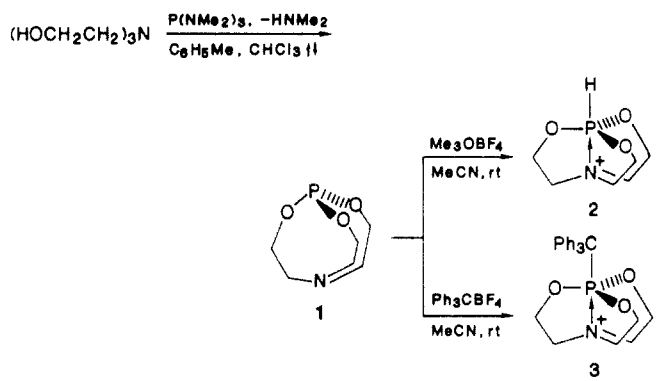
Scheme I



Results and Discussion

In the synthesis of **2**, $CHCl_3$ is used as a cosolvent to solubilize the $(HOCH_2CH_2)_3N$.[1] Using $CDCl_3$ as a substitute cosolvent we isolate only **2** in the same yield (6%), thus ruling out $CHCl_3$ as the proton source. The other cosolvent, toluene, is another potential proton source, since alkylation of aromatics by carbenium ions involves proton release.[6] However, substitution of heptane for the toluene consolvent gave only **2**, although in somewhat lower yield (4%). Repetitions of the synthesis with $Et_3OBF_4/C_6H_5Me/CHCl_3$, $MeOS(O)_2CF_3/C_6H_5Me/CHCl_3$, $MeOS(O)_2CF_3/C_6H_5Me/CDCl_3$, or $MeOS(O)_2CF_3$/heptane/$CHCl_3$ also gave only **2** in comparable yields (ca. 6%). Although these alkylating agents are unlikely sources of protons, $CD_3OS(O)_2CF_3$ was synthesized[6] and reacted with **1** using C_6H_5Me and $CHCl_3$ as cosolvents. Again, **2** was formed in 6% yield. We believe it unlikely that adventitious water could be present in sufficient quantity to lead to the formation of **2** in 6% yield, especially in view of the rather stringent precautions that were taken to insure anhydrous conditions.[1,3] Moreover, the yield of **1** is consistently about 6% using Me_3OBF_4, Et_3OBF_4, $MeOS(O)_2CF_3$, and $CD_3OS(O)_2CF_3$. It would be fortuitous if the amount of adventitious water were also so constant. Substitution of D_3CCN for MeCN as a solvent for the alkylating agent again gave only **2**.

The yield of **2** is low owing to the rather low yield of **1** (ca. 10%). Furthermore, intermediate **1** is unstable with respect to polymerization[7] and must be derivatized in situ.[1] In the course of repeatedly synthesizing **1**, we noticed that its yield is maximized at ca. 10% by slowly adding the reactants simultaneously over a 24-h period (even though the evolution of $HNMe_2$ is not complete at this time) and by maintaining a 1:1 molar ratio of reactants. The lack of complete $HNMe_2$ evolution indicates that $(HOCH_2CH_2)_3N$ is also not entirely consumed when the alkylating agent is added. We conclude, therefore, that alkylation of the alcohol groups accurs with proton release for the formation of **2** (as well as for the protonation of any unalkylated $HNMe_2$ present in solution).

In a previous publication we reported that **3** is formed when Ph_3CBF_4 is reacted with **1** (Scheme I). We now find that this reaction is erratic, giving either **3** or **4** or a mixture of these two products. The competition of OH groups for Ph_3C^+ is expected to be weaker than for Me_3O^+, thus accounting for the formation of **3** in the former case. The factors influencing the variable nature of the reaction of **1** with Ph_3C^+ have not been identified.

Experimental Section

Phosphatrane **1** was synthesized by a modification[8] of the route given earlier.[1] To the room-temperature reaction mixture were added the alkylating agents dropwise (in 100 mL of MeCN) in 20% molar excess over the $(HOCH_2CH_2)_3N$ used in the preceding reaction. The resulting crude **2** which precipitated was filtered and extracted with 2 × 25 mL of hot MeCH, and the solvent was removed under vacuum. After washing the residue with 30 mL of Me_2CO, further purification was accomplished as described earlier.[1]

Acknowledgment. J.G.V. is grateful to the National Science Foundation for a grant in support of this research. We thank Xi Shikang for experimental assistance.

Registry No. **1**, 36712-66-0; **2**·BF_4, 58418-99-8; $(HOCH_2CH_2)_3N$, 102-71-6; $P(NMe_2)_3$, 1608-26-0.

(6) van Aken, D.; Castelijns, A. M. C. F.; Verkade, J. G.; Buck, H. M. *Recl. Trav. Chim. Pas-Bas* **1979**, *98*, 12.
(7) Booth, B. L.; Hazeldine, R. N.; Laali, K. *J. Chem. Soc. Perkin Trans. 1* **1980**, 2887.
(8) The polymerization that **1** undergoes may be similar to the ring-opening polymerization observed for a cyclic aminophosphine derivative of a furanoside (Penczek, S.; Baran, J.; Pretula, J.; Tapienis, G. *Proc. IUPAC Macromol. Symp. 28th* **1982**, 203; *Chem. Abstr.* **1983**, *98*, 89802g).

Proton NMR Studies of Self-Association in the Civet Constituent (+)-(*S*,*S*)-(*cis*-β-Methyltetrahydropyran-2-yl)-acetic acid

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Received January 24, 1986

Introduction

Self-association in carboxylic acid solutions has been extensively investigated,[1] as the nature, energetics, and geometry of the association complex formed is of great interest, particularly in the case of biologically produced carboxylic acids.

Dimerization of simple carboxylic acids in solution have been studied by ^1H NMR spectroscopy, but invariably such investigations were based upon changes in the chemical shifts of the acidic protons alone.[2] Chemical shifts of these protons, however, are highly dependent on trace impurities, and reproducible results are often difficult to achieve, even following careful purification of both solvent and substrate.

A particularly interesting case of self-association is that of (+)-(*S*,*S*)-(*cis*-β-methyltetrahydropyran-2-yl)acetic acid (**1**) a naturally occurring heterocyclic acid found in trace quantitites in Civet,[3] a perfume material secreted by a scent gland of the civet cat (*Viverra civetta*). We have recently completed its total synthesis[4] by taking advantage of the enantiomerically pure (*S*)-(+)-5-chloropentan-2-ol which was obtained from enzymatic reduction of the corresponding ketone with *Thermoanaerobium brockii* alcoholdehydrogenase (TBADH)[4,5] (Scheme I).

Interestingly, we observed strong concentration and temperature dependencies in the ^1H NMR spectrum of both the synthetic material **1** and an authentic sample.[6] These findings may explain the wide diversity in chemical shifts reported in the literature for synthetic samples of **1** prepared by various authors.[7] Chemical shift values

† Incumbent of the Joseph and Madeleine Nash Career Development Chair established by Fondacion Madelon, Zurich, Switzerland.
‡ Incumbent of Charls H. Revson Career Development Chair.

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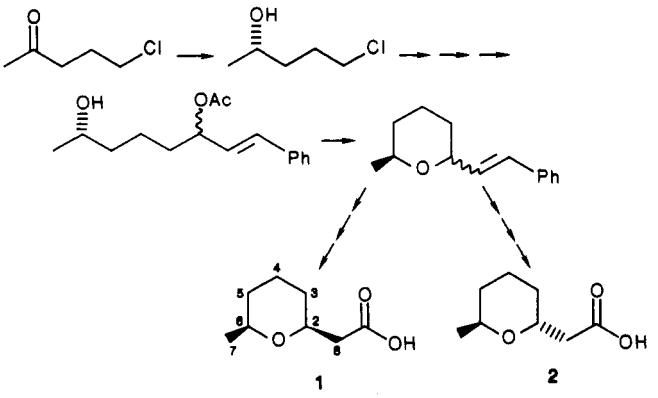
Scheme I



(measured as differences between the two C-8 methylene protons) range from 0.04[7e] and 0.05 ppm[3a] through 0.25[7a] to 0.42 ppm.[7f]

In this paper we report on the concentration and temperature dependencies of the absorptions of the relevant protons in cis and trans isomers **1** and **2**, respectively. The data were utilized as a multiple probe to study equilibrium dimerization in these compounds. The thermodynamic parameters of dimerization were extracted from the temperature dependence of the equilibrium constants.

Results and Discussion

We have monitored the chemical shifts of all protons in **1** (see Scheme I) as a function of concentration in dry $CDCl_3$. The signal corresponding to the acidic proton was not considered because of its sensitivity to trace impurities.[2] In order to minimize experimental errors, we utilized only those protons whose corresponding chemical shifts exhibit a conveniently large concentration dependence. These were the methyl protons and H-2, H-6, H-8, and H-8′ in both **1** and **2**. In **1**, overlap of the signals of the two C-8 methylene protons at very low concentrations prevented an accurate determination of their respective chemical shifts in that range (see Figure 1). The concentration dependence was measured at four different temperatures.

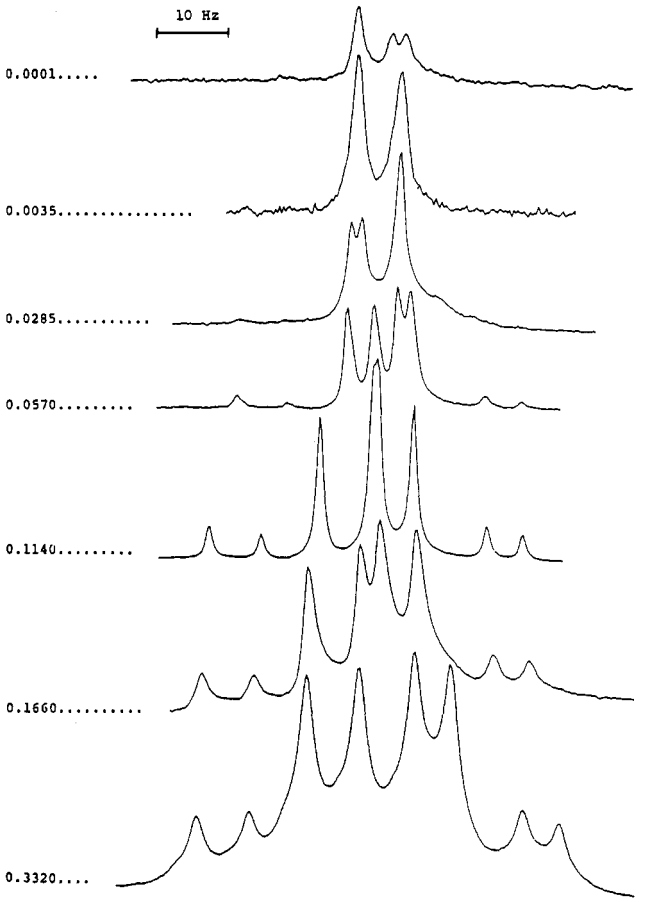


Figure 1. Spectral changes of the AB spin system at 293 K corresponding to the two C-8 methylene protons of **1** as a function of the total molar concentration (given on the left-hand side).

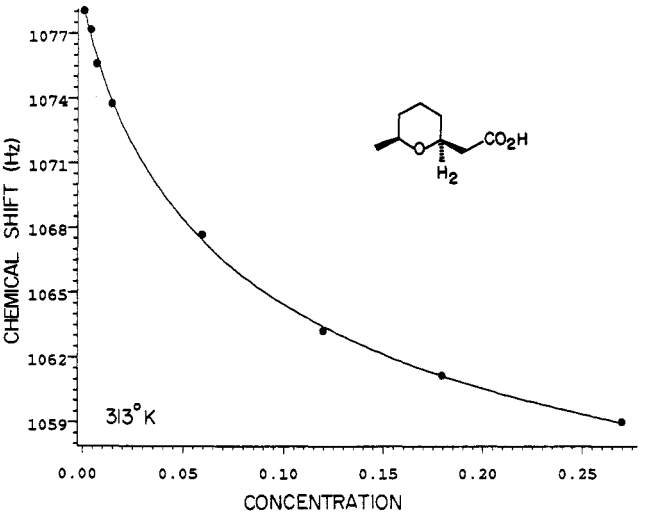


Figure 2. Plot of the changes in chemical shifts (in Hz) observed for the H-2 proton as a function of the total molar concentration of **1**. The line going through the experimental points represents the best fit as obtained from eq 2.

The basic assumptions and method used in analyzing the experimental results are presented below. It can be shown that in the case of monomer–dimer equilibrium[2b,c] the relevant proton chemical shift (δ) at a given total substrate concentration (C) is a weighted average of the monomer (δ_m) and dimer (δ_d) chemical shifts (eq 1), where

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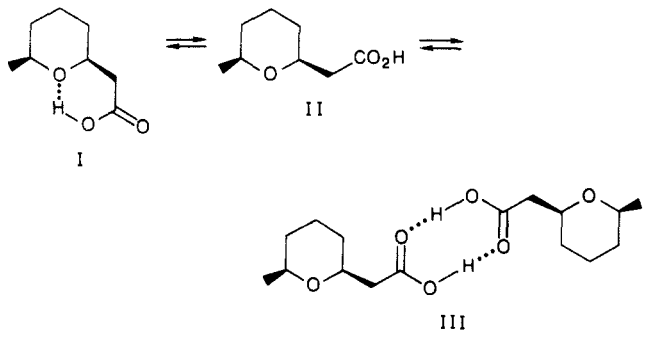
(6) We thank Dr. B. Maurer of Firmenich, Geneva, and Prof. D. Seebach of ETH, Zurich, for an authentic sample of compound **1**.

(7) For previous syntheses of the optically active natural product, see: (a) Seebach, D.; Pohmakotr, M. *Helv. Chim. Acta* **1979**, *62*, 843. Seebach, D.; Pohmakotr, M.; Schregenberger, C.; Weidmann, B.; Mali, R. S.; Pohmakotr, S., *Ibid.* **1982**, *65*, 419. (b) Lichtenthaler, F. W.; Klingler, F. D.; Jarglis, P. *Carbohydr. Res.* **1984**, *133*, in press. For synthesis of the racemic compound, see: (c) Semmelhack, M. F.; Bodurow, C. *J. Am. Chem. Soc.* **1984**, *106*, 1496. (d) Bates, H. A.; Deng, P. N. *J. Org. Chem.* **1983**, *48* 4479. (e) Kim, Y.; Mundy, B. P. *Ibid.* **1982**, *47*, 3556. (f) Ley, S. V.; Lygo, B.; Molines, H.; Morton, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1251.

Scheme II



I II III

C_m and C_d are the concentrations of monomers and dimers, respectively.

$$\delta = (C_m\delta_m + 2C_d\delta_d)/C \quad (1)$$

The process of dimerization at a given temperature, T, occurs with an apparent equilibrium constant ($K = C_d/C_m^2$) that is independent of concentration. Since $C = C_m + 2C_d$, it follows that

$$(\delta - \delta_m)/(\delta_d - \delta) = (-1 + \sqrt{1 + 8KC})/2 \quad (2)$$

Assuming that the spectral changes reflect the dimerization process only, we can obtain the temperate-independent limiting chemical shifts (and limiting coupling constants) for the monomer and the dimer at a given temperature by using eq 2 and an iterative three-parameter fit (Figure 2).

Temperature dependence of the limiting chemical shifts was found to be small with respect to the calculated errors, indicating that the relative populations of the two monomeric structures (I and II in Scheme II) are not significantly dependent on temperature (vide infra). Because the equilibrium between I and II is, by definition, also independent of concentration, this process is not expected to contribute to the measured chemical shift changes with concentration (see Figure 2). The observed concentration dependence of the chemical shift (in ppm/M) of a given proton was found to decrease with the distance of that proton from the dimerization reaction site. The van't Hoff plots[8] (see supplementary material) of the apparent K values obtained from these fits over a temperature range, yielded the thermodynamic parameters of free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). Provided that the temperature range is not too large (about 50 °C), these thermodynamic parameters are assumed to change little with temperature.

The study of concentration dependence was carried out at concentrations low enough to avoid complications arising from possible formation of associates higher than dimers (<0.3 M). The temperature range chosen was just broad enough to allow an accurate determination of the temperature dependence of K, but sufficiently far from the boiling or melting points of the solvent to minimize solvent effects on the observed chemical shifts. The calculated values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for 1 and 2 are given in Table I.

Most of the reported values for the $\Delta H°$ of dimerization of carboxylic acids in inert solvents fall between 50 and 75 KJ/mol. These include a broad variety of acids, such as formic, acetic, trifluoroacetic, benzoic, fatty acids, etc.[1,2] By comparison, the $\Delta H°$ values we found for acids 1 and 2 are significantly smaller (see Table I). In part, this difference may be attributed to the trend observed by

(8) Binsch, G. *Top. Stereochem.* **1969**, *3*, 121.

Table I. Thermodynamic Parameters for Self-Association of 1 and 2 at 25 °C

compd	K,[a] mol	$\Delta G°$,[b] KJ/mol	$\Delta H°$, KJ/mol	$\Delta S°$, J/(mol·deg)
1[c]	8.3 ± 0.2	−5.2 ± 0.1	−15.9 ± 0.3	−36 ± 1
1[d]	6.7 ± 2	−5.0 ± 2	−15.6 ± 0.3	−35 ± 7
2[e]	11.4 ± 0.6	−6.0 ± 0.4	−22 ± 2	−54 ± 5
2[d]	13.3 ± 3	−6.3 ± 2	−20 ± 2	−47 ± 13

[a] At 298 K, calculated directly from the van't Hoff fit. [b] Calculated by the relation: $\Delta G° = -RT \ln K$. [c] Data obtained from best fit values for the methyl (C-7) protons. [d] Data obtained from average values for all five signals corresponding to protons at positions 2, 6, 7, 8 and 8′. [e] Data obtained from best fit values for the proton at position 2.

Kimtys[2a] that a more sterically hindered carboxylic acid tends to have a smaller $\Delta H°$ of dimerization, but this effect is expected to reduce the $\Delta H°$ values by not more than 10 KJ/mol and cannot fully account for our observations.

Another factor that might contribute to lower $\Delta H°$ is related to the formation of intramolecular hydrogen bonds by the carboxyl group of 1 or 2. In principle, the carboxylic side chain may adopt either a cyclic, hydrogen-bonded structure I or the open form II (see Scheme II). If both monomeric structures (I and II) were present in comparable amounts in solution, the equilibrium constant between them would have to be explicitly considered when writing eq 1 and 2. Thus, the van't Hoff plots (see supplementary material) would not be linear. However, the experimental data fit the equations very satisfactorily, indicating that only one of these two forms is present in appreciable quantities. On the basis of reported estimates of enthalpy differences associated with intramolecular H bonds,[9] it is expected that formation of six-membered hydrogen-bonded ring structure I would stabilize each monomer by approximately 11–14 KJ/mol and reduce the value of $\Delta H°$ of dimerization by about 22–28 KJ/mol. Together with the steric effect (10 KJ/mol),[2a] this would nicely account for the difference between our data and those for previously reported carboxylic acids.

Although the respective standard enthalpies ($\Delta H°$) of the cis and trans compounds are significantly different (−16 and −22 KJ/mol, respectively), their Gibbs' free energies ($\Delta G°$) are small and quite close, a result of compensation by the $T\Delta S°$ term. The greater $\Delta H°$ of the trans isomer 2 relative to 1 may be a reflection of the greater stability of the cyclic form of monomer 1 relative to that of 2, due to steric considerations, with the latter releasing more energy upon dimerization.

The $\Delta S°$ difference, however, may be explained on the basis of relative conformer populations. It is expected that the trans acid 2 will exist in solution as a nearly equal mixture of its two chair conformers, each of the two side chains occupying either an axial or equatorial positions. In contrast, the cis isomer 1 is frozen in a chair conformation with both side chains taking up equatorial positions. Dimerization of either isomer significantly increases steric hindrance at the carboxylic group, favoring the conformer in which the carboxyl is equatorial. The expected resultant change in the relative population of conformers upon dimerization, which is relevant only for the trans isomer, may account for its more negative $\Delta S°$.

Conclusion

The concentration and temperature dependencies of the ^{1}H NMR absorptions of the heterocyclic carboxylic acids

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1 and 2 were used as a multiple probe to calculate the thermodynamic parameters of dimerization of each. Consequently, the energetics associated with intramolecular hydrogen bonding in these molecules could be derived with a high level of certainty. These findings are important for understanding and predicting preferred conformations of heterocyclic structures and in particular those of naturally occurring ionophores, such as nonactin, monensin, lasalocid, etc.,[10] and polyoxo macrolides, such as erythromycin, pikromycin, etc.[11] The conformations of such complex molecules have attracted the attention of chemists and biochemists in the past two decades, and also undoubtedly have an important bearing on structure-activity relationships of these antibiotics in biological systems.

Experimental Section

Samples of (+)-(*S,S*)-(*cis*-β-methyltetrahydropyran-2-yl)acetic acid (**1**) and (−)-(2*R*,6*S*)-(*trans*-β-methyltetrahydropyran-2-yl)-acetic acid (**2**) were prepared as reported.[4] NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 MHz using 5-mm o.d. NMR tubes. Samples of **1** and **2** were prepared as solutions in analytical grade $CDCl_3$ and various concentrations (0.27, 0.18, 0.12, 0.06, 0.015, 0.0075, 0.0037, and 0.00093 M) were made up by serial dilution. NMR spectra were taken at four different temperatures: 313, 293, 273, 253 K. For each concentration, the spectrum at each of the four temperatures was obtained after waiting at least 15 min to allow for equilibration. At the higher concentration, only eight scans were taken, while for dilute samples more scans (up to 100) were required. Tetramethylsilane (Me_4Si) was used as an internal standard. The spectra were generated by using a spectral window of 2400 Hz, 16 384 data points, a pulse width of 75°, a recycle time of 3.5 s, and a line broadening of 0.2 Hz. The results were processed on the IBM-3081 at the Weizmann Institute of Science by using the PROC NLIN package of the Statistical Analysis System (SAS). The spectra shown in Figure 1 were recorded on a Bruker WH-270 spectrometer operating at 270 MHz.

Acknowledgment. We wish to thank the Israel National Council for Research and Development for their generous support. Dr. Hugo E. Gottlieb of Bar-Ilan University is acknowledged for providing access to their Bruker AM-300 spectrometer.

Registry No. 1, 69493-11-4; 2, 69493-16-9.

Supplementary Material Available: Van's Hoff plot for H-2 in compound 1 (1 page). Ordering information is given on any current masthead page.

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Intramolecular Hydrogen Bonding Enhances the Rate of Nucleophilic Cleavage in Alkyl–Aryl Ethers

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Cleavage of alkyl–aryl ethers in acid solution is generally accepted to require equilibrium protonation of the ether oxygen prior to nucleophilic displacement of phenol from the alkyl carbon atom by halide ion.[1] Such protonation serves to polarize the alkyl carbon–oxygen bond, making the carbon more susceptible to nucleophilic attack, and to convert phenoxide into a neutral phenol leaving group. A variety of mild and selective ether cleaving reagents, active in nonaqueous solvents, have been reported in which protonation has been replaced by the coordination of Lewis acids to the ether oxygen.[2] Increasing the nucleophilicity of the halide ion through phase-transfer catalysts,[3] in situ generation of HI in nonaqueous solvents,[4] or the use of high temperatures and poorly solvating solvents[5] also leads to ether cleavage by halide ions in the absence of aqueous acid.

We postulated that if the C–O activation requirement could be met by an intramolecular hydrogen bond to the basic ether oxygen atom, selective nucleophilic ether cleavage by halide ion could be effected at moderate temperatures in a basic solvent such as pyridine. The original motivation for the studies reported here was the observation that pyridine hydriodide (py–HI) or anhydrous lithium iodide in pyridine at 50 °C modified fractions of a bituminous coal in a manner consistent with ether cleavage.[6] However, we have previously shown that monofunctional ethers such as anisole, benzyl phenyl ether, and dioctyl ether are not cleaved by py–HI below 200 °C.[7] Since ortho, but not para, anisic acid was demethylated by py–HI in pyridine at 85–115 °C, we suggested that intramolecular hydrogen bonding activated the alkyl C–O bond toward nucleophilic attack by iodide ion.

Royer and co-workers have shown that molten pyridine hydrogen halide salts (py–HX) will dealkylate methoxy aromatics at elevated temperatures (190–230 °C) and that the rates of these reactions are retarded by the presence of free pyridine or quinoline.[8] We have also shown[7] that py–HI converts anisole, benzyl phenyl ether, phenyl phenethyl ether, and cyclohexyl phenyl ether to the phenol and hydrocarbon[9] when heated without solvent in evacuated, sealed tubes at 210 °C but that these and other monofunctional alkyl–aryl ethers are more than 90% recovered after 4 days in pyridine solutions containing excess HI at 115 °C. Anhydrous LiI in boiling collidine (174 °C) demethylates methoxy naphthalene[5a] and converts 1,2-dimethoxybenzene into 2-methoxyphenol but does not demethylate *p*-anisic acid.[5b] *p*-Anisic acid, 2-methoxyphenol, and 2-benzyloxyphenol are also recovered unchanged from pyridine solutions of py–HI or LiI after three days at 115 °C.[7]

In order to further test the hypothesis that intramo-

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0022-3263/86/1951-4291$01.50/0