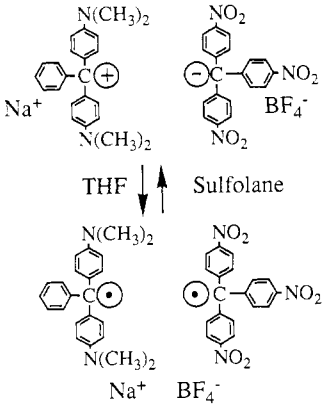
a sample produced by the reaction of the 4,4′,4″-trinitrotrityl bromide with mercury.[12] When this experiment was repeated with sulfolane (tetramethylenesulfone) as solvent only a trace of radical could be detected at the highest sensitivity. This highly polar solvent is an excellent medium for conducting carbocation–carbanion coordination reactions[9] since it is not attacked readily by either type of species and its high dielectric constant (ϵ = 43.3) stabilizes ions relative to other species—in this case radicals.

The above experiments demonstrate that single electron transfer from the carbanion to the carbocation occurs readily in THF (ϵ = 7.5) to produce a higher concentration of radicals than in sulfolane where the ions are stabilized by electrostatic solvation. *Evidence that electron transfer is reversible* in this system was obtained by diluting a THF solution of radicals, formed as described above, with an equal volume of sulfolane. Within the time needed to transfer the sample and obtain the ESR spectrum, the signal had decreased sharply and the carbanion absorbance had increased. A corresponding dilution experiment adding an equal volume of THF to a sulfolane solution of the cation (6.5 mM) and anion (6.3 mM) salts produced rapid development of an ESR signal.



In order to test the effect of solvent polarity on the ESR signal intensity of this system, two aliquots of 4,4′,4″-trinitrotrityl radical (produced by the reaction of trinitrotrityl bromide with mercury)[11,12] from a stock solution were diluted separately with equal volumes of THF and sulfolane, and spectra from these two solutions were compared under identical saturation conditions. Within experimental error, the ESR signal intensity for a given concentration of 4,4′,4″-trinitrotrityl radical was found to be the same in THF and sulfolane. These control experiments indicate that the solvent effects on 4,4′,4″-trinitrotrityl radical, used to monitor the equilibrium between ions and radicals, is due to changes in concentration of the radical rather than medium effects on its excitation energy.

We have not as yet been able to follow the corresponding spectral change for the radical derived from malachite green. If the system described above is truely at equilibrium, its concentration must vary in response to solvent variation exactly as the radical derived from the carbanion does.

Difficulties in making quantitative comparison of ESR spectra have so far prevented the exact analysis of these preliminary results in terms of equilibrium constants. Nonetheless, they provide very strong evidence that organic radicals and ions can engage in reversible equilibrium which can be shifted in favor of either species by manipulation of the solvent polarity.

These experiments show that single electron transfers and two-electron coordination can apparently exist at equilibrium as well as under kinetic conditions of competitive product formation. It is customary to think of radicals, carbanions, carbocations, and covalent bonds as species that are separated from each other by large differences in energy and conditions. Clearly, if structures and conditions are right they may coexist at equilibrium.

Acknowledgment. This work was supported by NSF Grant CHE-8412976 for which we are most appreciative.

(11) All ESR measurements reported in this paper were taken at room temperature with a Varian E-9, X-band EPR spectrometer fitted with the E-231 multipurpose and E-232 dual-sample cavities and with the sample contained within an E-248 aqueous solution sample cell.

(12) Lewis, G. N.; Lipkin, D.; Magel, T. T. *J. Am. Chem. Soc.* **1944**, *66*, 1579.

Novel Oxygenation of Pyridine and Quinoline Rings Using Acetyl Hypofluorite

Shlomo Rozen,* David Hebel, and Dov Zamir

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University Tel-Aviv 69978, Israel

Received December 3, 1986

Reagents with active fluorine have, most naturally, been used in organic chemistry for fluorination purposes. In the early stages these reagents were based on various fluorine salts, while more recently elemental fluorine and reagents derived directly from it have also been employed for introducing fluorine.[1] It is very unusual to use this most reactive element as an instrument for obtaining fluorine free products. We wish to report such a reaction which leads to a family of difficult to prepare compounds, namely, 2-oxygenated pyridine and quinoline derivatives.

Apart from Chichibabin's aminations, nucleophilic substitutions of the pyridine ring are remarkably difficult. Reaction with KOH, for example, yields only traces of 1*H*-2-pyridone,[2] while autoclave treatment with $CuSO_4$ of some substituted derivatives such as 3-picoline at 300 °C gives the corresponding pyridones in less then 7% yield.[3] Thus, up to now, the only practical method for introducing the oxygen atom at the 2-position has been to prepare the *N*-oxide moiety which then requires to be rearranged by prolonged heating with either acetic anhydride[4] or $SbCl_5$.[5]

As a step toward our goal of introducing elemental fluorine to organic synthesis methodology, a few years ago we prepared, for the first time, acetyl hypofluorite, AcOF,[6] which soon proved itself to be a useful fluorinating agent.[7] Surprisingly, when we reacted this reagent with pyridine (**1**) for a short time even at −75 °C, no fluorinated products were detected and only 2-acetoxypyridine (**2**) was obtained in 85% yield.[8] Similar results were observed

(1) See, for example: Rozen, S.; Gal, C.; Faust, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6860. Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. Rozen, S.; Brand, M. *J. Org. Chem.* **1985**, *50*, 3342. Rozen, S.; Ben-Shushan, G. *J. Org. Chem.* **1986**, *51*, 3522. Adcock, J. L.; Robin, M. L. *J. Org. Chem.* **1983**, *48*, 2437. Barnette, W. E. *J. Am. Chem. Soc.* **1984**, *106*, 452.

(2) Chichibabin, A. E. *Chem. Ber.* **1923**, *56*, 1879.

(3) Tomasik, P.; Woszczyk, A. *Tetrahedron Lett.* **1977**, *25*, 2193.

(4) Katada, M. *J. Pharm. Soc. Jpn.* **1947**, *67*, 51.

(5) Yamamoto, J.; Imagawa, M.; Yamauchi, S.; Nakazawa, O.; Umezu, M.; Matsuura, T. *Tetrahedron* **1981**, *37*, 1871.

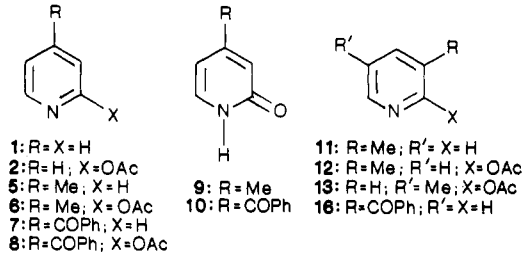
(6) Rozen, S.; Lerman, O.; Kol, M. *J. Chem. Soc., Chem. Commun.* **1981**, 443.

(7) (a) Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49*, 806. (b) Rozen, S.; Brand, M. *Synthesis* **1985**, 665. (c) Rozen, S.; Lerman, O.; Kol, M.; Hebel, D. *J. Org. Chem.* **1985**, *50*, 4753. (d) Jewett, D. M.; Potocki, J. F.; Ehrenkaufer, R. E. *J. Fluorine Chem.* **1984**, *24*, 477. (e) Visser, G. W. M.; Halteren, B. W.; Herscheid, D. M.; Brinkman, G. A.; Hoekstra, A. *J. Chem. Soc., Chem. Commun.* **1984**, 655.

(8) In a typical reaction, about 20 mmols of the heterocyclic derivative was dissolved in about 20 mL of precooled (−75 °C) $CHCl_3$ and added at this temperature to 30–35 mmols of AcOF solution prepared according to ref 5 and 6. The reaction was monitored by TLC or NMR until a full conversion was achieved. In some cases it was necessary to raise the reaction temperature as indicated in the text. In still other cases, it was found that a slow addition of the AcOF solution to the substrate was preferable. The final products, both new and known, were chromatographically purified and their physical and spectroscopic data were in perfect agreement with the proposed structure as well as with either an authentic sample or with the data described in the literature.

0002-7863/87/1509-3789$01.50/0

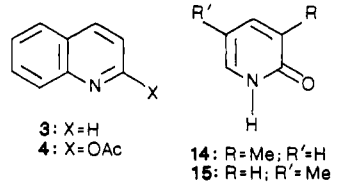
with quinoline (**3**), producing, almost instantaneously, 2-acetoxyquinoline (**4**) in higher than 90% yield. In both cases raising the temperature of the reaction to 0 °C did not change its outcome.



1: R = X = H
2: R = H; X = OAc
5: R = Me; X = H
6: R = Me; X = OAc
7: R = COPh; X = H
8: R = COPh; X = OAc

9: R = Me
10: R = COPh

11: R = Me; R′ = X = H
12: R = Me; R′ = H; X = OAc
13: R = H; R′ = Me; X = OAc
16: R = COPh; R′ = X = H



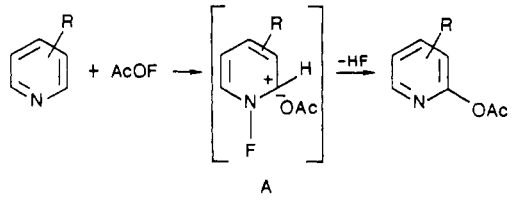
3: X = H
4: X = OAc

14: R = Me; R′ = H
15: R = H; R′ = Me

Pyridine substituted at the 4-position, such as 4-methylpyridine (**5**), reacted with AcOF to form 2-acetoxy-4-methylpyridine (**6**) in 75% yield, though a higher temperature, −10 °C, was required. Similar results were obtained with 4-benzoylpyridine (**7**) which after a short reaction with acetyl hypofluorite was transformed to the previously unknown 2-acetoxy derivative **8** (oil) in 90% yield. Both **6** and **8** were quantitatively hydrolyzed with water at 50 °C to the corresponding pyridones **9**[9] and **10**, mp 160 °C (from EtOAc).

When the substitutent was chosen to be in the 3-position, as in 3-methylpyridine (**11**), a 1:1 mixture of 2- and 5-acetoxy-3-methylpyridines (**12** and **13**)[10] was formed in 75% yield. These acetoxy derivatives were separated and then quantitatively hydrolyzed to the corresponding pyridones **14** and **15**.[9]

It is unlikely that the substitution proceeds via any radical pathway, since the addition of radical inhibitors or initiators such as nitrobenzene or benzoyl peroxide does not affect the outcome of the reaction. We believe that the first step is an attack of the electrophilic fluorine of the AcOF on the nitrogen lone pair electrons producing the ion pair A. Subsequent collapse of the ion pair and elimination of HF is strongly encouraged by the restoration of the aromaticity of the heterocyclic ring. Similar reaction pathway was found with electrophilic aromatic fluorination using AcOF.[7a]



A

This mechanism is supported by several observations. First, no acetoxylation was observed with 2-substituted pyridine rings. In the case where an electron-donating substituent is present as in 2-methyl- or 2-methoxypyridine, a ready addition across the region between the electron-donating substituent and the nitrogen takes place, but then no easy pathway for elimination of HF is possible and the resulting reactive diene system reacts further with AcOF to give many unidentified products. On the other hand, an electron-withdrawing group at the same position, as with 2-chloro- or 2-cyanopyridine, completely inhibits the reaction by reducing the basicity of the nitrogen and preventing the first addition step and there is full recovery of the starting material. The mechanism is also in accordance with the reaction of 3-benzoylpyridine (**16**) with AcOF, where the ^{19}F NMR has a signal at −63.4 ppm which is very characteristic to *N*-fluoropyridone derivatives.[11] It should also be mentioned that similar electrophilic attack of F_2 on the nitrogen atom of the pyridine ring was successfully used for fluorination purposes by Purrington[11] and Umemoto.[12]

In conclusion, it seems that the remarkable synthetic potential of elemental fluorine includes not only the ability to construct fluorine-containing compounds, but also to facilitate other difficult chemical transformations.

Acknowledgment. We thank the Fund for Basic Research administrated by the Israel Academy of Science and Humanities for supporting this research.

(9) Bell, C. L.; Egan, R. S.; Bauer, L. *J. Heterocycl. Chem.* **1965**, *2*, 420.
(10) Oae, S.; Kozuka, S. *Tetrahedron* **1964**, *20*, 2691.
(11) Purrington, S. T.; Jones, W. A. *J. Org. Chem.* **1983**, *48*, 762. Purrington, S. T.; Jones, W. A. *J. Fluorine Chem.* **1984**, *26*, 43.
(12) Umemoto, T.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 3271. Umemoto, T.; Kawada, K.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 4465.

Linear Free Energy Relationships for Excimers

Klaas A. Zachariasse* and Gert Duveneck

Max-Planck-Institut für biophysikalische Chemie
Abteilung Spektroskopie, Am Fassberg
D-3400 Göttingen, Federal Republic of Germany

Received February 18, 1987

We wish to report a linear free energy relationship, correlating ΔH and ΔS for intramolecular excimer formation. Such linear free energy relationships have been found for a great variety of chemical and physical phenomena.[1] However, for excited-state complexes, in contrast to electron donor–acceptor complexes in the electronic ground state,[2] linear ΔH–ΔS relationships have not previously been observed.

For intermolecular excimers and other excited state complexes ΔS has been assumed to be independent of the system with a value of the order of −80 J K^{-1} mol^{-1}, which was thought to be the expectation value for a molecular association process.[3] This assumption was based on the apparent constancy of the ΔS data for excimers in the literature.[3a,4] It also fitted the notion that a major contribution to ΔS for excimers comes from the reduction of the number of the degrees of freedom when an excimer, having two molecules in a rigid sandwich structure, is formed from two spatially uncorrelated molecules. It then appeared to be self-evident that intermolecular excimers and exciplexes with ΔH values smaller than −24 kJ/mol would not be easily detectable at room temperature, as under these conditions ΔG would be positive. However, as a notable exception to this expectation, efficient exciplex formation ($k_a = 7.1 \times 10^9$ s^{-1} at 25 °C) was recently observed for perylene/Ag^+ in methanol, with $\Delta H \approx -4$ kJ/mol and $\Delta S \approx +22$ J K^{-1} mol^{-1}.[5] The possibility that even weakly stabilized complexes in the excited state can be readily formed will be discussed on the basis of the ΔH–ΔS compensation relation to be presented here.

In Figure 1, the values for ΔH and ΔS for the intramolecular excimers of a series of dipyrenylalkanes in a variety of alkane solvents and in toluene are plotted. These compounds form ex-

(1) (a) Leffler, J. E. *J. Org. Chem.* **1955**, *77*, 334. (b) Exner, O. *Prog. Phys. Chem.* **1973**, *10*, 411. (c) Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438. (d) Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2772.
(2) (a) Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*; Springer: Berlin, 1961. (b) Person, W. B. *J. Am. Chem. Soc.* **1962**, *84*, 536. (c) Foster R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. (d) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.
(3) (a) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (b) Zachariasse, K. A. Ph.D. Thesis, Free University, Amsterdam, 1971. (c) Klöpffer, W. In *Organic Molecular Photophysics*: Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1.
(4) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.
(5) Läufer, A. G. E.; Dreeskamp, H.; Zachariasse, K. A. *Chem. Phys. Lett.* **1985**, *121*, 523.

0002-7863/87/1509-3790$01.50/0