theless, these ¹⁵N results establish that the adenine N1 is protonated in the low-pD, G(syn) structure of this A-G mispair, while in the high pD, G(anti) structure, it is not.

Summary. We have shown that the adenine N1 atom in the A-C and A-G mispairs studied is protonated at pD values above those of the monomer pK. These experiments provide the first direct evidence for protonation of a specific nitrogen in a mispair and demonstrate further the potential utility of ^{15}N labeling to probe DNA structural details.

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Supplementary Material Available: Details of the syntheses and purifications of 1 and 2, together with ¹⁵N NMR and ¹H NMR spectra (7 pages). Ordering information is given on any current masthead page.

[1,3] Sigmatropic Rearrangement of Allyl Vinyl Ethers at Ambient Temperature in 3.0 M Lithium Perchlorate-Diethyl Ether

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The intervention of the [1,3] sigmatropic rearrangement during the course of a Claisen rearrangement is a rare event, witnessed previously only in a few cases¹ where the typical [3,3] process is energetically and/or sterically unfavorable.^{2,3} We report that allyl vinyl ethers undergo unprecedented [1,3] sigmatropic rearrangement at ambient temperature in 3.0 M lithium perchlorate-diethyl ether.⁴

In a preliminary set of experiments, a 0.2 M solution of allyl vinyl ether 1 in 3.0 M lithium perchlorate-diethyl ether was shown to undergo exclusive [1,3] sigmatropic rearrangement after 1 h at ambient temperature, giving rise to a 90% yield of 2 and 3 in a 5:1 ratio. Use of 5.0 M lithium perchlorate-diethyl ether gave



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(4) For the effect of lithium perchlorate-diethyl ether on the rate of the Diels-Alder reaction, see: Grieco, P. A., Nunes, J. J.; Gaul, M. D. J. Am. Chem. Soc. 1990, 112, 4595. In addition, lithium perchlorate solutions in diethyl ether have previously been employed to accelerate reactions with polarized transition states, see: Winstein, S.; Smith, S.; Darwish, D. J. Am. Chem. Soc. 1959, 81, 5511. Pocker, Y.; Buchholz, R. F. J. Am. Chem. Soc. 1970, 92, 2075.

 Table I.
 [1,3] Rearrangement of Allyl Vinyl Ethers Employing 3.0

 M Lithium Perchlorate in Diethyl Ether^a



^aAll reactions were conducted at ambient temperature employing a 0.2 M solution of allyl vinyl ether in 3.0 M lithium perchlorate-diethyl ether. ^b Isolated yields. ^cApproximately 3% of the [3,3] sigmatropic product was isolated. ^dApproximately 2% of the [3,3] sigmatropic product was obtained. ^eApproximately 1% of the Claisen product along with 28% of an elimination product was observed. ^fThe β :a ratio was 5:1.

rise within 10 min to 2 and 3 in the same ratio. Use of 1.5 M lithium perchlorate in diethyl ether gave rise to a 98% yield of 2 and 3 in a ratio of 7.5:1; however, under these conditions the rate of the reaction was slowed, requiring 24 h to go to completion. Interestingly, exposure of the corresponding C(12) epimeric allyl vinyl ether to 3.0 M lithium perchlorate in diethyl ether gave rise after 1 h to a 94% yield of the [1,3] rearranged products 2 and 3 in a 5:1 ratio. Our observations stand in sharp contrast to our earlier studies on the Claisen rearrangement of 1 in aqueous medium,⁵ wherein unprotected allyl vinyl ether 1 in watermethanol (2.5:1) was observed to undergo exclusive [3,3] sigmatropic rearrangement at 80 °C. The facile [1,3] rearrangement observed above, coupled with the synthetic potential of this novel carbon-carbon bond forming reaction, led us to probe the generality of lithium perchlorate-diethyl ether induced [1,3] sigmatropic rearrangements of allyl vinyl ethers.

The procedure employing 3.0 M lithium perchlorate in diethyl ether to promote [1,3] rearrangement of allyl vinyl ethers is applicable to a variety of substrates (Table I). In all cases studied, [1,3] sigmatropic rearrangement is the major reaction pathway; however, traces of products arising from [3,3] sigmatropic rearrangement and, in a few cases, elimination with formation of dienes have been observed.

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The data in Table I as well as the data for allyl vinyl ether 1 suggest that the [1,3] rearrangement products observed may arise via dissociated ions followed by recombination. Note that the vinyl ether derived from verbenol (entry 5) gives rise to the [1,3]-rearranged product with exclusive inversion of configuration at the allylic carbon atom, suggesting that the [1,3] rearrangement is concerted. However, the formation of the observed product can also be rationalized via dissociated ions followed by recombination from the least hindered face of the molecule. In order to determine to what extent allyl vinyl ethers ionize in the presence of 3.0 M lithium perchlorate-diethyl ether, a crossover experiment was carried out employing allyl vinyl ethers 4 and 5, each 0.1 M in 3.0 M lithium perchlorate-diethyl ether. After 1.5 h at ambient temperature, there was obtained, in excellent yield, a mixture of aldehydes 6 and 7 and ketones 8 and 9 in a ratio of 1.0:1.8:1.5:1.6, suggesting that dissociated ions are involved.



The data reported above for substrate 1 imply that the reaction rate for the [1,3] rearrangement is dependent upon the concentration of lithium ion. In order to probe this point further, allyl vinyl ether 10 was exposed to lithium perchlorate in acetone.⁶ The rearrangement of a 0.2 M solution of 10 in 1.8 M LiClO₄-acetone gave rise to a rate constant of 8.31×10^{-5} s⁻¹ as compared to a rate constant of $2.05 \times 10^{-5} \text{ s}^{-1}$ in 1.0 M LiClO₄-acetone. In contrast, exposure of 10 to 1.8 M tetra-n-butylammonium perchlorate in acetone did not give rise after 1 week to any [1,3] or [3,3] rearrangement. In 5.0 M LiClO₄-acetone the rearrangement of 10 was so fast that only a lower limit for the reaction rate (ca. $2.46 \times 10^{-2} \text{ s}^{-1}$) could be established. The rate accelerations observed for the [1,3] rearrangements in lithium perchlorateacetone are in keeping with lithium ion catalysis; however, additional factors may be operational in order to account, in the case of 10, for the greater than 1000-fold increase in reaction rate observed in going from 1.0 M to 5.0 M LiClO₄-acetone.



We anticipate that the mildness and efficiency of promoting [1,3] rearrangements of allyl vinyl ethers in lithium perchlorate-diethyl ether will find considerable use in organic chemistry.

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Gas-Phase Reactivity of Fullerene Anions

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Fullerenes have attracted considerable interest since 1985, when Kroto, Smalley, and co-workers first deduced their existence.¹ This interest has grown dramatically² since the recent report of a convenient synthesis of macroscopic quantities of C_{60} and C_{70} .³ Very little has been published on the gas-phase reactions of fullerenes, primarily because they are exceptionally unreactive. C_{60} and C_{70} are unreactive with NO, CO, SO₂, and NH₃ and react only slowly with H₂ and O₂ at partial pressures up to 120 Torr in a laser vaporization plasma.⁴ $C_{2n}^{+5.6}$ and C_{2n}^{-7} clusters (*n* > 10) have been found to be generally unreactive. This work examines the chemistry of the fullerene anions C_{60} and C_{70} ("fullerides") with various neutral molecules under thermal conditions in a flow reactor and gives the first examples of gasphase reactions of fullerides, most significantly the formation of adducts with NO₂.

All experiments were performed at 298 K in a flowing afterglow-triple quadrupole apparatus.⁸ The fullerenes are synthesized by using an arcing method described previously,³ extracted with refluxing benzene, and washed with diethyl ether to give a mixture of primarily C_{60} (\approx 90%) and C_{70} (\approx 10%). Small amounts of other carbon clusters are also seen. A solution containing ca. 1 mg of C_{60} and C_{70} in toluene or hexanes is applied to all exposed surfaces of an electron-impact (EI) ionization source at the upstream end of the flow tube and allowed to dry. The fullerenes sublime when the electron-emission filament is heated during operation. The electron energy is set at 20 V to minimize ionization of other species present and decomposition of the fullerenes. Electron attachment to gas-phase fullerenes or dissociative attachment to adsorbed material on the collection grid of the EI source produces the fullerides. The anions are entrained in a flow of helium or argon in the tube (P = 0.4 Torr) and thermalized by ca. 10⁵ collisions with the bath gas. Ions in the flow tube are gently extracted into a region of differential pumping, mass-analyzed in the first quadrupole of an Extrel triple-quadrupole mass analyzer, and detected.8

 C_{60}^{-} and C_{70}^{-} do not react at a significant rate with a range of acids including H₂O, (CH₃)₂CHOH, CF₃CH₂OH, C₂H₅-COOH, and CF₃COOH, as shown by the lack of depletion of the parent ion signal upon addition of ≥ 1 mTorr of acid to the flow tube. The lack of proton transfer from trifluoroacetic acid is particularly noteworthy because of its high acidity ($\Delta G_{acid} = 317$ kcal/mol). This indicates either that $C_{60}H$ and $C_{70}H$ are extremely strong acids ($\Delta G_{acid} \leq 317 \text{ kcal/mol}$) or that there is a kinetic barrier to proton abstraction. Both explanations are consistent with the extensive charge delocalization in these ions.

 C_{60} and C_{70} react very slowly $(k < 10^{-13} \text{ cm}^3/\text{s})$ under flowtube conditions with BF₃, an extremely strong Lewis acid. Since

⁽⁶⁾ Acetone was employed as the solvent because in diethyl ether the reaction rates for the [1,3] rearrangement were too fast to be measured by ¹H NMR. In addition, tetra-n-butylammonium perchlorate is insoluble in ether. Reactions were carried out 0.2 M in substrate in sealed NMR tubes at 22 °C. Note that the reaction of 10 in 3.0 M LiClO₄-Et₂O gave rise after 1 h to an 86% isolated yield of aldehyde 11.

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