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.

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(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 $\Delta G°_{(g)}$ 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).

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

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(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).

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(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.

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Received July 19, 1979

Coupling of Nonvicinal Glycols by Low-Valent Titanium

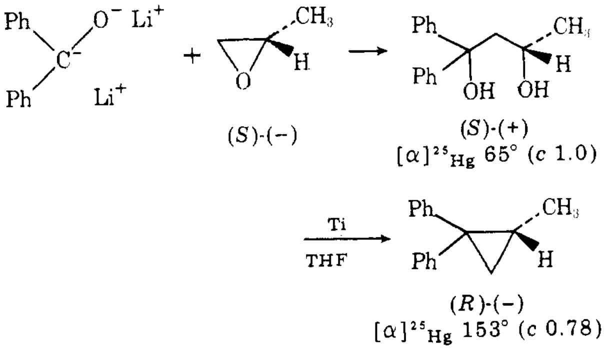
Sir:

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.

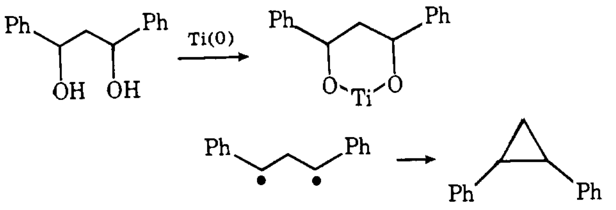
Since the absolute configuration of 1-methyl-2,2-diphenylcyclopropane had been established in our laboratory many years ago,[7] this hydrocarbon was selected as the target compound.

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.*



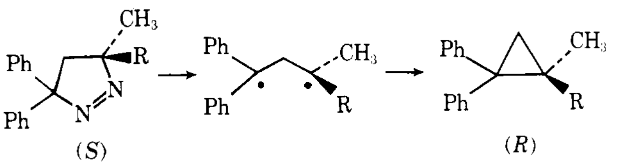
(1)

The result is significant to the understanding of the mechanism of the reaction. Baumstark[6] has postulated a diradical intermediate for this reaction (eq 2). At least for our system



(2)

this mechanism can be excluded based on the results that we had obtained previously.[11] The thermal decomposition of pyrazolines are known to proceed via a singlet diradical mechanism[12] (eq 3). The diradical produced from the pyrazoline

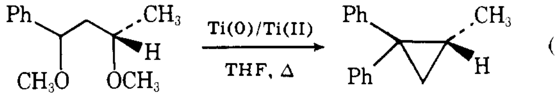


(3)

R = COOR, CH_2OH

decomposition is similar in structure to that which would be produced from the reductive coupling of 1,1-diphenyl-1,3-butanediol. In the case of pyrazoline decomposition, the stereochemistry of the reaction is that of *retention of configuration* as well as high optical purity. However, the reductive coupling proceeds with *inversion of configuration and not retention.*

One must also comment on another observation. Why did the reductive coupling occur in ours and Baumstark's cases and not in others?[4,5] The reason for this, we believe, is that both our systems contain phenyl groups in either the 1 or 3 positions. The aromatic moieties are essential as electron acceptors. This would also account for the observation by Van Tamelen and Schwartz[1] that coupling only occurred with benzylic and allylic alcohols. The cyclic titanium(II) dialkoxide intermediate is not essential for the reaction to occur, although it may perhaps be an intermediate for 1,3-glycols. For example, the reaction of the dimethyl ether derivative of 1,1-diphenyl-1,3-butanediol with the McMurry reagent produced, inter alia, a 60% isolated yield of the cyclopropyl hydrocarbon (eq 4). The stereochemical result is identical with that obtained for the corresponding 1,3-glycol, *complete inversion of configuration.*

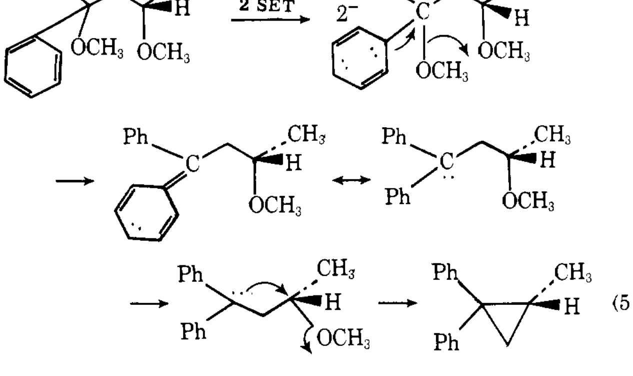


(4)

(*S*)-(−) $[\alpha]^{25}_{Hg}$ 15° (*c* 1.77)

(*R*)-(−) $[\alpha]^{25}_{Hg}$ 153° (*c* 0.49)

Our observations led us to postulate the mechanism shown in eq 5 for this reaction.

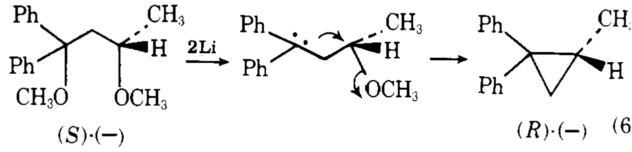


(5)

This mechanism presupposes two things: one, that electron transfer can occur to the phenyl ring from either a Ti(0) or Ti(II) species, and two, that the anion formed at C-1 can displace a methoxide ion.

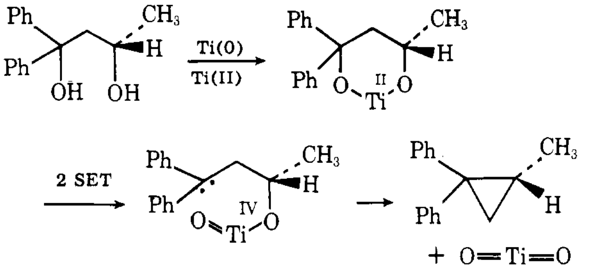
The oxidation of Ti(II) to Ti(IV) occurs very readily and this is an attractive species to undergo single electron transfers (SET), although Ti(0) to Ti(II) is also a good candidate.[13] The nucleophilic displacement of methoxide has its precedence in the work of Köbrich.[14]

Consistent with the proposed mechanism is our result on the reaction of 1,1-diphenyl-1,3-dimethoxybutane with lithium metal (eq 6). This reaction, too, involves two SETs to the phenyl ring and is a general method for the cleavage of phenyl carbinyl ethers.[15] Of significance is that this reaction produces hydrocarbon of >92% inverted configuration. This result is completely analogous to that obtained using the McMurry reagent.



(6)

In the case of 1,3-glycols, the titanium has another purpose besides providing electrons. It also converts the hydroxyl groups into good leaving groups. We view the reaction as proceeding as depicted in eq 7.



(7)

The Ti(0) or Ti(II) reacts with the glycol to give a six-membered cyclic Ti(II) intermediate.[16] This intermediate undergoes a 2 SET transfer from the Ti(II) to the benzene ring to yield a diphenylcarbinyl anion–Ti(IV) species which by an S_N2 intramolecular displacement of TiO_2 yields the hydrocarbon. The reactions described have a bearing on the general topic of 1,3 eliminations.[17-19]

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(18) All new compounds gave correct elemental analyses and IR and NMR spectra consistent with the structure. All optical rotations were recorded at 5461 Å with a Bendix-Ericson Model 143A polarimeter using chloroform as a solvent. An authentic sample of 1-methyl-2,2-diphenylcyclopropane[7] gave [α] ±151° (c 1.18).
(19) Acknowledgement is made to to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Received August 13, 1979

Sensitivity Enhancement in ^{15}N NMR: Polarization Transfer Using the INEPT Pulse Sequence

Sir:

In a previous communication[1] a new pulse sequence was described which allows the NMR signals of nuclei with low magnetogyric ratio to be enhanced by the transfer of polarization from protons scalar coupled to the weak nucleus. This technique has now been evaluated for the case of a simple ^{15}N spectrum in natural abundance, that of the blocked dipeptide benzyloxycarboxylglycylglycyine methyl ester, giving substantial improvements in sensitivity both for proton coupled and for decoupled spectra.

Three main factors contribute to the low sensitivity of ^{15}N NMR: the low natural abundance (0.37%), its low resonant frequency, and the negative sign of its magnetogyric ratio. The first of these can only be overcome by the use of isotopically enriched materials, but the problems caused by the other two factors can be alleviated to some extent by suitable experimental methods. The use of wide-band proton decoupling can lead to an increase in the ^{15}N signal of up to four times, by the nuclear Overhauser effect;[2] however, since the magnetogyric ratios of the proton and the ^{15}N nucleus have opposite signs, if the dipole–dipole mechanism on which the Overhauser effect depends does not dominate the ^{15}N T_1, then proton irradiation can actually reduce or entirely suppress the signal. This situation is sufficiently common that many nitrogen spectra must be run using gated proton decoupling[3] in order to suppress the Overhauser effect.

A more satisfactory solution to the problem is to transfer spin polarization from protons to ^{15}N via proton–nitrogen scalar couplings. Not only does this lead to a tenfold increase in the ^{15}N polarization owing to the higher magnetogyric ratio of the proton, but an additional improvement in sensitivity can result from the faster spin-lattice relaxation of protons, since this governs the rate at which experiments may be repeated. Cross polarization via Hartmann–Hahn contact in the rotating frame is familiar in solid-state NMR[4,5] and has recently been applied to liquid-state high-resolution NMR with considerable success.[6-9] The principal disadvantage of this technique is its sensitivity to any mismatch between the proton and nitrogen radio frequency fields, which makes necessary the construction of probe coils doubly tuned for ^{15}N and protons, a procedure which reduces the basic ^{15}N sensitivity. This problem can be avoided by the use of the INEPT pulse sequence[1] (insensitive nuclei enhanced by polarization transfer).

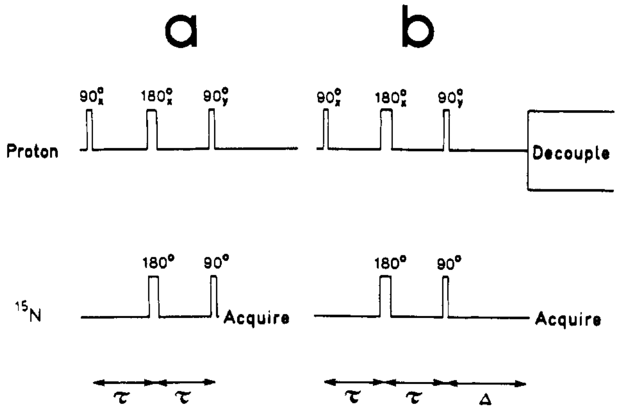

Figure 1. Pulse sequences used for obtaining INEPT enhanced spectra (a) without proton decoupling and (b) with proton decoupling. For the spectra of Figure 2a τ was 2.5 ms and Δ5 ms.

Figure 1 illustrates the pulse sequences used to obtain enhanced proton coupled and decoupled spectra by the INEPT method. The mechanism of the basic experiment has already been described in detail;[1] a ^{15}N modulated proton spin echo is used to invert one ^{15}N satellite of each proton directly coupled to nitrogen, which leads to the full proton Boltzmann spin polarization appearing across the connected ^{15}N transitions. This leads to proton coupled multiplet intensity ratios of $-1{:}+1$ for NH groups, $-1{:}0{:}+1$ for NH_2, and $-1{:}-1{:}+1{:}+1$ for NH_3. Since proton decoupling immediately after the ^{15}N 90° pulse would collapse the antiphase signals and hence lose any enhancement, the extra delay in Figure 1b is inserted in order to bring the multiplet components in phase before the onset of decoupling. The optimum value for the delay τ is $1/(4J_{NH})$, while that for Δ is $1(2J_{NH})$ for doublets and $1/(4J_{NH})$ for triplets. Since most one-bond proton–nitrogen couplings lie in the range of 60–90 Hz and the polarization transferred shows only a sine dependence on J, a single value of τ generally suffices to give good enhancements for all protonated nitrogens.

Spectra of a 1 M solution of blocked glycylglycine[10] in deuteriochloroform obtained using the pulse sequences of Figure 1 are shown in Figure 2a. For comparison, spectra obtained by conventional methods using the same total time of 10 min are shown in Figures 2b and 2c. Figure 2b shows the spectra obtained with Overhauser enhancement, using gated decoupling to obtain an enhanced spectrum.[11] In separate experiments the nuclear Overhauser enhancement was found to be the theoretical maximum of −4 within experimental error. Figure 2c shows a proton coupled spectrum obtained without nuclear Overhauser enhancement, and a proton decoupled spectrum obtained using only 40-s time averaging with continuous proton decoupling, in order to show the effect of removing the Overhauser enhancement without the need for artificially long interpulse delays. All experimental conditions were chosen to optimize sensitivity for the different techniques employed, using proton and nitrogen T_1 values of 1 and 3 s, respectively, estimated from progressive saturation experiments.

Spectra were obtained using the low-band multinuclear system of a Bruker WH 400 spectrometer, operating at 40.5 MHz for ^{15}N with 15-mm-diameter sample tubes. The only nonstandard feature of the spectrometer used was the provision of a computer-controlled 90° phase shift on the decoupler channel. The pulse sequence was generated using a machine code patch to the standard Bruker FT NMR software.

Despite the low pulse power (ν_1 = 1.6 kHz for ^{15}N) of the particular broad-band probe used, ~80% of the predicted

0002-7863/80/1502-0428$01.00/0