octadien-2-ol (**9**),[11] was formed exclusively when the myrcene monoepoxide (**10**) was subjected to the usual reaction sequence.

The best current method for the epoxide–allylic alcohol conversion, discovered by Cope,[12] and thoroughly developed by Crandall[13] and Rickborn,[14] involves isomerization with strong base. Although often an excellent procedure, the results in Table I reveal several situations where our new, milder method would be preferred. Medium ring epoxides such as **11** give very little allylic alcohol with the base procedure.[12a,b] Rigid epoxides, similar to α- (**12**) and β-Δ^2-cholestene oxides (**13**) often give mixtures with the base methods,[14a] whereas we obtained only the allylic alcohols expected from initial (step a) diaxial opening of the epoxides. Terpenoid epoxides, such as **8**, **10**, and **16**, give exclusively the allylic alcohols resulting from attack by base on a methyl proton.[13b,14a] Finally, the almost neutral selenium procedure should succeed in situations where strong base would not be tolerated.

In a typical procedure, 12.0 g (0.04 mol) of diphenyl diselenide[15] was dissolved in 200 ml of absolute ethanol. Sodium borohydride (3.07 g, 0.081 mol) was added in batches, while stirring mechanically under nitrogen, until the bright yellow solution turned colorless.[16] (*Caution!* reduction of the diselenide is exothermic and vigorous hydrogen evolution occurs.) After addition of the epoxy methyl ether (**16**) (13.2 g, 0.071 mol) the reaction mixture was refluxed for 2 hr. The solution was cooled and 100 ml of THF added. Then 76 ml (0.83 mol) of 30% hydrogen peroxide was added over a period of 1 hr, while cooling the mixture in an ice bath, such that the temperature did not exceed 20°. After 2 hr the elimination was complete by tlc. The resulting slurry was diluted with water and extracted with ether. The organic phase was washed several times with aqueous sodium carbonate, dried (Na_2SO_4), and concentrated to give an orange oil, which upon vacuum distillation (77° (0.3 mm)) gave 10.4 g (79%) of the *E* allylic alcohol (**17**).

We are finding that organoselenium compounds have great potential as synthetic reagents and will soon report on two other diphenyl diselenide derived reagents.[17] Use of diphenyl diselenide as a stoichiometric reagent should be comparable in expense to the use of triphenylphosphine. However, unlike triphenylphosphine, diphenyl diselenide is easily regenerated from its oxidation products (seleninic acid **6**), and this oxidation product, being water soluble, is easily separated from the usual organic products. *Caution!* Selenium compounds are toxic and should be handled accordingly.

Acknowledgment. We thank Dr. Günther Ohloff of Firmenich et Cie., Geneva, for kindly providing ir and nmr spectra of the rose oxides. We are grateful to the National Science Foundation (GP-30485X), Eli Lilly, Hoffmann-La Roche, and the Mobil Foundation for support of this research.

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[11] This terpene was first isolated and characterized by R. M. Silverstein, J. O. Rodin, D. L. Wood, and L. E. Brown, *Tetrahedron*, **22**, 1929 (1966). A recent synthesis gave a mixture of the desired compound and its isomer, 2-methyl-6-methylene-1,7-octadien-3-ol: T. Moore, A. Komatsa, and K. Ueda, U. S. Patent 3,433,839 (1969); *Chem. Abstr.*, **70**, P 114701*e* (1969).

[12] (a) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1965); (d) A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958).

[13] (a) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964); (b) J. K. Crandall and L. Chang, *ibid.*, **32**, 435, 532 (1967); (c) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

[14] (a) B. Rickborn and R. P. Thummel, *J. Org. Chem.*, **34**, 3583 (1969); (b) R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970); (c) R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971); (d) C. L. Kissel and B. Rickborn, *ibid.*, **37**, 2060 (1972).

[15] This odorless, yellow solid was easily prepared on a 2.5 *M* (based on bromobenzene) scale by a modification of the *Organic Syntheses* procedure for the preparation of selenophenol: D. G. Taster, *Org. Syn.*, **III**, 771 (1955). The above procedure is followed except that the crude ethereal selenophenol solution is not distilled, but rather filtered, then diluted with ~1500 ml of 95% ethanol containing a few pellets of potassium hydroxide. Oxygen or air is bubbled through the stirred solution until the odor of selenophenol disappears (overnight). Filtration affords the yellow diselenide which may be used without further purification. Concentration of the filtrate affords further diselenide; the total yield is ~71%, mp 63°.

[16] B. Sjöberg and S. Herdevall, *Acta Chem. Scand.*, **12**, 1347 (1958). This is a convenient method for reducing diselenides. However, there are a number of less expensive alternatives for reduction to the desired anion **2**: see, W. H. H. Günther, *J. Org. Chem.*, **31**, 1202 (1966), and references cited therein. We originally prepared ethanolic solutions of **2** by reaction of selenophenol with NaOEt, but the stench of selenophenol encouraged use of the diselenide route.

[17] K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, unpublished results.

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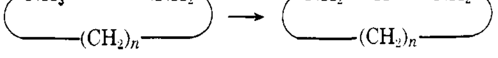
Quantitative Evaluation of Intramolecular Strong Hydrogen Bonding in the Gas Phase[1,2]

Sir:

Strong hydrogen bonding and solvation of ions in the gas phase have been the subjects of several recent experimental[3] and theoretical investigations.[4] By studying long range interactions between functional groups in gas-phase basicity studies,[5,6] we have been able to observe *intramolecular* strong hydrogen bonding and evaluate some of the energetic parameters for formation of such bonds as a function of ring size.

Diaminoalkanes show dramatically higher (by 6–14 kcal/mol) gas-phase basicities (GB's) than primary amines of comparable polarizability (Table I).[7] This effect must result from intramolecular strong hydrogen bonding between the ammonium ion and the other terminal amino group (eq 1). Allen's *ab initio* calcula-



(1)

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[1] Presented in part in Abstracts of the 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, June 4–9, 1972.

[2] Supported by NSF Grant No. GP-15628. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[3] (a) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968); (b) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); (c) T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 3671 (1972).

[4] (a) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970); (b) W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.*, **5**, 463 (1970); (c) N. DePaz, S. Ehrenson, and L. Friedman, *J. Chem. Phys.*, **52**, 3362 (1970).

[5] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

[6] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

[7] See ref 6 for an evaluation of polarizability effects on gas-phase basicities.

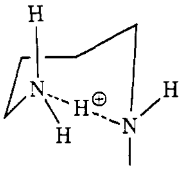
Table I. Gas-Phase Basicities of Diaminoalkanes[a]

Compound	GB,[b] $-\Delta G°_{\text{prot}}(g)$	$-T\Delta S°_{\text{prot}}$[c]	PA,[b] $-\Delta H°_{\text{prot}}(g)$	$-\Delta H°_{\text{ring form}}$
$NH_2CH_2CH_2NH_2$	220.2	11.8	232.0	>9.7
$NH_2CH_2CH_2CH_3$	213.7	8.6	222.3	
$NH_2CH_2CH_2CH_2NH_2$	225.7	12.6	238.3	>15.5
$NH_2CH_2CH_2CH_2CH_3$	214.3	8.6	222.8	
$NH_2CH_2CH_2CH_2CH_2NH_2$	228.3	15.0	243.3	20.2
$NH_2CH_2CH_2CH_2CH_2CH_3$	214.6	8.6	223.1	
$NH_2CH_2CH_2CH_2CH_2CH_2NH_2$	226.6	14.7	241.3	18.1
$NH_2CH_2CH_2CH_2CH_2CH_2CH_3$	214.7	8.6	223.2	
$NH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2$	226.6	15.5	242.1	18.8
$NH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	214.8	8.6	223.2	
$CH_3OCH_2CH_2NH_2$	215.9	11.8	227.7	>4.9
Morpholine	215.2	8.3	223.5	
Piperidine	222.0	8.3	230.3	
Piperazine	220	8.3	228	

[a] All values in kcal/mol. [b] Relative GB's are ±0.2 kcal/mol by multiple overlap of $\Delta G°$'s. [c] $T\Delta S$ term includes the entropy of free proton, the entropy from symmetry change, and the entropy of ring closure approximately estimated from the alkane ⇄ cycloalkane equilibrium for analogous hydrocarbons: D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969. $T = 298°K$.

tions for the strong hydrogen bond in $H_2O\cdot\cdot H\cdot\cdot H_2O^+$ give an energy minimum at 36.9 kcal/mol relative to $H_3O^+ + H_2O$ and an sp^2 staggered geometry at oxygen.[4a] The O··H··O bond has an O–O distance of 2.38 Å with the proton symmetrically disposed on the line between the oxygens in contrast to weak hydrogen bonds with linear, but asymmetric, hydrogen bonds.[8]

The proton affinity (PA) of 1,4-diaminobutane (Table I) was calculated from the observed GB assuming that the entropy of ring formation for hydrogen bonding is about the same as for hexane ⇄ cyclohexane ($T\Delta S° = -6.4$ kcal/mol).[9] The proton affinity of *n*-pentylamine should be a good model for the expected PA of 1,4-diaminobutane if the latter did *not* form a strong intramolecular hydrogen bond on protonation.[11] Thus the enthalpy for intramolecular strong hydrogen bond formation (eq 1, $n = 4$) would be about 20.2 kcal/mol = PA (1,4-diaminobutane) − PA (*n*-pentylamine). Dreiding models indicate that a linear hydrogen bond can be accommodated in a ring of this size (structure **1**)



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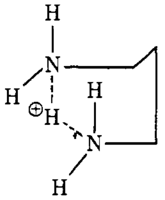

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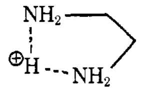

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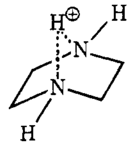

4

with no angle strain, but a small amount of eclipsing strain (*ca.* 3.5 kcal/mol) would be expected.[12] This strain energy and the enthalpy of ring formation can be combined to give an approximate enthalpy of a strain-free hydrogen bond of 24 kcal/mol.[13] As expected from consideration of strain energy models,[12] the enthalpies of hydrogen bond formation in the seven and eight membered rings are lower (by 1–2 kcal/mol) than the six-membered ring because of eclipsing and transannular interactions. For 1,3-diaminopropane and 1,2-diaminoethane the hydrogen bonds in structures **2** and **3** are probably bent by about 30°. In addition, **3** suffers angle strain (C–C–N ≈ 100°) at the ring carbons. The acyclic model primary amines for **2** and **3** do not take the expected inductive lowering of the PA by the amino groups into account. This makes the 9.7 and 15.5 kcal/mol values lower limits on the enthalpies of ring closure. Models for inductive effects in the gas-phase basicities must be chosen with care to prevent intramolecular hydrogen bonding from obscuring the inductive effects.[14] The proton affinities of piperazine and morpholine, relative to piperidine, may be good models for inductive effects since the bridged ions (*e.g.*, **4**) would be expected to suffer a large angle strain.[15] These models lead to estimates of *ca.* 1 kcal/mol and 2 kcal/mol for the inductive effects for **2** and **3**, respectively. This places the strain energy of **2** at about 8 kcal/mol and that of **3** at about 12 kcal/mol.[16]

We anticipate that this method of detecting intramolecular ring formation with gas-phase basicities will

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(8) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(9) Usually the entropy of proton transfer is nearly zero (ref 10) but for proton transfer from a simple amine to a diamine capable of intramolecular hydrogen bonding there should be a large ΔS. Temperature-dependent equilibrium constants will be measured to verify this assumption.

(10) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

(11) The inductive lowering of the PA by the electronegative amino group would be expected to be small (<1 kcal/mol) at this chain length.

(12) For some models of strain energies in cyclic systems, see P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(13) This value compares well with the 24.8 kcal/mol value for $NH_3 - NH_4^+ \rightarrow NH_3\cdot\cdot H\cdot\cdot NH_3^+$ and the 21.7 kcal/mol value for $CH_3NH_2 + CH_3NH_3^+ \rightarrow CH_3NH_2\cdot\cdot H\cdot\cdot NH_2CH_3^+$: P. Kebarle, private communication (see also ref 3a).

(14) Even in 2-methoxyethylamine the inductive effect is not large enough to overcome the energy of hydrogen bonding, but 2,2,2-trifluoroethylamine has a proton affinity *ca.* 16 kcal/mol below ethylamine.

(15) The strain energy of norbornane is 17.5 kcal/mol (ref 12) and the hydrogen bond is bent by *ca.* 55°.

(16) When strain energies and inductive effects can be better estimated it will be possible to evaluate the energetic effect of bending these strong hydrogen bonds. It appears from these preliminary data that a 30° bend in the hydrogen bond of **2** may cause a strain of *ca.* 5 kcal/mol.

be a very general one.[17] It is capable of giving quantitative information on the energetics of strong hydrogen bonding which will allow a better evaluation of the importance of intramolecular processes in the gas phase and solution.[18]

[17] Beauchamp has reported that proton bound dimerization of dimethoxyalkanes (but not dihydroxyalkanes) is inhibited by intramolecular hydrogen bond formation (ref 3c). All of our diaminoalkanes formed proton bound dimers from 10^{-4} to 10^{-3} Torr with equal facility. This further supports Beauchamp's conclusion that a nonbridging hydrogen is needed for dimerization.

[18] The solution thermodynamic data for protonation of diaminoalkanes in water indicate that intramolecular hydrogen bonding is not important and that inductive effects are felt strongly for short chain lengths. The long chain diamines behave in solution nearly like analogous *n*-alkylamines.

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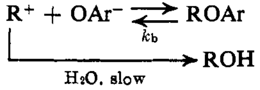
Interaction of Phenols with the Tri-*p*-anisylmethyl Cation

Sir:

The effects of ionic and nonionic solutes upon the rate and equilibrium constants for the attack of water upon the tri-*p*-anisylmethyl cation (R^+) have been explained in terms of ion pairing and changes in solvent structure.[1,2] In extending earlier work,[2] we used phenoxide ions as nucleophiles by taking hydroxide ion in an excess of the phenol, so that the phenoxide ion concentration was that of the initial hydroxide ion. The concentrations of phenoxide ions were 3×10^{-3} *M* and of phenol 0.06–0.25 *M*. (All the rate measurements were made using a Durrum–Gibson stopped flow spectrophotometer.[2]) The reaction gives an equilibrium mixture of R^+ and ROAr which in a few seconds gives the thermodynamically stable ROH (*cf.* the reaction of R^+ with azide ion[2]).



The rate constants fit eq 1, where k_f^0 is the rate constant

$$\log (k_f/k_f^0) = a[\mathrm{ArOH}] \qquad (1)$$

extrapolated to zero phenol.[3] The values of k_f^0, a, and the equilibrium constant $K = k_f/k_b$ are given in Table I. Values of k_f and K for the reaction of R^+ with other anionic nucleophiles are included for comparison.

This stabilization of R^+ by phenols is confirmed by the observation that phenols decrease the reactivity of R^+ toward water, and increase the equilibrium formation of R^+ in dilute acid, as measured by $-H_R$.[4]

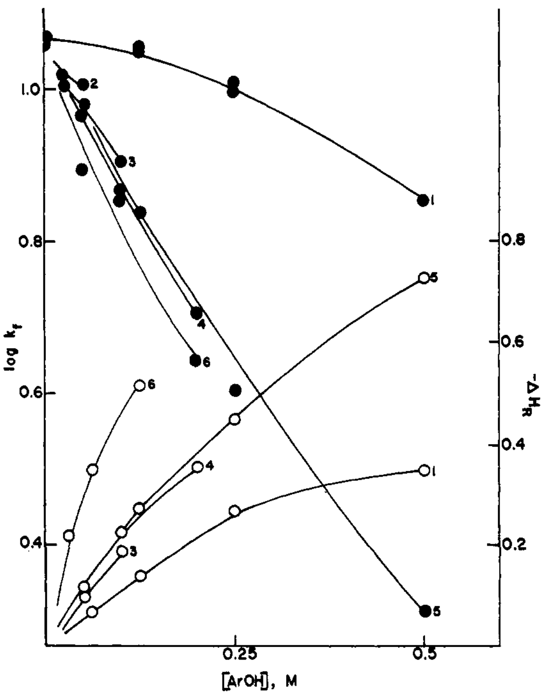


Figure 1. Inhibition of the reaction of R^+ and water at 25.0° by phenols (left-hand scale, solid points), and increase of $-H_R$ by phenols (right-hand scale, open points). Substituents: (1) none; (2) *p*-Me; (3) *p*-OMe; (4) *m*-OME; (5) *m*-OH; (6) 3,5-$(OH)_2$.

Table I. Reaction of Tri-*p*-anisylmethyl Cation with Phenoxide Ions and Other Anionic Nucleophiles[a]

Nucleophile	k_f, l. mol^{-1} sec^{-1}	a[b]	K, l. mol^{-1}
$C_6H_5O^-$	1.05×10^5	-1.0	1.6×10^4
p-$MeC_6H_4O^-$	2.5×10^5		
p-$MeOC_6H_4O^-$	4.25×10^5	-2.1	2.4×10^4
m-$MeOC_6H_4O^-$	1.42×10^5		2.3×10^3
OH^-	8.2×10^3[c]		Large
N_3^-	5×10^6[c]		6.6×10^4
CN^-	2.7×10^3[d]		Large

[a] In water at 25.0°. [b] For reaction of ArO^- and R^+ in the presence of ArOH, eq 1. [c] Reference 2. [d] Measured using the methods described in ref 2.

Some examples of this behavior are shown in Figure 1. In 3 *M* HCl or $HClO_4$, where the equilibrium is wholly toward R^+, added phenols shift the broad maximum of R^+ at 482 nm slightly toward larger wavelengths.[6] With 1 *M* resorcinol $\Delta\lambda_{max} = +7$ nm and with 0.063 *M* phloroglucinol $\Delta\lambda_{max} \sim +2$ nm. Phenols have only a small effect on the protonation of *p*-nitroaniline, and cyclohexanol (up to 0.1 *M*) does not increase $-H_R$. (However, H_R is affected by relatively high concentrations of many nonionic solutes.[1])

Electron-donating substituents in the phenols increase both their ability to stabilize R^+ and the nucleophilicity of the phenoxide ions (Figure 1 and Table I).

There is extensive evidence for interactions between cations and aromatic compounds,[7] and it has been suggested that π complexes are intermediates in aromatic

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[1] M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 474 (1972).

[2] C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, **94**, 3536 (1972).

[3] Hydrogen bonding between phenol and phenoxide ion could reduce the nucleophilicity of the latter, although it is probably unimportant in water. It does not explain the effects on H_R or on the reaction with water, and leads to the prediction that inhibition of the phenoxide ion reaction should increase with increasing phenol acidity in disagreement with experiment.

[4] For discussions of acidity functions, see ref 5.

[5] R. H. Boyd in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

[6] These shifts are similar to that of +8 nm given by 1 *M* NaOTos, for which $\Delta H_R = -0.65$, and which strongly inhibits reactions of R^+ with H_2O and OH^-.

[7] E. J. F. Duynstee and E. Grunwald, *Tetrahedron*, **21**, 2401 (1965); J. Gordon and R. L. Thorne, *J. Phys. Chem.*, **73**, 3643, 3652 (1969); J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972).