

NMR Spectra. All NMR spectra were obtained by using a Bruker WH-360 spectrometer. The spectra were measured from dilute CDCl_3 solutions with Me_4Si as an internal standard for ^1H and ^{13}C NMR spectra while external boron trifluoride etherate was used to calibrate the ^{11}B NMR spectra.

Where possible the ^1H NMR spectral assignments were made from the relative intensities of the signals. The assignment of the olefinic signals of 3 and 4 could be made since the protons trans to boron show signals broadened by coupling to ^{11}B , while the geminal protons do not.¹⁵ The relative assignment of the olefinic protons of 7 and 9 was made from the ^{119}Sn satellite signals. The protons trans to tin are more strongly coupled than the geminal protons.¹⁶ These olefinic signals show first-order AB patterns.

In the ^{13}C NMR spectra of 3 and 4 the relative assignment of the olefinic signals could be made since the signal for the α -carbons were broadened by ^{11}B quadrupole relaxation while those of the β -carbons were not.¹⁷ The relative assignment of the olefinic signals of 7 and 9 was based on the larger value of $^1J(^{119}\text{Sn}^{13}\text{C})$ than $^2J(^{119}\text{Sn}^{13}\text{C})$.¹⁶

MO Calculations. The STO-3G calculations¹⁸ were performed on an Amdahl 470-V8 computer by using a computer program by Binkley et al.¹⁹ The geometries employed were as follows. Bond lengths (in angstroms) for 1 and 3: C_1C_2 , 1.494; C_2C_3 , 1.546; C_3C_4 , 1.54; C_4C_5 , 1.36; C_5C_6 (C_5B_6), 1.54; all CH, 1.08; BH, 1.16. Bond angles for 1 and 3: $\text{C}_1\text{C}_2\text{C}_3$, 61.1° ; $\text{C}_1\text{C}_3\text{C}_2$, 57.7° ; all internal angles in the six-membered rings, 120° . Bond lengths (in angstroms) for 4: C_1C_3 , 1.54; C_3C_4 , 1.54; C_4C_5 , 1.36; C_5B_6 , 1.54; C_1H , 1.09; other CH, 1.08; BH, 1.16. Bond angles for 4: $\text{C}_1\text{C}_3\text{C}_2$, 109.5° ; all internal angles in the six-membered ring, 120° .

4,4-Dimethyl-1,1-dibutylstannacyclohexa-2,5-diene. A solution of lithium diisopropylamide was prepared by treating 3.1 g (31 mmol) of diisopropylamine in 30 mL of tetrahydrofuran with 9.6 mL of 2.13 N *n*-butyllithium in hexane. This was added to 6.4 g (20 mmol) of 4-methyl-1,1-dibutyl-1-stannacyclohexa-2,5-diene⁸ in 25 mL of tetrahydrofuran at -78°C . The color changed to a dark green-brown on addition. After 15 min addition of an excess (7 g) of methyl iodide discharged the color. The reaction mixture was added to 100 mL of water. After separation of the layers, the aqueous layer was extracted with 70 mL of ether. The combined organic fractions were washed with water and then dried over anhydrous sodium sulfate. Distillation afforded 2.6 g (39%) of product: bp 105°C (0.5 torr); mass spectrum, *m/e* (relative intensity) 328 (0.43, M^+ for $\text{C}_{15}\text{H}_{28}^{120}\text{Sn}$), 271 (100, $\text{M} - \text{C}_4\text{H}_9$); ^1H NMR (CDCl_3) δ 0.88 (t, $J = 7.3$ Hz, 6 H), 0.94 (t, $J = 7.8$ Hz, 4 H), 1.11 (s, 6 H), 1.32 (m, 4 H), 1.50 (m, 4 H), 5.95 (d, $J = 14.6$ Hz, 2 H, $^2J(^{119}\text{SnH}) = 84$ Hz), 6.44 (d, $J = 14.5$ Hz, 2 H, $^3J(^{119}\text{SnH}) = 123$ Hz). ^{13}C NMR (CDCl_3) δ 10.53, 13.62, 26.89, 29.11 (C_4H_9), 31.98 (CH_3), 40.6 (C), 122.2 ($^1J(^{119}\text{Sn}^{13}\text{C}) = 391.85$ Hz, CH), 156.8 (CH). Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{Sn}$: C, 55.06; H, 8.64. Found: C, 54.99; H, 8.72.

6,6-Dibutyl-6-stannaspiro[2.5]octa-4,7-diene. In the same manner, 1,1-dibutyl-4-(β -bromoethyl)stannacyclohexa-2,5-diene⁷ (4.2 g, 10.3 mmol) was treated with 10.5 mmol of lithium diisopropylamide. The reaction mixture was allowed to stir at 25°C for 2 h and then worked up as before. Distillation of the mixture gave the product: 2.10 g (62%); bp $90-95^\circ\text{C}$ (0.001 torr); Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{Sn}$: mass spectrum, *m/e* 269 ($\text{M}^+ - \text{C}_4\text{H}_9$); ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.3$ Hz, 6 H), 0.94 (s, 4 H), 0.96 (t, $J = 7.9$ Hz, 4 H), 1.33 (m, 4 H), 1.52 (m, 4 H), 5.74 (d, $J = 14.3$ Hz, $^2J(^{119}\text{SnH}) = 113$ Hz), 6.00 (d, $J = 14.2$ Hz, $^3J(^{119}\text{SnH}) = 84$ Hz); ^{13}C NMR (CDCl_3) δ 11.0, 13.6, 26.9, 29.1 (C_4H_9), 19.7 ($\text{c-C}_2\text{H}_4$), 122.62 (CH, $^1J(^{119}\text{Sn}^{13}\text{C}) = 391.85$ Hz), 153.0 (CH). Anal. Calcd

for $\text{C}_{15}\text{H}_{28}\text{Sn}$: C, 55.42; H, 8.06. Found: C, 55.47; H, 8.13.

1,4,4-Trimethylboracyclohexa-2,5-diene. 1,1-Dibutyl-4,4-dimethyl-1-stannacyclohexa-2,5-diene (2.6 g, 8 mmol) was cooled to -78°C under an argon atmosphere. Methylboron dibromide (1.5 g, 8 mmol) was added dropwise with stirring. A large precipitate formed. The reaction mixture was allowed to warm to 25°C . The product was purified by pot-to-pot distillation at 25°C (1.5 torr): mass spectrum, *m/e* (relative intensity) 120 (12, M^+ for $\text{C}_8\text{H}_{13}^{11}\text{B}$), 105 (100, $\text{M} - \text{CH}_3$); ^1H NMR (CDCl_3) δ 0.78 (s, 3 H), 1.12 (s, 6 H), 6.35 (d, $J = 11.8$ Hz, 2 H), 6.95 (d, $J = 11.8$ Hz, 2 H). ^{13}C NMR (CDCl_3) δ 9.7 (br s, BCH_3), 26.7 (CH_3), 41.9 (C), 131.9 (br s, BCH), 164.5 (CH); ^{11}B NMR δ 58.3. Anal. Calcd for $\text{C}_8\text{H}_{13}\text{B}$: C, 80.07; H, 10.92. Found: C, 79.86; H, 11.02.

6-Methyl-6-boraspiro[2.5]octa-4,7-diene. To a solution of 1.5 g (4.2 mmol) of 6,6-dibutyl-6-stannaspiro[2.5]octa-4,7-diene in 10 mL of pentane at -78°C was added 0.79 g (4.2 mmol) of methylboron dibromide in 10 mL of pentane. During the addition, the color darkened and a precipitate formed. The mixture was allowed to warm to 25°C for 1 h. After removal of the solvent at reduced pressure, the product (0.4 g, 80%) was collected by pot-to-pot distillation at 25°C (0.3 torr): mass spectrum, *m/e* (relative intensity) 118 (79, M^+ for $\text{C}_8\text{H}_{11}^{11}\text{B}$), 103 (100, $\text{M} - \text{CH}_3$); ^1H NMR (CDCl_3) δ 0.89 (s, 3 H), 1.59 (s, 4 H), 6.59 (d, $J = 11.7$ Hz, 2 H), 6.70 (d, $J = 11.5$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 9.3 (br s, BCH_3), 18.7 ($\text{c-C}_2\text{H}_4$), 31.3 (C), 134.7 (br s, BCH), 159.4 (CH). ^{11}B NMR (CDCl_3) δ 56.5. Anal. Calcd for $\text{C}_8\text{H}_{11}\text{B}$: C, 81.44; H, 9.40. Found: C, 81.05; H, 9.27.

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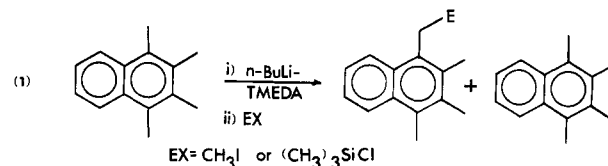
The Anion from 2,3-Dimethylnaphthalene/Tetramethylethylenedi- amine/*n*-Butyllithium: An Unusual Ambident Aromatic Nucleophile

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We were interested in improving the bromination of 2,3-dimethylnaphthalene (1) to 2-bromomethyl-3-methylnaphthalene (2), which we have used previously in connection with the synthesis of benzannulated dimethyldihydropyrenes.¹ Hart's procedure,² which uses excess *n*-BuLi/tetramethylethylenediamine (TMEDA) for monoanion formation in a series of polymethylnaphthalenes, followed by an electrophilic quench as shown, for example, in eq 1, seemed to offer a most attractive synthesis of 2.



We thus employed these conditions with 1 but found somewhat unexpected results. Quenching the deep red anion 3 with D_2O or with CH_3I gave the expected benzylic

(15) A similar broadening is observed in the ^1H NMR spectrum of 1-methylboracyclohexa-2,5-diene (see ref 14).

(16) Petrosyan, V. S. *Prog. Nucl. Magn. Reson. Spectrosc.* 1977, 11, 115.

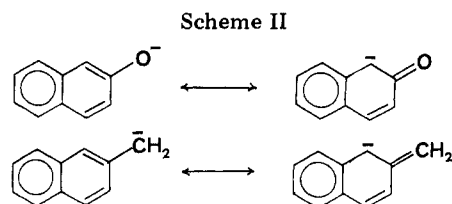
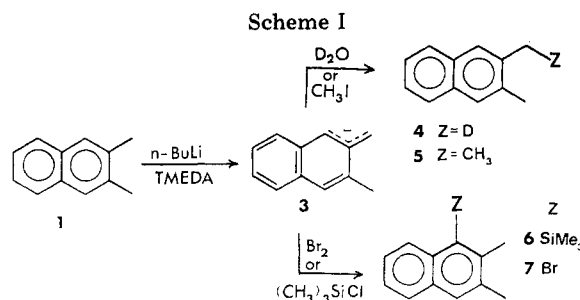
(17) For a similar effect for trivinyl borane see: Hall, L. W.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* 1975, 97, 4527.

(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1969, 51, 2657. Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *Ibid.* 1970, 52, 2769.

(19) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H.-B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "Gaussian 80—An ab initio Molecular Orbital Program"; Carnegie-Mellon University: Pittsburgh, PA; 1980.

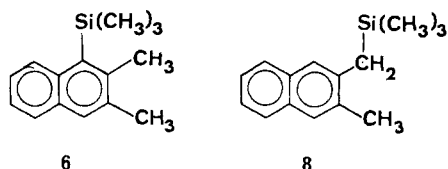
(1) R. H. Mitchell, R. J. Carruthers, and L. Mazuch, *J. Am. Chem. Soc.*, 100, 1007 (1978).

(2) E. Dunkelblum and H. Hart, *J. Org. Chem.*, 44, 3482 (1979).



products 4 and 5, whereas when $(\text{CH}_3)_3\text{SiCl}$ or Br_2 was used, the unexpected ring-substitution products 6 and 7 were formed (Scheme I). Other electrophiles tried included CCl_4 , CBr_4 , $\text{BrCH}_2\text{CH}_2\text{Br}$, CH_3COCH_3 , PhCHO , and PhCH_2Br ; however, only 1 was readily identified from the products.

The identification of 4, 5, and 7 was made from their definitive NMR and mass spectra and/or by comparison with authentic material.³ Identification of the trimethylsilane 6 is not trivial, however, since in their ^1H NMR spectra the chemical shift of the trimethylsilyl protons on an aryl ring or at a benzylic position are very similar, as are the protons of an aromatic methyl relative to the methylene protons of an $\text{ArCH}_2\text{SiR}_3$.⁴ To distinguish between 6 and 8, integration values must be used, and in similar compounds this had led to incorrect assignments in the past.⁵ The identity of the product was thus established chemically. It is known⁶ that benzylsilanes do not undergo protodesilylation readily; e.g., they give proton exchange without loss of the silyl group, whereas arylsilanes undergo extremely easy protodesilylation. In fact 6 on treatment with methanol-sulfuric acid⁷ readily returned 1, confirming its identity as 6 rather than 8.



It would thus seem that the anion 3 is ambident. Whereas ambident allyl anions are well-known,⁷ the analogous benzylic ones are much less common⁸ and hence

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(4) D. J. Couglin and R. G. Salomen, *J. Org. Chem.*, **44**, 3784 (1979); M. Bullpitt, W. Kitching, W. Adcock, and D. Dodrell, *J. Organomet. Chem.*, **116**, 161 (1976).

(5) D. Seyferth and S. C. Vick, *J. Organomet. Chem.*, **141**, 173 (1977); R. J. Wroczynski, M. W. Baum, D. Kost, K. Mislou, S. C. Vick, and D. Seyferth, *ibid.*, **170**, C29 (1979).

(6) T. H. Chan and I. Fleming, *Synthesis*, 761 (1979); D. Häbich and F. Effenberger, *ibid.*, 841 (1979).

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(8) To our knowledge no ambident benzylic anion has been demonstrated. Benzylic anions have been generated by using *n*-BuLi/TMEDA, but the authors⁹ indicate that there is no evidence to believe that such anions are ambident. More recent work¹⁰ also indicates that ring metalation can occur for *o*-xylene, but again there is no evidence that these species are ambident. Our calculations also support this data (see Table II).

Table I. Calculations of Excess π Charge and HOMO Coefficients (C^2) Using π -SCF, CNDO/2, and Hückel Molecular Orbital Methods at the 1-Position and on the 2-Methyl for 2,3-Dimethylnaphthalene^a

method	π charge		C^2	
	1-ring	2-methyl	1-ring	2-methyl
π -SCF	-0.225	-0.399	0.253	0.465
CNDO/2	-0.315	-0.518	0.255	0.456
HMO	-0.245	-0.523	0.232	0.524

^a Full calculations for all atoms are deposited as supplementary material.

Table II. π -SCF Calculations of Excess π Charge and HOMO Coefficients (C^2) at Selected Positions for Several Methyl Aromatics^a

compound	position	π charge	C^2
toluene	CH_3	-0.445	0.527
	2	-0.146	0.152
<i>o</i> -xylene	4	-0.198	0.159
	1- CH_3	-0.459	0.509
	4	-0.195	0.156
1-methylnaphthalene	6	-0.159	0.156
	CH_3	-0.333	0.394
1,4-dimethylnaphthalene	2	-0.185	0.208
	4	-0.226	0.217
	1- CH_3	-0.348	0.384
1,4,5,8-tetramethylnaphthalene	2	-0.184	0.198
	1- CH_3	-0.380	0.384
	2	-0.188	0.198

^a Full calculations for all atoms are deposited as supplementary material.

are worthy of some comment. It is well-known that the naphthalene nucleus in its compounds displays bond-fixation properties,¹¹ which result in, for example, β -naphthoxides being more ambident¹² than phenoxides. It is possible that this same tendency to bond localize (Scheme II), enhances the stability of a β -naphthylmethyl ion and results in this ion behaving more closely like the allyl ion.

Molecular orbital calculations¹³ clearly demonstrate (Table I) that with hard electrophiles (where excess charge predominates) or with soft electrophiles (where frontier orbital control predominates¹⁴) attack is possible at either the benzylic or aryl positions for 3 although the former is favored to some extent. Presumably the steric bulk of $\text{Si}(\text{CH}_3)_3$ and Br favor attack on the ring. This results in considerably less crowded molecules than would result from attack at the benzylic position, which is favored by the much smaller CH_3 and D. (This is readily seen by using molecular models). D^+ is the hardest electrophile used, and hence the Coulombic term becomes more important, favoring attack at the position of highest electron density (the benzylic position).

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(10) J. Klein, A. Medlik, and A. Y. Meyer, *Tetrahedron*, **32**, 51 (1976).

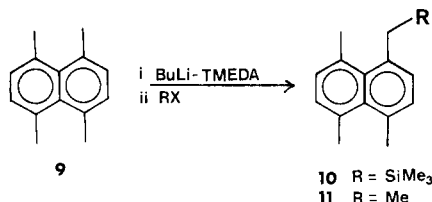
(11) For reviews see L. S. Efron, *Russ. Chem. Rev.*, **29**, 66 (1960); G. M. Badger, *Q. Rev. Chem. Soc.*, **5**, 147 (1951).

(12) See, for example, G. Bram, N. Geraghty, G. Nee, and J. Seyden-Penne, *J. Chem. Soc., Chem. Commun.*, 325 (1980).

(13) Standard Hückel molecular orbital (HMO), Pariser-Parr-Pople (PPP), π -SCF, and CNDO/2 methods were used as described by us in detail in R. H. Mitchell, R. V. Williams, R. Mahadevan, Y. H. Lai, and T. W. Dingle, *J. Am. Chem. Soc.*, **104**, 2571 (1982). A full description of all variations tried has been deposited as supplementary material.

(14) S. A. Shevelev, *Russ. Chem. Rev.*, **39**, 844 (1970); I. Fleming, "Frontier Orbitals and Organic Chemical Reactions"; Wiley: Chichester, 1976; pp 40-66.

As a consequence of these results, we wonder if perhaps the anion of 9, which Hart² has reported to give the ben-



zylic products 10 and 11 on quenching with $(\text{CH}_3)_3\text{SiCl}$ and CH_3I , respectively, is also ambident. Our calculations (Table II) suggest that it might be, and because of the severe steric effect in 1,8-naphthalenes,¹⁵ we would anticipate again that ring substitution would be preferred for trimethylsilyl chloride. As with 6, assignment of the product identity by spectroscopic means is liable to error.

Similar calculations with the anions of 1-methyl- and 1,4-dimethylnaphthalene (see Table II) suggest that substitution on the ring adjacent to the benzylic group is a possibility, though perhaps not as likely as for 1. We have also calculated the results expected for 1,2,3,4-tetramethyl- and 1,2,3,4,5,8-hexamethylnaphthalene, and these calculations agree with the experimental results found by Hart.² While synthetically we have made no attempt to examine the scope of this effect, we hope that this note will caution others to take cognizance of it in their investigations.

Experimental Section

¹H NMR spectra were determined in CDCl_3 on a Perkin-Elmer R32 (90 MHz) spectrometer (Me_4Si as internal standard). GC-mass spectra were recorded on a Finnigan 3300 mass spectrometer using methane chemical ionization. Relative intensities are reported in parentheses.

General Procedure. *n*-Butyllithium (5 mmol in hexane (3.4 mL)) was added to TMEDA (0.8 mL, 5 mmol) in a flame-dried flask, under N_2 at 0 °C with stirring. After 15 min a solution of 2,3-dimethylnaphthalene (156 mg, 1 mmol) in THF (5 mL, distilled from LiAlH_4) was added. The mixture was kept at 0 °C for a further 15 min and then was allowed to warm to ~20 °C and stirred for 24 h. The appropriate electrophile ($(\text{CH}_3)_3\text{SiCl}$, Br_2 , CH_3I , or D_2O ; 5.5 mmol) was then added, and the resulting mixture was stirred again for 24 h. Water and CH_2Cl_2 were then added, and the organic extract was dried (MgSO_4) and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel with pentane as eluant. Product purity and identity were established by ¹H NMR and GC-mass spectrometry.

No attempts have been made to optimize yields, but in all cases some 1 is returned, and this is not reduced by longer reaction times; it is possibly formed by 3 acting as a base with some of the electrophiles or solvent or on workup.

2-(Deuteriomethyl)-3-methylnaphthalene (4): an oil in about 80% yield; ¹H NMR δ 7.75–7.55 (m, 2, H-5,8) 7.50 (s, 2, H-1,4), 7.45–7.25 (m, 2, H-6,7), 2.30 (br s, ~5, CH_2D , CH_3 ; this peak was broadened due to D coupling); GC-MS (CI), *m/e* 186 (M + 29, 15), 185 (<5), 158 (M + 1, 95), 157 (M, 100) 156 (M - 1, 32). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{D}$: C, 91.67; H + D, 8.33. Found C, 91.33; H + D, 8.30.

2-Ethyl-3-methylnaphthalene (5): an oil in about 75% yield; ¹H NMR δ 7.85–7.65 (m, 2, H-5,8), 7.58 (s, 2, H-1,4), 7.45–7.25 (m, 2, H-6,7), 2.75 (q, *J* = 7.5 Hz, 2, CH_2CH_3), 2.42 (s, 3, Ar CH_3), 1.30 (t, *J* = 7.5 Hz, 3, CH_2CH_3); GC-MS (CI), *m/e* 199 (M + 29, 8), 171 (M + 1, 100), 170 (M, 90) 169 (M - 1, 14), 155 (M - 15, 31). Anal. Calcd for $\text{C}_{13}\text{H}_{14}$: C, 91.71; H, 8.29. Found: C, 91.65; H, 8.17.

2,3-Dimethyl-1-(trimethylsilyl)naphthalene (6): an oil in about 70% yield; ¹H NMR δ 7.85–7.25 (m, 5, Ar H) 2.41 and 2.29 (s, ~3 each, Ar CH_3), 0.05 (s, 9, $\text{Si}(\text{CH}_3)_3$); GC-MS (CI), *m/e* 257 (M + 29, 4), 229 (M + 1, 42), 228 (M, 48), 73 ($\text{Si}(\text{CH}_3)_3^+$, 100).

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Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{Si}$: C, 78.88; H, 8.83. Found: C, 79.20; H, 8.69.

Reaction of this compound at ~20 °C with 1:1 methanol- H_2SO_4 returned 2,3-dimethylnaphthalene (1) in essentially quantitative yield.

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Registry No. 1, 581-40-8; 3, 84498-93-1; 4, 84498-94-2; 5, 31032-94-7; 6, 84498-95-3.

Supplementary Material Available: Molecular orbital calculations for all atoms (4 pages). Ordering information is given on any current masthead page.

Transition-State Pliability in N-to-N Proton Transfer

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Partial atomic charges and bond orders in transition states are commonly estimated from isotope effects and Brönsted coefficients. Transition states with, for example, "0.20 partial atomic charge" or "0.37 fraction of reaction progress" abound in the literature.^{1,2} Importantly, and this is seldom stated explicitly, a partial charge or bond order in a transition state almost certainly represents a weighted average derived from an array of transition-state geometries. In this respect partial bonds resemble intermolecular hydrogen bonds where greater than half the population can deviate by 20° or more from linearity.³ Since chemists have, however, little notion as to the pliability of transition states, they are unable to assign significance to numbers such as "62% bond breakage". Does this value mean that most transition-state contributors fall within the 62 ± 5% range? Or is the distribution curve broad so that a substantial number of contributors possess greater than 72% or less than 52% bond breakage? One would like to know, in short, the width of the potential valley in which the transition state lies.

We have attacked the problem of transition-state pliability both experimentally and theoretically. In the experimental approach, we synthesized rigid hydroxy acids for which the lactonization trajectories differ while other parameters (OH/C=O distances and ring strain in the lactones) remain constant.⁴ It was found that within the confines of a 10° angle variation, lactonization rates are invariant. In the present paper, we utilize the MINDO/3 method to secure energies⁵ for N-to-N proton transfer in $\text{NH}_2\text{CH}_2\text{NH}_3^+$. Calculations, employing a Davidson-Fletcher-Powell optimization subroutine, were used initially to locate the minimum position of the mobile proton

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(2) I. M. Kovach, J. P. Elrod, and R. L. Schowen, *J. Am. Chem. Soc.*, **102**, 7530 (1980).

(3) W. L. Jorgensen and M. Ibrahim, *J. Am. Chem. Soc.*, **102**, 3309 (1980).

(4) F. M. Menger and L. E. Glass, *J. Am. Chem. Soc.*, **102**, 5404 (1980).

(5) Semiempirical methods such as MINDO/3 have limitations, some of which are discussed in M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977). These limitations are not so important in our calculations because we are concerned with changes in energy rather than with absolute energy values.