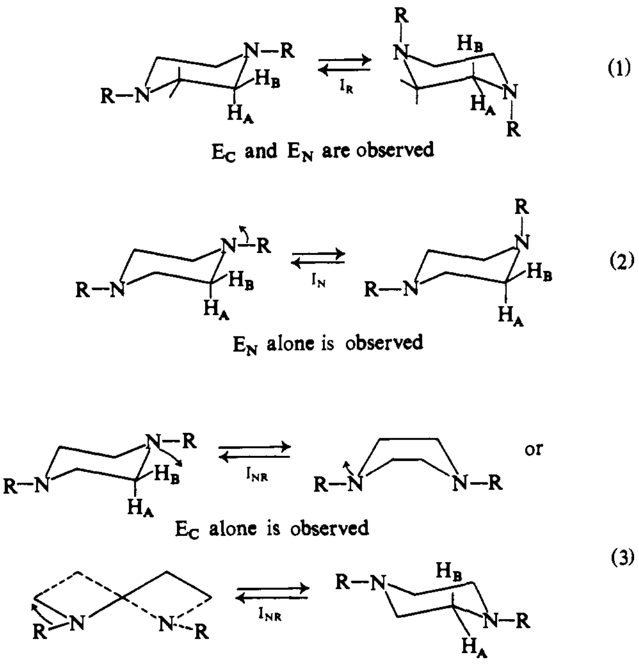


Figure 1. Conformational isomerizations and nmr site exchanges in N,N′-dialkylpiperazines.

the high inversion rate of N-*t*-butylpiperidine[2]) is a combined process, I_{NR}, allowing E_C and not E_N through a boat or twist intermediate (Figure 1, eq 3).

t-Butyl substituents are most likely to promote such an inversion, I_{NR}, because of the large energy[3] (≃5 kcal/mol) necessary to bring them into an axial position through an I_N inversion, although both I_{NR} and I_N processes may exist with less bulky substituents as in N,N′-dimethylpiperazine (P). Moreover, the *cis*-1,4-di-*t*-butyl isomer probably assumes a predominant (≃98%) diequatorial twist conformation,[4] which is a suitable intermediate for the more direct I_{NR} movement and which is generally supposed to have a slightly lower energy level than the corresponding chair conformation.[5] We examine this case using an already described method of competitive protonation.[6]

In an acidic solution ($D_2O + DCl$; pD ⩽3) with a 0.2 *M* amine at 33°, a single *t*-butyl nmr signal is observed. Ring protons display an AA′BB′ spectrum (Figure 2) due to the unique diequatorial chair conformation of the dication AD_2^{2+}, at 100 MHz $\Delta\nu_{ae} = 51.6 \pm 1$ Hz, $J_{gem} = -15.2 \pm 0.7$ Hz, $J_{aa} = 11.0 \pm 0.5$ Hz, $J_{ee} = 1.5 \pm 0.5$ Hz, $J_{ae} = 6.0 \pm 0.3$ Hz.

The solution is made progressively more basic from pD 2.0 to 4.6. In this pD range the dication is predominant (100–96%, taking $pK_1 = 5.36$, $pK_2 = 10.02$, $\log \gamma_\pm = -0.218$). An exchange E_C is evidenced by a coalescence of the AA′BB′ spectrum, whose line shapes have been exactly computed, for the first time, by a method described elsewhere.[7] The mean lifetimes, τ, of one conformation AD_2^{2+} are: 0.200, 0.092, 0.050, and 0.0175 sec at pD 3.45, 3.80, 4.20, and 4.64, respectively. A plot of log 1/τ as a function of the pD yields a straight line (L) whose slope is exactly unity.

This conformational flip from AD_2^{2+} to AD_2^{2+*} (species marked with an asterisk have undergone E_C) must go through the transient monocation AD^+ or free diamine A having the same diequatorial chair conformation

$$AD_2^{2+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} AD^+ \text{ (or A) } \underset{k_A}{\overset{k_A}{\rightleftarrows}} AD^{+*} \text{ (or A*) } \underset{k_1}{\overset{k_2}{\rightleftarrows}} AD_2^{2+*}$$

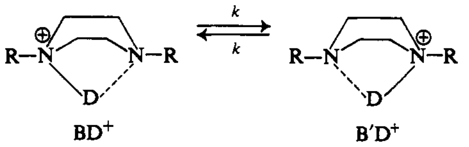
with[6] $1/\tau = k_1k_A/k_2$ (supposing k_1 and $k_2 \gg k_A$). The slope of L agrees only with a monocation intermediate (in which case, $\log(k_1/k_2) = \text{pD} - pK_1 + 2 \log \gamma_\pm$); its intercept yields k_A: $k_A = 1.55 \times 10^3$ sec^{-1}.

Now AD^+ must flip to AD^{+*} through a primary inversion, I_{NR}, of its free nitrogen leading to a different monocation BD^+ (in a twist or boat form). BD^+ is then carried into $B'D^+$, the same form of the molecule as the original (*cf.* below), giving AD^{+*} through the opposite inversion, I_{NR}

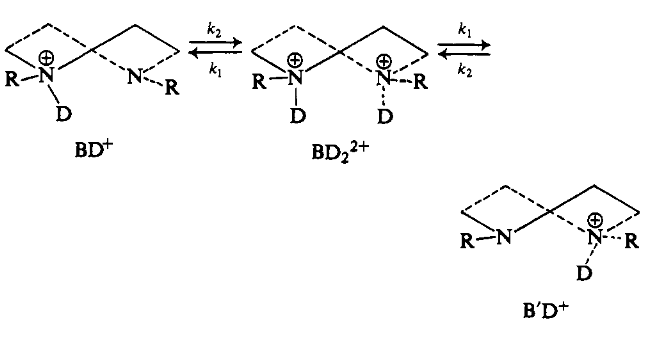
$$AD^+ \underset{k'_N}{\overset{k_N}{\rightleftarrows}} BD^+ \underset{k}{\overset{k}{\rightleftarrows}} B'D^+ \underset{k_N}{\overset{k'_N}{\rightleftarrows}} AD^{+*}$$

According to this scheme $k_N = 2k_A\alpha$, with $\alpha = 1 + k'_N/2k$.

Lastly, the process turning BD^+ into $B'D^+$ may arise from: (a) dedeuteration of nitrogen 4 (nitrogen 1 being redeuterated meanwhile), through a deuteron transfer, which may be either intramolecular (and so, very fast) on a twist or a boat deuteron-bonded conformation



in which case $k_N \simeq 2k_A$, or intermolecular with a symmetrical transient twist or boat dication BD_2^{2+}



In this case, the coefficient $\alpha \simeq 1 + k'_N/k_2$ may have a value between 1.01 and 2.0, as k'_N (10^5–10^7 sec^{-1}) is not small compared to k_2 (10^6–10^7 sec^{-1}).

(b) A ring inversion, I_R, of a transient dication BD_2^{2+} (twist conformation of the above formula through a half-chair intermediate)

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(2) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 44.

(4) R. D. Stolow, P. M. McDonagh, and M. M. Bonaventura, *J. Am. Chem. Soc.*, **86**, 2165 (1964).

(5) D. L. Robinson and D. W. Theobald, *Quart. Rev.* (London), **21**, 314 (1967).

(6) M. Saunders and F. Yamada, *J. Am. Chem. Soc.*, **85**, 1882 (1963); J. J. Delpuech and M. N. Deschamps, *Chem. Commun.*, 1188 (1967); J. J. Delpuech and Y. Martinet, *ibid.*, 478 (1968).

(7) J. J. Delpuech, *Mol. Phys.*, **14**, 567 (1968).

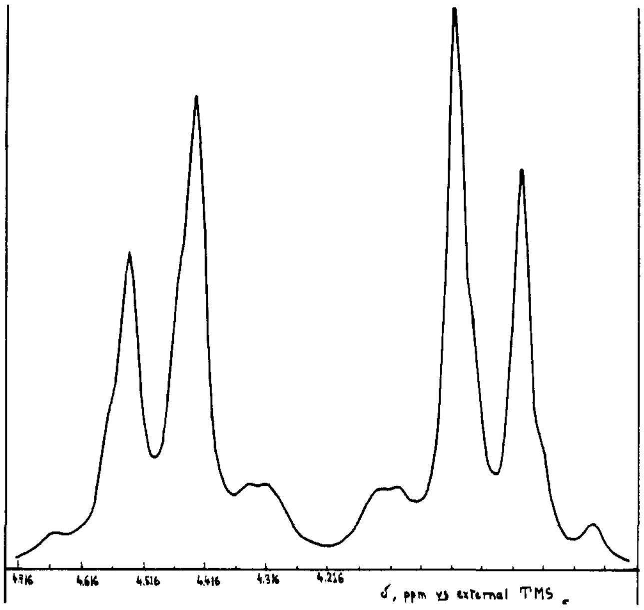

Figure 2. 100-MHz nmr spectrum of the ring protons of N,N′-di-*t*-butylpiperazinium dichloride at pD ≤3.

$$\mathrm{BD^+} \underset{k_1}{\overset{k_2}{\rightleftarrows}} \mathrm{BD_2}^{2+} \underset{k_R}{\overset{k_R}{\rightleftarrows}} \mathrm{BD_2}^{2+*} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{BD^{+*}} \quad (\equiv \mathrm{B'D^+})$$

In this case, the parameter $\alpha \simeq 1 + (k'_N/k_2)[1 + (k_1/2k_R)]$ may have an unobserved dependence on pD, through k_1 ($k_1 = 10^4\text{–}10^6$ sec^{-1}), and because the unknown ratios k'_N/k_2 and k_1/k_R are not necessarily small. The possibility that I_R could be the rate-determining step must be rejected here, because $\tau = k'_N/(k_N k_R)$ would become independent of the pD. In the unlikely event of a primary I_N nitrogen inversion (with BD^+ and BD_2^{2+} in equatorial–axial chair conformations), the same equation is obtained and the same remarks can be made.

We may then infer that our results are evidence—however not yet sufficiently conclusive to exclude the other alternatives—for a double consecutive I_{NR}-type nitrogen inversion of the monocation with deuteron transfer, whose rate constant has the value $k_N = 2k_A = 3.10 \times 10^3$ sec^{-1}. This is 100 times smaller than that obtained for P (2×10^5 sec^{-1} at 44°[8]) for a supposed I_N inversion (and the parameter α equal to 1).

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(8) J. L. Sudmeier and G. Occupati, *J. Am. Chem. Soc.*, **90**, 154 (1968).

(9) To whom requests for reprints should be sent.

J. J. Delpuech,[9] Y. Martinet, B. Petit
Faculté des Sciences de Grenoble
38-Grenoble, France
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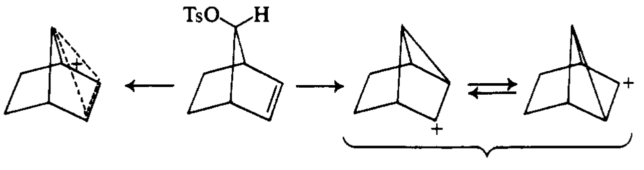
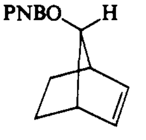
Evidence for the Symmetrical Nature of the 7-Norbornenyl Cation

Sir:

The cation derived from the solvolysis of *anti*-7-norbornenyl tosylate (**1**) has been described as both a symmetrical, highly delocalized species[1,2] (**2**) and as a rapidly equilibrating pair of classical ions[3] (**3**). We now report data which support the view that the acetolysis of **1** produces the ion **2** and not the rapidly equilibrating pair of ions represented by **3**. Our position is based on a study of the rates and products obtained from the solvolysis of the series of *p*-nitrobenzoates, **4**, **5**, and **6**. We have found that the increase in rate in going from no methyl groups, to one methyl group, to two methyl groups on the double bond represents a "cumulative effect" of the methyls and not a "statistical effect" (which might be expected for the second methyl group if classical equilibrating ions were formed).



2 **1** **3**



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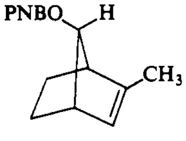

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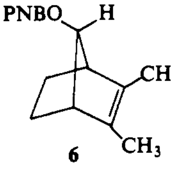
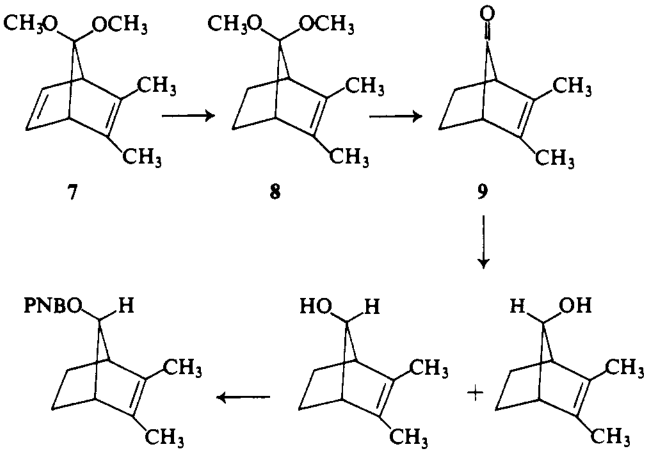


6

The *p*-nitrobenzoate **6** was prepared as shown below[4]



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(1) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(2) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

(3) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(4) Satisfactory elemental analyses have been obtained on all new compounds.