(10) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973,** *95*, 5833.

(11) (a) Katz, T. J.; Lee, S. J.; Acton N. *Tetrahedron Lett.* **1976,** 4247. (b) Katz, T. J.; Acton, N. *Ibid.* **1976,** 4251. (c) Katz, T. J.; Hersh, W. H. *Ibid.* **1977,** 585. (d) McGinnis, J.; Katz, T. J.; Hurwitz, S. *J. Am. Chem. Soc.* **1976,** *98*, 605. (e) Katz, T. J.; McGinnis, J.; Altus, C. *Ibid.* **1976,** *98*, 606. (f) Lee, S. J.; McGinnis, J.; Katz, T. J. *Ibid.* **1976,** *98*, 7818.

(12) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974,** *7*, 174.

(13) With some initiators *tert*-butylacetylene failed to polymerize while other acetylenes did,[14] and once the resulting polymer was not characterized.[15]

(14) (a) Tsumura, R.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1964,** *37*, 1889. (b) Meriwether, L. S.; Colthup, E. C.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961,** *26*, 5155. (c) Hübel, W.; Hoozgand, C. *Chem. Ber.* **1960,** *93*, 103.

(15) Voronkov, M. G.; Pukhnarevich, V. B.; Sushinskava, S. P.; Annenkova, V. Z.; Andreeva, N. I. *Bull. Acad. Sci. USSR* **1976,** *25*, 1591.

(16) (a) Mauret, P.; Guerch, G. *C.R. Acad. Sci., Ser. C* **1972,** *274*, 1340. (b) Lutz, E. F. *J. Am. Chem. Soc.* **1961,** *83*, 2551.

(17) (a) Kawai, W. *Kogyo Kagaku Zasshi* **1966,** *69*, 1994. (b) Takegami, Y.; Suzuki, T.; Fuji, M. *Ibid.* **1967,** *70*, 1796.

(18) Green, M. L. H.; Knight, J.; Mitchard, L. C.; Roberts, G. G.; Silverthorn, W. E. *J. Chem. Soc., Chem. Commun.* **1972,** 987.

(19) 2-Butyne and 3-hexyne fail to polymerize with some initiators effective for terminal alkynes.[6i,14b]

(20) Sasaki, N.; Masuda, T.; Higashimura, T. *Macromolecules* **1976,** *9*, 664.

(21) (a) Mauret, P.; Megné, J.; Guerch, G. *C.R. Acad. Sci., Ser. C* **1973,** *275*, 415. (b) Mauret, P.; Pellegrina, M.; Guerch, G. *Ibid.* **1975,** *281*, 235. (c) Mauret, P.; Guerch, G.; Martin, S. *Ibid.* **1977,** *284*, 747.

(22) Polyphenylacetylene is an auburn solid, polypropyne and poly(1-hexyne) are orange, and poly(*tert*-butylacetylene) and poly(2-butyne) are white.

(23) The ^{13}C NMR spectrum of polypropyne in $CDCl_3$ consists of broad resonances at 134 (–CH=) and 20 ppm (CH_3).

(24) The IR spectrum of poly(1-hexyne)[25] and the ^{13}C NMR,[20] ^{1}H NMR, and IR spectra[26] of polyphenylacetylene match those published. The IR spectrum of polypropyne resembles those in the literature[17] except that peaks attributable to oxidation are missing. The IR spectrum of the insoluble poly(2-butyne) in KBr exhibits peaks at 2970 (s), 2920 (s), 2850 (m), 2710 (vw), 1440 (m), 1365 (m), 1095 (m), 1040 (sh), and 1030 cm^{-1} (m). The soluble polymer exhibits the same spectrum, but with two weak unexplained absorptions added at 1260 and 800 cm^{-1}.

(25) Natta, G.; Mazzanti, G.; Pregaglia, G.; Peraldo, M. *Gazz. Chim. Ital.* **1959,** *89*, 465.

(26) The ^{1}H NMR values resemble those of a polymer formed from phenylacetylene, cobalt trisacetoacetate, and triethylaluminum,[27] believed to have mainly *Z* ("trans") stereochemistry. The IR spectrum resembles that of a polymer formed by WCl_6 in benzene, believed to contain both *Z* and *E* units.[2]

(27) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977,** *15*, 2497.

(28) Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961,** *83*, 3200.

(29) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966,** *5*, 1837.

(30) Masuda, T.; Thieu, K.-Q.; Sasaki, N.; Higashimura, T. *Macromolecules* **1976,** *9*, 661.

(31) Unpublished results of William Hersh in this laboratory: cycloocta-1,5-diene–tungsten tetracarbonyl at 50 °C during 16 h with 100 equiv of norbornene gives a 100% yield of polynorbornenamer, while $(C_6H_5)_3PW(CO)_5$ at 54 °C during 13 days gives a 0.7% yield.

(32) (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975,** *99*, 309. (b) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976,** *109*, 2026. (c) Dötz, K. H. *ibid.* **1977,** *110*, 78. (d) A paper by Wood et al. (Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101*, 3210) records a related example.

(33) (a) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974,** *12*, 11. (b) Ito, T.; Shirakawa, H.; Ikeda, S. *Ibid.* **1975,** 13, 1943. (c) Watson, W. H., Jr.; McMordie, C. W., Jr.; Landes, L. G. *J. Polym. Sci.* **1961,** *55*, 137. (d) Kleist, F. D.; Byrd, N. R. *J. Polym. Sci., Polym. Chem. Ed.* **1969,** *7*, 3419.

Thomas J. Katz,* Steven J. Lee
Department of Chemistry, Columbia University
New York, New York 10027

Received July 12, 1979

Theoretical Calculations of the Aqueous Medium Effects on the Basicities of Primary Amines[1]

Sir:

The success of ab initio molecular orbital theory in treating substituent effects on gas-phase acidities and basicities[2] (i.e., energy changes for isodesmic proton transfer reactions) suggests its applicability in treating appropriate aqueous medium effects. For neutral acids and bases, aqueous medium effects on proton-transfer equilibrium have recently been shown to be highly specific, ranging from ~0 to 35 p*K*.[3,4] Evidence has been presented which indicates that the principal cause of the aqueous medium effects on the basicities of nitrogen and oxygen bases is the selective stabilization imparted by formation of complexes between water and the ammonium or the oxonium ions.[4] These complexes involve hydrogen bonding of at least one water molecule at each protonic "active site" of the ion. For example, consider the following equilibria:

$$(CH_3)_2OH^+{}_{(g)} + (CH_3)_2S_{(g)} \rightleftharpoons (CH_3)_2SH^+{}_{(g)} + (CH_3)_2O_{(g)} \quad (1)$$

$$\Delta G°_{(g)} = -8.0 \text{ kcal/mol}^5$$

$$(CH_3)_2OH^+{}_{(aq)} + (CH_3)_2S_{(aq)} \rightleftharpoons (CH_3)_2SH^+{}_{(aq)} + (CH_3)_2O_{(aq)} \quad (2)$$

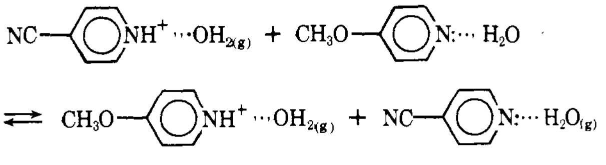
$$\Delta G°_{(aq)} = +62 \text{ kcal/mol}^3$$

The free-energy changes for these two reactions correspond to an aqueous medium effect which increases (and reverses) the apparent basicity of $(CH_3)_2O$ relative to $(CH_3)_2S$ by 10.3 p*K* units. This result is reproduced approximately by the difference in gas-phase binding energies of a single water molecules attached to $(CH_3)_2OH^+$ relative to $(CH_3)_2SH^+$ [6] (i.e., $\Delta G°$ for the hypothetical "model" reaction

$$(CH_3)_2OH^+\cdots OH_{2(g)} + (CH_3)_2S_{(g)} \rightleftharpoons (CH_3)_2SH^+\cdots OH_{2(g)} + (CH_3)_2O_{(g)} \quad (3)$$

$$\Delta G° \simeq +4. \text{ kcal/mol}$$

agrees approximately with that for reaction 2 and accounts for most of the reversed basicity difference observed between the gas and aqueous phases). A few related equilibria involving single molecule attachment have been scrutinized both experimentally and by means of ab initio molecular orbital theory. In general the theoretical calculations have been moderately successful in reproducing the experimentally observed free energies (e.g., eq 4).



(4)

$$\Delta G°_{(4)} = -13.7 \text{ kcal/mol}^{7,8}$$
$$\Delta E°_{(4)(STO\text{-}3G)} = -14.6 \text{ kcal/mol}^7$$

We report here the successful application of ab initio molecular orbital theory at the STO-3G level[9] to the calculation of the known medium effects of water (up to 8.5 p*K* units) on the basicities of primary amines.[3] The results are summarized in Table I. Typical are the results for two categories of substituent effects. The first equilibrium

$$CF_3CH_2NH_3^+{}_{(g)} + CH_3CH_2NH_{2(g)} \rightleftharpoons CH_3CH_2NH_3^+{}_{(g)} + CF_3CH_2NH_{2(g)} \quad (5)$$

$$\Delta G°_{(5)} = -14.6 \text{ kcal/mol}^{10}$$

has been the subject of a recent analysis[11] which indicates that the two ions, $CF_3CH_2NH_3^+$ and $CH_3CH_2NH_3^+$, are stabilized to a comparable degree by charge induced dipole interactions; destabilization of the $CF_3CH_2NH_3^+$ ion by the inductive-field effect (unfavorable internal charge-dipole interaction) therefore accounts for most of the observed $\Delta G°$ value. It has generally been argued that charge dispersal to the solvent effectively increases the distance between the centroids of charge and substituent dipole moment. It was further suggested that the extent of this charge dispersal is sufficient to reduce the destabilization of $CF_3CH_2NH_3^+{}_{(aq)}$ by a factor of ~2, thus accounting for the observed free energy for the aqueous phase proton transfer equilibrium[3]

0002-7863/80/1502-0424$01.00/0

Table I. Observed and Calculated Medium Effects of Aqueous Solution on Proton Transfer Equilibria for Substituted Methylammonium Ions, $\Delta G°_{(g)} - \Delta G°_{(aq)}$ and $\Delta E°_{(g)calcd} - \Delta E°_{(calcd,\ model)}$, Respectively,[a] for the Reaction Shown

$$RNH_3^+ + R_0NH_2 \rightleftarrows R_0NH_3^+ + RNH_2$$

	$q_{-NH_3^+}$[b]	$\Delta_{(aq)}\Delta G°_{(obsd)}$	$\delta_{(aq)}\Delta E°_{(calcd\ model\ A)}$	$\delta_{(aq)}\Delta E°_{(calcd\ model\ B)}$	$\delta_{(aq)}\Delta E°_{(calcd\ model\ C)}$
R = $N{\equiv}CCH_2$	+0.661				
R_0 = CH_3CH_2	+0.617	−11.6	−11.4	−9.9	−9.0
R = CF_3CH_2	+0.644				
R_0 = CH_3CH_2	+0.617	−7.7	−8.3	−7.3	−7.2
R = CH_3CH_2	+0.617				
R_0 = CH_3	+0.637	2.9	3.3	3.1	3.1
R = $(CH_3)_3C$	+0.589				
R_0 = CH_3	+0.637	8.0	8.5	8.4	7.8

[a] $\delta_{(aq)}\Delta G°_{(obsd)} = \Delta G°_{(g)} - \Delta G°_{(aq)}$ at 298 K for the reaction indicated and $\delta_{(aq)}\Delta E°_{(calcd)} = \Delta E°_{(g)(calcd)} - \Delta E°_{(g)(calcd\ model)}$, where $\Delta G°_{(g)}$ and $\Delta E°_{(g)(calcd)}$ refer to the simple proton-transfer equilibrium in the gas phase, $\Delta G°_{(aq)}$ refers to the same formal reaction in dilute aqueous solution at 298 K, and $\Delta E°_{(g)(calcd\ model)}$ refers to the gas-phase proton-transfer reaction in which both RNH_3^+ and $R_0NH_3^+$ are stabilized by three H-bond acceptor water molecules and RNH_2 and R_0NH_2 are stabilized by either one H-bond donor water molecule (model A), no water molecules (model B), or one H-bond donor water molecule and two H-bond acceptor water molecules (model C). [b] $\Sigma q_N + \Sigma q_H$ values calculated for RNH_3^+.

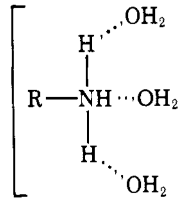
$$CF_3CH_2NH_3{}^+{}_{(aq)} + CH_3CH_2NH_{2(aq)} \rightleftarrows CH_3CH_2NH_3{}^+{}_{(aq)} + CF_3CH_2NH_{2(aq)} \quad (6)$$

$$\Delta G°_{(6)} = -6.9 \text{ kcal/mol}^{12}$$

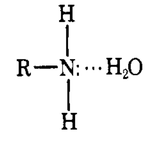
The aqueous medium effect, $\delta_{(aq)}\Delta G° = \Delta G°_{(5)} - \Delta G°_{(6)} = -7.7$ kcal/mol, corresponds to the free energy of the hypothetical equilibrium process

$$\begin{aligned} &CF_3CH_2NH_3{}^+{}_{(g)} + CH_3CH_2NH_3{}^+{}_{(aq)} + CF_3CH_2NH_{2(aq)} + CH_3CH_2NH_{2(g)} \\ &\rightleftarrows CF_3CH_2NH_3{}^+{}_{(aq)} + CH_3CH_2NH_3{}^+{}_{(g)} + CF_3CH_2NH_{2(g)} + CH_3CH_2NH_{2(aq)} \quad (7) \end{aligned}$$

We have assumed that the effects of water (aq) in reaction 7 (as well as reaction 8 below) may be modeled by the stabilizing effects of forming the corresponding cationic trihydrate complexes[13-15] (**1**) and by the single water complexes (**2**) for



1



2

the neutral amines. The "overall" process given by eq 7 then corresponds to an isodesmic process. Therefore, it is subject to only relatively small entropy effects[12] and should be reasonably well described by ab initio calculations. Indeed, the result obtained theoretically at the STO-3G level, $\delta_{(aq)}\Delta E°_{(7)(calcd)} = (\Delta E°_{(5)} - \Delta E°_{(6)})_{(calcd)} = -8.3$ kcal/mol is in excellent agreement with the experimental value of $\delta_{(aq)}\Delta G°_{(7)} = \Delta G°_{(5)} - \Delta G°_{(6)} = -7.7$ kcal/mol.

Next, consider the proton-transfer equilibrium

$$t\text{-}BuNH_3{}^+{}_{(g)} + CH_3NH_{2(g)} \rightleftarrows CH_3NH_3{}^+{}_{(g)} + t\text{-}BuNH_{2(g)} \quad (8)$$

$$\Delta G°_{(8)} = +8.0 \text{ kcal/mol}^{10}$$

The much greater gas-phase basicity of *tert*-butylamine has been ascribed principally to the greater charge-induced dipole stabilization of t-$BuNH_3^+$ compared with $CH_3NH_3^+$.[16] It has been estimated[11] that this effect accounts for ~6 kcal mol^{-1}, the remaining 2 kcal mol^{-1} being due to a relatively small inductive effect. In aqueous solution, the dispersal of ionic charge to H-bonded solvent molecules has been estimated to reduce the polarizability effect to zero and the inductive effect to ~1 kcal/mol (there is also probably some small effect of steric hindrance to solvation of the *tert*-butyl ammonium ion[17]). The observed aqueous medium effect,[3] corresponding to the overall process of eq 9, is ~6 p*K* units—which reduces the apparent basicity of t-$BuNH_{2(aq)}$ to essentially that for $CH_3NH_{2(aq)}$:

$$\begin{aligned} &t\text{-}BuNH_3{}^+{}_{(g)} + CH_3NH_3{}^+{}_{(aq)} + t\text{-}BuNH_{2(aq)} + CH_3NH_{2(g)} \\ &\rightleftarrows t\text{-}BuNH_3{}^+{}_{(aq)} + CH_3NH_3{}^+{}_{(g)} + t\text{-}BuNH_{2(g)} + CH_3NH_{2(aq)} \quad (9) \end{aligned}$$

$$\delta_{(aq)}\Delta G°_{(9)} = +8.0 - 0.0 = +8.0 \text{ kcal/mol}^{10}$$

The theoretical calculations, carried out with the structural assumptions noted above, again give excellent agreement with the experimental value: $\delta_{(aq)}\Delta E°_{(9)(calcd)} = +8.5$ kcal/mol. The agreement between theory and experiment for reactions 7 and 9, as well as for a number of other systems summarized in Table I, provides supporting evidence for the structural assumptions which we have made, i.e., for the nature of the dominant species present in aqueous solution. Table I also lists the results of calculations made with the assumption of either no hydrogen-bonded complex formation with the free amines (model B) or of amine trihydrate formation involving two hydrogen-bonded water molecules acting as acceptors plus a single hydrogen bonded water acting as a donor (model C). It is clear that the hydration state of the neutral amines has relatively little effect on the results, although agreement does appear to be most satisfactory for calculations made with the single hydrogen-bonded donor water molecule (model A). The only reasonable alternative explanation for the good agreement between the observed and calculated results is that the theory has systematically overestimated the differential stabilizing effects of water on the complex formation. The overestimates of the stabilities of the assumed trihydrates of RNH_3^+ might be comparable with the stabilizing effects in aqueous solution that are instead due to a water cluster (perhaps of three water molecules) attaching to each of the cation protonic sites. It is known that polar solvents decrease the formation constants for hydrogen-bonded complex formation.[18] Thus it could be conceived that this effect on the formation of H-bonded water clusters to the RNH_3^+ ions in water coincidentally brings the experimental results in agreement with the overcalculations of the differential stabilization due to the formation of the trihydrates.

In order to investigate this issue, we have carried out limited calculations using the split-valence 4-31G basis set.[19] For $CH_3NH_3^+$, $N{\equiv}CCH_2NH_3^+$, and $CH_3CH_2NH_3^+$, the theoretically calculated binding energies of the three water molecules are as follows: STO-3G, 77.3, 84.2, and 74.3 kcal/mol, respectively; 4-31G, 53.2, 63.0, and 50.1 kcal/mol, respectively. The only experimental value available is ~43 kcal/mol for $CH_3NH_3^+$.[20] Thus, while the absolute 4-31G calculation is much closer to the experimental value, the differential hydration energies (the critical quantities in our calculations of the aqueous medium effects on relative base strengths) between these three ions are nearly the same at both levels of theory. If anything, the differential hydration energies are slightly greater (not less) at the 4-31G level. These results therefore appear to favor our first interpretation. However, experimental values for the energies of binding of three water molecules to all of the RNH_3^+ ions of Table I are needed as a critical test.

Trends in the charge distributions obtained in the STO-3G calculations are also instructive. These results show that ca. +0.34 of the ionic charge in all five of the RNH_3^+ ions of Table I is transferred to the three bonded water molecules of the trihydrated primary ammonium ions. Further, nearly half of this charge is transferred from the R group.[21] That is, the centroid of positive charge is very substantially moved away from the R group in the trihydrated ion-molecule complexes compared with the corresponding anhydrous ions. As expected for the internal inductive effects, the total charge of the $-NH_3^+$ moiety increases in the sequence t-Bu < C_2H_5 < CH_3 < CH_2CF_3 < CH_2CN. The overall increase for the anhydrous ions is greater (from +0.589 to +0.661) than that for the corresponding trihydrated ions (from +0.427 to +0.477). Also as expected, the effect of R on charges in the neutral amines is entirely second order in comparison with that in the ions. All of the present results provide theoretical support for the simplified interpretations[3,11] which have been made of the aqueous medium effects and encourage further experimental and theoretical studies of "model" gas-phase reactions as a means to further understanding of aqueous solution acid-base behavior.

References and Notes

(1) This work was supported in part by a grant from the Public Health Service.

(2) See, for example, R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Wiley-Halstead, New York, 1975, p 31.

(3) R. W. Taft, J. F. Wolf, J. L. Beauchamp, G. Scorrano, and E. M. Arnett, *J. Am. Chem. Soc.*, **100,** 1240 (1978).

(4) R. W. Taft in "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum, New York, 1979, pp 271-293.

(5) J. F. Wolf, R. G. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99,** 5417 (1977). The results reported therein have been corrected for a small ICR cell temperature factor, which has subsequently been shown to apply.

(6) The difference in the free energy of binding a *single* water molecule to $(CH_3)_2OH^+$ is assumed to be approximately the same as the corresponding quantity for H_3O^+ compared with $(CH_3)_2SH^+$ compared with H_3S^+; cf. P. Kebarle, *Annu. Rev. Phys. Chem.*, **28,** 445 (1977), and D. K. Bohme, private communication.

(7) Result calculated from $\Delta G^\circ_{(g)}$ for the simple photon-transfer equilibrium (corrected as indicated in note 6) together with the estimated free energies of H-bond complex formation of the substituted pyridines [E. M. Arnett, B. Chawia, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99,** 5729 (1977)] and the free energies of attachments of a single water molecule to the gaseous substituted pyridinium ions (ref 8).

(8) W. R. Davidson, J. Sunner, and P. Kebarle, *J. Am. Chem. Soc.*, in press.

(9) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969). All calculations have been performed on a Harris Slash 6 minicomputer using the Gaussian 77 series of programs. (b) D. J. DeFrees, B. A. Levi, S. K. Pollack, E. Blurock, and W. J. Hehre, to be submitted to Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(10) From ref 3 with correction indicated in footnote 5.

(11) R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. DeFrees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **100,** 7765 (1978).

(12) P. Love, R. B. Cohen, and R. W. Taft, *J. Am. Chem. Soc.*, **90,** 2455 (1968).

(13) Cf. P. Kebarle, *Annu. Rev. Phys. Chem.*, **28,** 445 (1977).

(14) Structures were obtained for $CH_3NH_3^+$, CH_3NH_2, $CH_3NH_3^+(H_2O)_3$, and $CH_3NH_2(H_2O)$ by optimization of all independent geometrical parameters subject only to overall symmetry constraints. Structures for the remaining systems were obtained by attaching substituents to these parent compounds using standard model [J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89,** 4253 (1967)] bond lengths and angles. Full details will be presented in our upcoming full report.

(15) Kebarle has previously emphasized that ion solvation energies may be well reproduced by the interactions of the ions with the first solvent molecules; cf. P. Kebarle, W. R. Davidson, M. French, J. B. Cumming, and T. B. McMahon, *Faraday Discuss. Chem. Soc.*, **No. 64,** 220 (1977).

(16) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90,** 5636, 6501 (1968).

(17) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79,** 5441 (1957).

(18) Cf. L. Joris, J. Mitsky, and R. W. Taft, *J. Am. Chem. Soc.*, **94,** 3438 (1972), and references cited therein.

(19) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54,** 724 (1971).

(20) This value is estimated from the binding energy of four water molecules to NH_4^+, 57.5 kcal/mol, and the binding energy of one water molecule to $(CH_3)_3NH^+$, 14.5 kcal/mol; cf. P. Kebarle in ref 6.

(21) The 4-31G calculations show essentially the same amount of charge (ca. +0.17) is transferred from the R group to the three water molecules.

M. Taagepera, D. DeFrees, W. J. Hehre,* R. W. Taft*
Department of Chemistry, University of California, Irvine
Irvine, California 92717

Received July 19, 1979

Coupling of Nonvicinal Glycols by Low-Valent Titanium

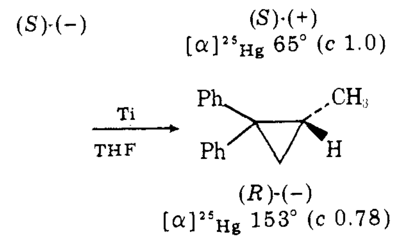
Sir:

Basing their strategy on the knowledge that Ti(II) can be readily oxidized to Ti(IV), Van Tamelen and Schwartz[1] treated the sodium salts of benzyl and allyl alcohol with $TiCl_4$ to produce the corresponding dichlorotitanium(IV) dialkoxide, which was then reduced with potassium to the titanium(II) dialkoxides. Thermolysis of the titanium(II) dialkoxide intermediate yielded TiO_2 and the coupling product bibenzyl or biallyl. Since then, low-valent titanium(II) has been used in the pinacolic coupling of carbonyls and in the reductive coupling of carbonyls to olefins.[2,3]

Ti(0) has also been used to convert vicinal diols into their corresponding olefins.[4] Although several attempts to couple 1,3-diols reductively were abortive,[4,5] Baumstark[6] reported that the reaction of a 3:2 mixture of 1,3-diphenyl-1,3-propanediol[7] with the McMurry reagent $TiCl_3$-$LiAlH_4$ resulted in the formation of a 4:1 mixture of *trans*- and *cis*-1,2-diphenylcyclopropane. The object of this communication is not only to clarify why certain 1,3-glycols reductively couple[6] and others do not,[5] but also to determine the stereochemistry of the reaction to gain some insight into the mechanism of the reaction.

Since the absolute configuration of 1-methyl-2,2-diphenylcyclopropane had been established in our laboratory many years ago,[7] this hydrocarbon was selected as the target compound.

The optically active (S)-(+)-1,1-diphenyl-1,3-butanediol was prepared in excellent yield by reacting the dilithium derivative of benzophenone[8] with (S)-(−)-propylene oxide.[9] The reaction of the glycol with the McMurry reagent $TiCl_3$-$LiAlH_4$[10] gave, inter alia, a 65% isolated yield of *optically pure* (R)-(−)-1-methyl-2,2-diphenylcyclopropane (eq 1). *Moreover, the configuration at C-3 of the 1,1-diphenyl-1,3-butanediol had been inverted.*



(1)