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

$$[PyH^+] = [PyH^+]_{added} + [HCl]_0 \qquad (7)$$

$1/k_{exch}$ 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 0.59×10^{-3} and 0.31×10^{-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 RNHMe$_2^+$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. 10^3 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 $1/k_{exch}$ vs. [PyH$^+$]$_{added}$ is $1/kK_e$[RNHMe$_2^+$][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 [RNHMe$_2^+$] of 0.32 and 0.16 M, respectively. The constancy of this rate constant, over a 2-fold variation in [RNHMe$_2^+$], 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

$$v = k_{exch}[RNHMe_2^+] =$$
$$kK_e[RNHMe_2^+]^2[Py]/[PyH^+] + k_2[RNHMe_2^+][Py] \quad (8)$$

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 $k_2 = 1.4 \times 10^2$ M^{-1} 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 $k = 5 \times 10^6$ M^{-1} s^{-1}. This value is consistent with the upper limit of 3×10^7 M^{-1} 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[RNHMe$_2^+$]/[HCl]$_0$. Therefore their observed $\Delta H^\ddagger$ of 4 kcal/mol must equal $\Delta H^\circ + \Delta H^\ddagger$, where ΔH° and $\Delta H^\ddagger$ apply to eq 2 and 3, respectively. If ΔH° is the same in chloroform as it is in aqueous solution[7] (or even in the gas phase, for model amines[9]), then $\Delta H^\ddagger = 0$. It then follows that $\Delta S^\ddagger$ 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 observed[4] 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.

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

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Interest continues in this and other laboratories[1] in the synthesis of twisted alkenes. This has prompted investigations into the potential coupling of "di-*tert*-butylcarbene fragments" to form the elusive[2] and highly sterically congested[3] 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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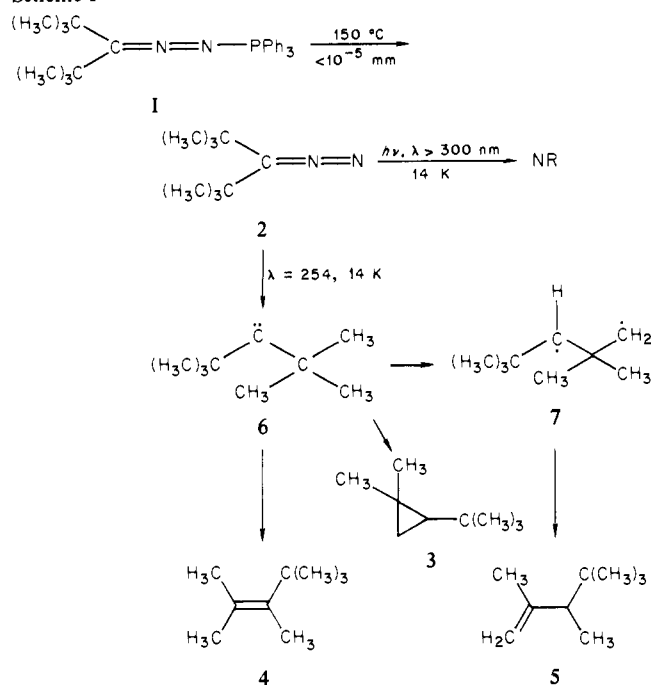
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Scheme I

adduct, **1** (Scheme I), under reduced pressure. Irradiation at long wavelengths ($\lambda > 300$ nm) produced no change, but irradiation at 254 nm, followed by collection and separation (GLPC), allowed the isolation of three major products in a 5:3:2 ratio. These were identified as 1,1-dimethyl-2-*tert*-butylcyclopropane (**3**), 2,3,4,4-tetramethyl-2-pentene (**4**), and 2,3,4,4-tetramethyl-1-pentene (**5**), respectively. Monitoring of the progress of the photolysis by infrared spectroscopy showed that the composition of the product mixture was fairly constant. The three major products (**3–5**) accounted for all of the major bands observed at low temperatures. The azine was not formed under these conditions.[4a] Products **3** and **4** represent classic reactivity of a carbene such as **6**. The origin of **5** is not obvious. Hydrogen atom transfers (via a tunneling mechanism) have precedent under these conditions.[6] Conceivably, **7**, thus formed, could rearrange to **5** and possible also represent a source of **3**.

The gradual warming after the photolysis was uneventful with the exception of the disappearance, at temperatures >100 K, of a moderately intense band observed at 1290 cm⁻¹. The band was determined to be associated with a primary photoproduct by monitoring its intensity during the early stages of photolysis. This band was also present when **2** was irradiated while matrix isolated in argon.[7] Subsequent irradiation of **2** in an outgassed 2-methyltetrahydrofuran glass at 20 K revealed the characteristic ESR spectrum of a triplet. The observation of a stable ESR signal at 20 K indicates that the triplet is the molecule's ground state or is within a few cal/mol of the ground state. Although stable at low temperatures, the ESR spectrum disappeared irreversibly at temperatures in excess of 70 K. The zero-field parameters ($|D/\hbar c| = 0.689 \pm 0.005$ cm⁻¹ and $|E/\hbar c| = 0.039 \pm 0.002$ cm⁻¹) fully support the assignment of the triplet spectrum as di-*tert*-butylcarbene (**6**). The $|D/\hbar c|$ parameter is at least a factor of 5 larger than expected for a triplet biradical such as twisted tetra-*tert*-butylethylene.[8] We did not detect any triplet biradical spectra upon scanning the appropriate spectral region between 2500 and 41 000 G, specifically the product of 1,3 hydrogen

migration, **7**.[9] The $|D/\hbar c|$ parameter of di-*tert*-butylcarbene is comparable to that observed by Wasserman for CF_3–$\ddot{C}$–CF_3 (0.7444 cm⁻¹).[10] The parameter is, as expected, much larger than the $|D/\hbar c|$ values of aryl- and diarylcarbenes. Recent calculations suggest that di-*tert*-butylcarbene should have a singlet ground state.[11] We suspect that the *tert*-butyl groups force the bond angle (vida infra) open sufficiently to raise the singlet above the triplet.

The zero-field parameters indicate that this carbene is not linear. The $|E/D|$ ratio predicts a bond angle about the central carbon of ~143°. This value is surprisingly similar to the value of 138° found in triplet methylene and of 140° found for CF_3–$\ddot{C}$–CF_3.[10] Clearly, even with the bulky *tert*-butyl groups present, the historical proposal[12,13] that triplet carbenes are linear has not proven correct. Further structure-stability correlations and kinetic measurements are in progress to clarify why this highly congested carbene should show this surprising resistance to rearrangement.

Registry No. 1, 56956-22-0; **2**, 54396-68-8; **6**, 81158-97-6.

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Anodic Oxidation of Heterocumulenes in Acetonitrile

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Studies on the electrochemical oxidation of organic compounds containing an allenic-type bond are rare. Recently we reported on the oxidation of allenic hydrocarbons in methanol[1] and in acetonitrile.[2] The present communication reports, for the first time, on the anodic oxidation of cumulenes possessing an $N{=}C{=}y$ bond in which y = N, O, or S. All compounds studied undergo α cleavage predominantly, similar to what was previously reported for the anodic oxidation of ketones[3] and alkyl halides.[4]

Dicyclohexylcarbodiimide (**1**), di-*tert*-butylcarbodiimide (**2**), cyclohexyl isocyanate (**3**), and cyclohexyl isothiocyanate (**4**) were potentiostatically oxidized at the Pt anode in acetonitrile–LiClO₄ solutions, by employing a three-compartment cell with Ag/0.1 N AgNO₃ as the reference electrode. The oxidation of **1**, **2**, and **4** was terminated when the current dropped to its background value, generally after passing ~1 F/mol. The reaction of **3** was arbitrarily terminated after passing 1 F/mol, because of a high background current. In all the former cases pulses to 0 V (for 0.5 s every 35 s) were required to maintain a decent current since

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