terpretation of the metal effect on aldol-type stereoselection. Until now, it seems that the possibility through the α -metallo ketone form has been neglected. There is the possibility that erythro selection of triphenyltin enolates proceeds through the α -stannyl ketone form. Certain copper enolates, prepared from the conjugate addition of Me₂CuLi to α,β -unsaturated carbonyl compounds, undergo erythro-selective condensations.²² This result can be explained by the intervention of α -cupric ketones, and such species are frequently suggested in many other reactions.²³ The most recent reports on erythro-selective condensations are also interesting in this respect.24

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(25) Note Added in Proof: After the submission of this paper, two conflicting papers on tin enolates appeared: three selective reactions of isolated R_3Sn enolates (Shenvi, S; Stille, J. K. *Tetrahedron Lett.* **1982**, 627) and erythro selective condensations of divalent tin enolates (Mukaiyama, T.; Stevens, R. W.; Iwasawa, N. Chem. Lett. 1982, 353).

Nitrogen to Nitrogen Proton Transfer. Significance of Large Negative Entropies of Activation

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In studying the kinetics of proton exchange of N,N-dimethylcyclohexylamine hydrochloride, catalyzed by bases such as pyridine (eq 1, R = cHx), Menger, Singh, and Bayer¹ have

$$RNHMe_2^+ + Py \xrightarrow{\kappa_2} RNMe_2 + PyH^+$$
 (1)

observed that ΔS^* in chloroform as solvent is large and negative, ca. -30 eu. They also found a Hammett ρ value of -6.4 and a Brønsted β value of 1.1 (for variations of the catalyzing base) and normal reactivity for 2,6-di-tert-butylpyridine, without any steric retardation. These latter results suggested that the transition state resembles products, so that the charge contents of reactant and transition state would not differ appreciably. The large negative ΔS^* was then interpreted in terms of ion-pair dissociation. We now wish to show that eq 1 is not the correct mechanism for the proton exchange. Instead, we propose that the mechanism is a chain reaction, with eq 1 as initiation step and with a propagation step whose transition state is consistent with a large negative ΔS^*

The mechanism of any exchange reaction must be symmetrical.² To take eq 1 as the rate-limiting step implies that its reverse must also be the rate-limiting step, since the transition states are identical. We therefore should adapt eq 1 by explicitly writing it as reversible (eq 2). Of course, the PyH⁺ must return a

$$\text{RNHMe}_{2}^{+} + \text{Py} \frac{k_{2}}{k_{-2}} \text{RNMe}_{2} + \text{PyH}^{+}$$
 (2)

different proton to the amine, in order to qualify as exchange. However, we are then led to consider whether PyH⁺ is the only acid that can return a proton.

Might $RNHMe_2^+$ also serve (eq 3)? Each occurrence of either



Figure 1. Kinetics of proton exchange of N,N-dimethylcyclohexylamine hydrochloride (0.16 and 0.32 M) in chloroform at 34 °C, catalyzed by 2.47×10^{-3} M added Py and inhibited by added PyH⁺.

$$RNHMe_2^+ + RNMe_2 \rightleftharpoons RNMe_2 + RNHMe_2^+$$
 (3)

eq 2 or eq 3 represents one proton exchange, but which is faster? Even though RNHMe₂⁺ is a much weaker acid than PyH⁺, rate constants for thermoneutral proton transfer involving nitrogen or oxygen are nearly as large as those for exergonic proton transfers.³ Therefore the rate of protonation by the more abundant RNHMe₂⁺ is likely to be even greater than the rate of protonation by PyH⁺. Thus we expect eq 3 to be a faster reaction than eq 2. This suggests that the dominant mechanism of exchange is likely to be eq 3, utilizing RNMe₂ generated through eq 2. Moreover, the mechanism of eq 3 automatically satisfies the requirement for symmetry. However, this leads to eq 4, which

$$v = k_{\text{exch}}[\text{RNHMe}_2^+] = k[\text{RNHMe}_2^+][\text{RNMe}_2] \quad (4)$$

does not fit Menger's observed kinetics, which is first order in $RNHMe_2^+$ and first order in Py (eq 5). Even if eq 4 is trans-

$$v = k_{\text{exch}}[\text{RNHMe}_2^+] = k_2[\text{RNHMe}_2^+][\text{Py}]$$
(5)

formed by assuming that the steady-state [RNMe₂] is governed by the equilibrium of eq 2, with equilibrium constant $K_e = k_2/k_{-2}$, the result (eq 6) still does not fit the observed kinetics, which is not second order in RNHMe₂⁺.

$$v = k_{\text{exch}}[\text{RNHMe}_2^+] = kK_e [\text{RNHMe}_2^+]^2[\text{Py}]/[\text{PyH}^+] \quad (6)$$

It is the purpose of this paper to demonstrate that eq 6 nevertheless describes the kinetics of the exchange. Equation 6 may be reconciled with eq 5, observed by Menger, if [RNHMe₂⁺]/ [PyH⁺] was constant throughout all Menger's kinetic runs. This would hold if the N,N-dimethylcyclohexylamine hydrochloride had been contaminated by some excess HCl, which would be converted to PyH⁺ under the conditions of the kinetic experiments. Indeed, the presence of excess HCl may be inferred from the stated requirement that the amine hydrochloride must be free of traces of unprotonated amine. Such contamination has been demonstrated⁴ previously even for amine salts recrystallized twice.

Figure 1 shows our evidence⁵ in favor of eq 6 over eq 5. It is quite clear that adding PyH^+ decreases k_{exch} , whereas eq 1 and 5 imply that k_{exch} should be independent of [PyH⁺]. The observed dependence on [PyH⁺] is sufficient to disprove eq 1 as the mechanism of exchange.

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⁽⁵⁾ Amine hydrochlorides were prepared from the amine (redistilled N,Ndimethylcyclohexylamine or Spectroquality pyridine) and HCl in ether. Kinetics of proton exchange in reagent chloroform were followed on a Varian EM-390 NMR spectrometer at 34 °C. Rate constants, including a statistical factor of 2, were determined from the valley-to-peak intensity ratio of the

N-methyl doublet,^{6a} as calculation from the line-shape equation.^{6b} (6) (a) Grunwald, E.; Jumper, C. F.; Meiboom, S. J. Am. Chem. Soc. 1962, 84, 4664. (b) Gutowsky, H. S.; Holm, C. H. J. Chem. Phys. 1956, 25, 1228.

The total $[PyH^+]$ is equal to the sum of the $[PyH^+]$ added and the $[PyH^+]$ produced from the excess HCl in the amine hydrochloride (eq 7). Therefore, according to eq 6 and 7, a plot of

$$[PyH^{+}] = [PyH^{+}]_{added} + [HCl]_{0}$$
(7)

 $1/k_{exch}$ vs. [PyH⁺]_{added} should be linear and intersect the horizontal axis at $-[HCl]_0$. Figure 1 contains two such plots, and they are indeed linear (r > 0.994). From those intersections, we determine that our $[HCl]_0$ was 0.59 \times 10⁻³ and 0.31 \times 10⁻³ M for $[RNHMe_2^+]$ of 0.32 and 0.16 M, respectively. Thus, the ratio $[HCl]_0/[RNHMe_2^+]$ is constant, corresponding to a contamination by 0.19 mole % HCl. This value varied from batch to batch, so it is understandable that our k_{exch} at zero $[PyH^+]_{added}$ differs from that of Menger et al. With another batch of RNHMe₂+Cl⁻, we find contamination by 0.22 mole % HCl, and this value, determined by kinetic analysis, could be verified independently as 0.21 mole % by titration with NaOH in methanol. Neutralization of this HCl with $RNMe_2$ produces a solution that shows extremely fast (k_{obsd} ca. 10³ s⁻¹) pyridine-catalyzed proton exchange, as expected from our mechanism. The fact that Menger et al. observed conveniently measurable rates is evidence that their amine hydrochloride too contained excess HCl.

It also follows from eq 6 and 7 that the slope of $1/k_{\text{exch}}$ vs. [PyH⁺]_{added} is $1/kK_e$ [RNHMe₂⁺][Py]. We may correct the [Py] for the amount that is converted to PyH⁺ by the HCl contamination. Then from the slopes in Figure 1 we may determine that $kK_e = 13.8$ and 14.9 M⁻¹ s⁻¹ for [RNHMe₂⁺] of 0.32 and 0.16 M, respectively. The constancy of this rate constant, over a 2-fold variation in [RNHMe₂⁺], is strong evidence for eq 6 and the mechanism of eq 3.

This mechanism represents a chain reaction, for which $RNMe_2$ is the chain carrier, eq 3 is the propagation step, and the forward and reverse reactions of eq 2 are initiation and termination steps, respectively. As stated above, protonation of $RNMe_2$ by $RNHMe_2^+$ (the propagation step) may be much more frequent than protonation by PyH⁺ (termination). This is the condition of long chains, and steady-state analysis of eq 2 and 3 then leads to eq 6. Without the assumption of long chains, steady-state analysis leads to eq 8. The influence of the second term in eq

$$v = k_{\text{exch}}[\text{RNHMe}_2^+] = kK_{\text{e}}[\text{RNHMe}_2^+]^2[\text{Py}] / [\text{PyH}^+] + k_2[\text{RNHMe}_2^+][\text{Py}] (8)$$

8 can be seen as a slight curvature in Figure 1, and kinetic data at higher concentrations of Py and PyH⁺ (off scale in Figure 1) indicate that $k_2 = 1.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. This value corresponds to a chain length of 50 under the conditions of Figure 1 with no added PyH⁺. Also, from kK_e and k_2 , we obtain $k/k_{-2} = 0.1$, which corroborates the statement above comparing rate constants for thermoneutral and exergonic proton transfers.

We are especially interested in the propagation step (eq 3). Unfortunately we cannot determine k for this step alone, but only kK_e . However, if K_e (eq 2) is the same in chloroform as it is in aqueous solution,⁷ then $k = 5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This value is consistent with the upper limit of $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for triethylamine (eq 3, R = Me) in aqueous solution,⁸ which is the only other rate constant reported for symmetrical proton transfer between tertiary amines.

This mechanism accounts for Menger's observed results. Comparison of eq 4, 6, and 7 shows that the k_2 of Menger et al.¹ is our $kK_e[\text{RNHMe}_2^+]/[\text{HCl}]_0$. Therefore their observed ΔH^* of 4 kcal/mol must equal $\Delta H^\circ + \Delta H^*$, where ΔH° and ΔH^* apply to eq 2 and 3, respectively. If ΔH° is the same in chloroform as it is in aqueous solution⁷ (or even in the gas phase, for model amines⁹), then $\Delta H^* = 0$. It then follows that ΔS^* for eq 3 is ca. -28 eu, quite close to the value that Menger et al. originally reported. However, this value now applies to a symmetrical transition state rather than one resembling products. A similar value, -29 eu, was previously observed⁴ for symmetrical proton transfer from trimethylamine hydrochloride to trimethylamine, but via a *tert*-butyl alcohol bridge. Such values are quite reasonable for such highly organized transition states, involving proton (and chloride) transfer from tertiary amine hydrochloride to tertiary amine. Also, the Hammett ρ of -6.4, the Brønsted β of 1.1, and the normal reactivity of 2,6-di-*tert*-butylpyridine all follow from the simple proportionality between k_{exch} and K_e (eq 6). These results are to be expected because a proton has already been transferred completely to the catalyzing base before the transition state (strictly, the propagation step) has been reached.

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Di-tert-butylcarbene: The Low-Temperature Photochemistry of Di-tert-butyldiazomethane

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Interest continues in this and other laboratories¹ in the synthesis of twisted alkenes. This has prompted investigations into the potential coupling of "di-*tert*-butylcarbene fragments" to form the elusive² and highly sterically congested³ tetra-*tert*-butylethylene. Our approach to this problem has utilized low-temperature methods in an effort to produce high concentrations of di-*tert*-butylcarbene so as to promote direct coupling. Although carbene coupling reactions are not common, there is precedent for this reaction at low temperatures.^{4a} Coupling of two methylene triplets is expected to occur with little or not activation energy.^{4b} Although tetra-*tert*-butylethylene was not detected, the carbene was found to be sufficiently stable to provide the *first direct observation of a hydrocarbon dialkylcarbene*.^{4c,5}

Di-tert-butyldiazomethane was deposited on a cesium iodide window and cooled to 14 K by pyrolyzing its triphenylphosphine

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