tert-Butylation of Pyridines, Quinolines, and Isoquinolines by *tert*-Butylmercury Halides[1]

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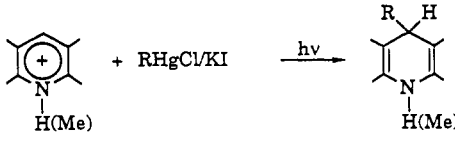
Abstract: Photolysis of *tert*-butylmercury halides with pyridinium or quinolinium salts leads to alkylation via the intermediacy of adduct radical cations. With simple pyridines or the 2-adducts from quinolines, the radical cations readily lose a proton to form a substituted pyridinyl radical which is easily oxidized by the alkylmercury halide. Addition of *t*-Bu• at the 4-position of the quinolinium ions, the 1-position of the isoquinolinium ions, or the 9-position of the acridinium ions, yields in the presence of KI the dihydro derivatives formed via electron transfer to the adduct radical cation from I^- or its ate-complex with the *tert*-butylmercury halide. A similar reductive alkylation is observed for the radical cations formed by the addition of *t*-Bu• to the β-position of the 4-vinylpyridinium ion or to the *N*-methylated cations derived from pyridine-3,4-dicarboximide, acridine, quinaldine, or isoquinoline. Competition between substitutive (oxidative) and additive (reductive) alkylation reflects the ease of proton loss from the intermediate adduct radical cation. Because of reversibility in adduct formation and variable rates of deprotonation of the adducts, yields of substitutive alkylation products are often not a true measure of the selectivity in the initial radical addition step. 4-*tert*-Butyl-1,4-dihydro-2-methylquinoline can be isolated from the photolysis of quinaldine with *t*-BuHgCl in the presence of KI/PTSA, methylated at C-3 by methyl iodide during the *tert*-butylation reaction, reduced by $NaBH_4$ upon workup, or oxidized to the quinoline at long reaction times. 4-*tert*-Butyl-1,4-dihydroquinoline reacts rapidly in the presence of PTSA and *t*-BuHgCl to form 2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline while 4-*tert*-butyl-2-chloro-1,4-dihydroquinoline is readily hydrolyzed to form the amide. Although 1-*tert*-butyl-1,2-dihydro-3-methylisoquinoline is isolable, 1-*tert*-butyl-1,2-dihydroisoquinoline reacts via the iminium ion to form 1,3-di-*tert*-butyltetrahydroisoquinoline and the de-*tert*-butylated product 3-*tert*-butyl-3,4-dihydroisoquinoline. De-*tert*-butylation with aromatization is also observed upon photolysis of 4-*tert*-butyl-3,4-dihydro-2,3-dimethylquinoline with *t*-BuHgCl.

Introduction

Photolysis of alkylmercury chlorides in pyridine solution forms the 2- and 4-alkylpyridines and Hg^0 in high yields.[2] With the photochemically more labile *t*-BuHgI,[3] or a mixture of *t*-BuHgCl and KI, the reaction proceeds more readily and dilute solutions of pyridines or quinolines in Me_2SO readily undergo *tert*-butylation. Alkylation may involve the attack of *t*-Bu• upon the free pyridine, upon a complex of the pyridine with *t*-BuHgX,[4] or upon the pyridinium ion formed as the substitution reaction 1

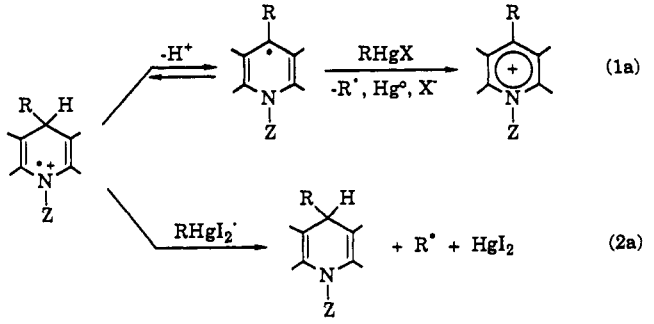
$$C_6H_5N + RHgX \xrightarrow{h\nu} RC_6H_4NH^+X^- + Hg^0 \qquad (1)$$

proceeds. Reductive alkylation is observed with some pyridine derivatives, particularly in the presence of PTSA and KI, e.g. with 4-vinylpyridine [to yield 4-(3,3-dimethylbutyl)pyridine], acridine, or 2-chloro- or 2-methylquinoline (quinaldine). Similar reductive alkylations are observed for the *N*-methylpyridinium ions derived from acridine, quinaldine, isoquinoline, or pyridine-3,4-dicarboximide (reaction 2).



(2)

Scheme I. (Z = H, Me, $Hg(R)X^-$)



(1a)

(2a)

Protonation of heteroaromatics is known to activate them toward radical additions.[5] Complexation with alkylmercury halides may have a similar effect. For some reactions of *t*-BuHgX/KI with pyridines, the promoting effect of protonation is quite strong, particularly for reactions that proceed exclusively by the reductive pathway of reaction 2. For oxidative alkylations proceeding via reaction 1, the promoting effect of protonation is often apparent only in the initial stages of the reaction.

The competition between oxidative and reductive alkylation is apparently controlled by the rate of proton removal from the initial adduct radical (Scheme I). Reaction 1a greatly predominates for simple pyridines, but when the proton in the adduct radical is not easily lost because of steric or stereoelectronic reasons, the reductive pathway of reaction 2a predominates (e.g. for acridine or 2-substituted quinolines). The system RHgI/KI is a unique one because of the presence of both the mild oxidizing agent required for reaction 1 (RHgI)[6] and the reducing agent (I^- or $RHgI_2^-$)[3] required for reaction 2.

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(1) Electron Transfer Processes. 56.

(2) Russell, G. A.; Guo, D.; Khanna, R. K. *J. Org. Chem.* **1985**, *50*, 3423.

(3) Russell, G. A.; Hu, S.; Herron, S.; Baik, W.; Ngoviwatchai, P.; Jiang, W.; Nebgen, M.; Wu, Y.-W. *J. Phys. Org. Chem.* **1988**, *1*, 299.

(4) Graddon, D. P.; Mondal, J. *J. Organomet. Chem.* **1978**, *160*, 377.

(5) Minisci, F.; Vismara, E.; Fontane, F.; Morini, G.; Serravalle, M.; Giordano, C. *J. Org. Chem.* **1987**, *52*, 730.

(6) Russell, G. A. *Acc. Chem. Res.* **1989**, *22*, 1.

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1,4-Dihydropyridines can be oxidized to the pyridinium ions in a radical fashion by RHgX via the removal of the hydrogen atom at C-4 by R· followed by electron transfer between the pyridinyl radical and RHgX.[7] This raises the possibility that an observed oxidative alkylation product can be formed via an initial reductive alkylation reaction. The results reported exclude this process for simple pyridines but support it for reactions of quinaldine.

Results and Discussion

Oxidative *tert*-Butylation of Pyridines. Photolysis of *t*-BuHgCl (0.2 M) in pyridine solution at 35 °C for 20 h yields the 2- and 4-*tert*-butylpyridines (94%) with the formation of 0.98 equiv of Hg^0.[2] Evidence for a free radical process in the alkylation of pyridines is conclusive, since there is no reaction in the dark. By use of the $(t\text{-Bu})_2NO^\cdot$ inhibition method, a kinetic chain length of 40 was measured for the ortho *tert*-butylation of neat γ-picoline by 0.2 M *t*-BuHgCl upon photolysis with a 275-W sunlamp (rate of radical formation 2 x 10^{-4} M min^{-1}).[8] With 0.2 M $CH_2{=}CH(CH_2)_4HgCl$ in neat pyridine at 35 °C, only cyclopentylcarbinyl-substituted pyridines are observed. This places an upper limit upon the rate constant for attack of the 5-hexenyl radical upon pyridine of 10^3 M^{-1} s^{-1}. Competition of Bu· (from BuHgCl) with $Me_2C{=}NO_2^-$ and pyridine in the presence of excess DABCO to preferentially complex BuHgCl leads to an estimated rate constant for Bu· attack on pyridine of 1 × 10^2 M^{-1} s^{-1} at 35 °C.[2] (A reasonable estimate for the rate constant for addition of Me· to pyridine at 65 °C in isooctane is 1.5 × 10^2 M^{-1} s^{-1}.[9])

The *o*/*p* ratio of *tert*-butylpyridines varies with the alkylation conditions and decreases as reaction 1 occurs, i.e., as the pyridinium ion is formed and as the concentration of *t*-BuHgX decreases.[10] In general, the *o*/*p* ratio is lower for conditions that favor a reversal of the radical addition step such as lower concentrations of the oxidizing agent (RHgX) and higher concentrations of a proton donor (which would affect the radical cation/pyridinyl radical equilibrium of Scheme I). In pyridine solution containing 1 M PTSA, the final *o*/*p* ratio increases from 0.75 with an initial concentration of RHgX (X = Cl or I) of 0.1 M to 0.95 with $[RHgX]_0$ = 0.5 M. In Me_2SO with 0.5 M pyridinium tosylate, the *o*/*p* ratio decreases to 0.48 with $[t\text{-BuHgI}]_0$ = 0.1 M. Without an added proton donor, the *o*/*p* ratio is 0.65 in Me_2SO (0.5 M pyridine, 0.1 M *t*-BuHgI) while in pyridine solution *o*/*p* = 1.1 with 0.1 M *t*-BuHgCl and 0.8 with 0.1 M *t*-BuHgI.

The photochemical reaction of *t*-BuHgI in pyridine-d_5 could be monitored by ^1H NMR. Figure 1 presents data demonstrating the decrease in the *o*/*p* ratio with decreasing *t*-BuHgI concentration and the effect of added DABCO on this ratio.

Photolysis of 0.2 M lutidine with 3 equiv of *t*-BuHgI in Me_2SO for 4 h forms 87% of the para *tert*-butylated derivative, 1.05 equiv of Hg^0, 0.5 equiv of $Me_2C{=}CH_2$, and 0.43 equiv of Me_3CH. The observed yields of $Me_2C{=}CH_2$ and Me_3CH are inconsistent with a reaction proceeding via initial formation of a dihydropyridine followed by oxidative radical reactions; the $Me_2C{=}CH_2$ and Me_3CH are apparently formed in the disproportionation of *t*-Bu·. In a 3-h reaction with 3 equiv of added PTSA, an 82% yield of 4-*tert*-butyllutidine was accompanied by formation of 0.18 equiv of $Me_2C{=}CH_2$ and 0.28 equiv of Me_3CH, a stoichiometry suggesting a small contribution from protonation of the organomercurial compound.

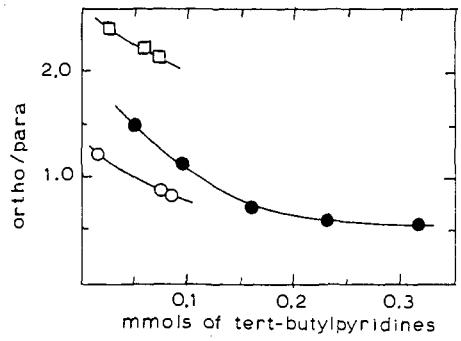


Figure 1. *o*/*p* ratio followed by ^1H NMR in the photostimulated reaction of *t*-BuHgI in 1 mL of pyridine-d_5: ○, 0.1 mmol of *t*-BuHgI; ●, 0.4 mmol of *t*-BuHgI; □, 0.1 mmol of *t*-BuHgI in the presence of 0.4 mmol of DABCO.

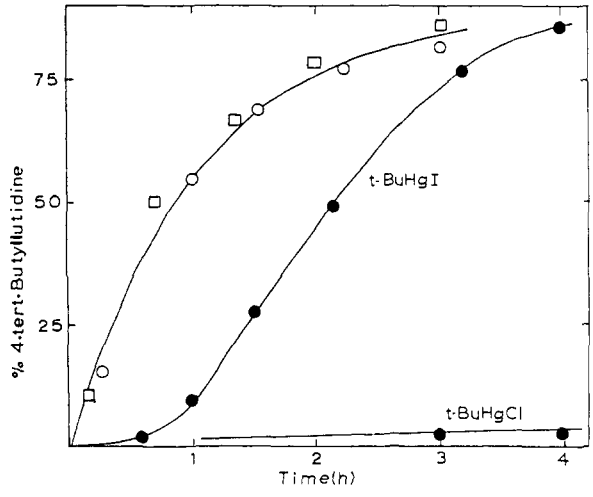


Figure 2. Photolysis of 0.2 M lutidine with 0.6 M *t*-BuHgX in Me_2SO-d_6 at 35 °C: ○, X = I with 0.6 M PTSA; □, X = I with 0.6 M PTSA and 0.6 M KI.

Figure 2 demonstrates the dramatic difference between *t*-BuHgCl and *t*-BuHgI in this photostimulated reaction. Figure 2 also demonstrates that the presence of PTSA has a relatively small effect in the latter stages of the reaction. However, the initial reaction of *t*-BuHgI with lutidine in the absence of PTSA is quite slow and shows a decided autocatalytic effect which we ascribe to the formation of the lutidinium ion as reaction 1 proceeds.[8] When the competitive reactivity of lutidine (k_l) and (*E*)-PhCH=CHI (k_s) toward *t*-Bu· is measured from the observed products in Me_2SO-d_6, the value k_l/k_s increases with time (Table I).

During the period in which the first 1% of the lutidine is *tert*-butylated, the relative reactivity of lutidine is no more than 1/50 that of (*E*)-PhCH=CHI. During the period from 1 to 2 h as the yield of 4-*tert*-butyllutidine increases from 11 to 29%, the average relative reactivity of lutidine is 0.6 times that of (*E*)-PhCH=CHI. In the presence of PTSA a much faster reaction occurs with little effect of time (i.e. % reaction) upon the observed relative reactivity of lutidine, which is 0.8–0.9 times that of the β-iodostyrene. Competitive reactions of the pyridinium ion (k_p) and (*E*)-PhCH=CHI (k_s) in Me_2SO with *t*-BuHgCl/KI under conditions where the *o*/*p* ratio is 0.9 give k_p/k_s = 15 at 35 °C, i.e., the pyridinium ion is ~19 times more reactive than the lutidinium ion in *t*-Bu· addition. In the presence of DABCO the competitive alkylation of pyridine and (*E*)-PhCH=CHI fails to form detectable amounts of the *tert*-butylpyridines; pyridine can be no more than 1/50 as reactive as (*E*)-PhCH=CHI. The rate constant for addition of *t*-Bu· to (*E*)-PhCH=CHI is estimated

(7) Kurosawa, H.; Okada, H.; Yasuda, M. *Tetrahedron Lett.* **1980**, *21*, 959. Kurosawa, H.; Okada, H.; Hattori, T. *Tetrahedron Lett.* **1981**, *22*, 4495.

(8) The photostimulated reaction of pyridine, γ-picoline, or lutidine with *t*-BuHgX initially shows autocatalytic behavior. The kinetic chain length was calculated from the time delay between the fast reactions which were approximately linear in time following the autocatalytic period. See Figure 2 for typical yield curves.

(9) Ingold, K. U. In *Free Radicals*; Kochi, J., Ed.; Wiley and Sons: New York, 1973; Vol. 1, p 93.

(10) At 60 °C the *o*/*p* ratio for *tert*-butylation of the pyridinium ion is reported to vary from 0.4 in H_2O to 2.5 in benzene.[5]

Table I. Competitive *tert*-Butylation of Lutidine and (*E*)-PhCH=CHI at 35 °C in Me_2SO-d_6[a]

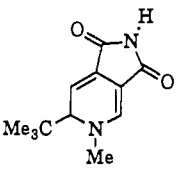
conc (M)			products (%)[b]		
t-BuHgI	PTSA	time (min)	"L"	"S"	k_l/k_s
0.50		30	1.1	41	0.02
0.50		60	11	61	0.13
0.50		120	29	73	0.26
0.50	0.50	10	13	15	0.86
0.50	0.50	30	29	33	0.84
0.375	0.50	30	24	29	0.80
0.25	0.50	30	19	22	0.83
0.50	0.50	50	50	57	0.84
0.50	0.50	90	62	65	0.92

[a] Solutions initially 0.125 M in lutidine and (*E*)-PhCH=CHI were irradiated by a 275-W sunlamp in Pyrex NMR tubes. [b] "L" = 4-*tert*-butyl-2,6-dimethylpyridine; "S" = (*E*)-Me_3CCH=CHPh. Yields were measured by ^1H NMR using DMF as an internal standard.

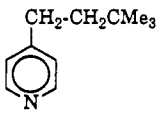
to be 2.5 × 10^4 M^{-1} s^{-1} on the basis of the measured relative reactivities of CH_2=CHP(O)$(OEt)_2$/(*E*)-PhCH=CHI = 19.2:1.0.[11,12]

The data of Table I indicate that reversibility is not a factor in the addition of *t*-Bu• to the lutidinium ion, since if the addition is reversible, it would be expected that the concentration of *t*-BuHgI would affect the observed reactivity; see reaction 1a of Scheme I. No effect was observed for a 2-fold change in the concentration of *t*-BuHgI. The presence of added KI also had no appreciable effect on the relative reactivities observed in the presence or absence of PTSA. When compared with the results observed for pyridine, it appears that reversibility in the addition of *t*-Bu• to a pyridinium ion may be more important for attack at the 2-position than for the 4-position.

Reductive *tert*-Butylation of Pyridine Derivatives. Reductive alkylation with *t*-BuHgCl/KI to form a 1,4-dihydropyridine derivative was not observed with simple pyridines in the presence of PTSA even in the case of 3,4-pyridinedicarboximide, which in Me_2SO yielded a mixture of the 2- (43%) and 6- (52%) substituted *tert*-butyl derivatives. However, in the presence of MeI the *N*-methylated cation underwent reductive alkylation to yield **1** and the 1,4-dihydro isomer. However, a similar reaction



1



2

with *N*-methyllutidinium iodide yielded only 4-*tert*-butyl-1,2,6-trimethylpyridinium iodide from ^1H NMR. Reductive alkylation products were formed exclusively from acridine, *N*-methylacridinium iodide, or 4-vinylpyridine (to form **2**) upon photolysis with *t*-BuHgCl/KI in Me_2SO.

(a) 4-Vinylpyridine. Photolysis of *t*-BuHgCl/KI with 4-vinylpyridine in Me_2SO in the presence of PTSA or TMSI leads to 4-(3,3-dimethylbutyl)pyridine (**2**) with the formation of only traces of Hg^0. Very little reaction is observed in the absence of KI even with *t*-BuHgI/PTSA. In the presence of PTSA the reaction proceeds by Scheme II. In the absence of added PTSA the observed relative reactivity of 0.025 M 4-vinylpyridine (k_v) and (*E*)-PhCH=CHI (k_s) toward *t*-Bu• depends upon the amount of KI added and, with 4 equiv of *t*-BuHgCl, increases from 3.4 with 2 equiv of KI to 7.2 with 4 equiv of KI (k_v/k_s = 9.8 with 4 equiv each of *t*-BuHgI and KI). An even more dramatic effect of KI is observed in the PTSA-promoted reaction with 4 equiv each of PTSA and *t*-BuHgI; k_v/k_s increases from ~4 without KI to ~600 with 4 equiv of KI. In a similar fashion with 4 equiv each of PTSA and *t*-BuHgCl, k_v/k_s increases from 36 to 208 to 470 with 2, 4, and 8 equiv of KI. We believe the effect of KI concentration must reflect reversibility in the *t*-Bu• addition step with the observed reactivity increasing with the concentration of the reducing agent (I^- or $RHgI_2^-$). In the absence of PTSA the reaction may involve the reversible addition of *t*-Bu• to a complex of 4-vinylpyridine and *t*-BuHgI to form **3**, which can be reduced by I^- or *t*-$BuHgI_2^-$ to **4** (reaction 3 with R = *t*-Bu). Exchange processes of **4** with HgI_2 could form **5** as a precursor to **2** formed upon hydrolytic workup. A direct conversion of **3** to **5** by an internal electron transfer (generating *t*-Bu•) seems reasonable but appears to be excluded by the requirement that excess KI is required for the reaction to occur even when *t*-BuHgI is used as the alkylation agent.

Scheme II. (R = *t*-Bu)

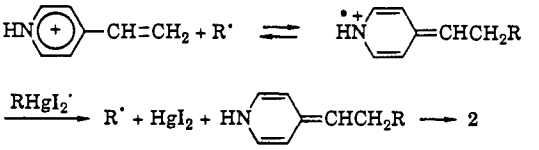


Table II. Photostimulated Reactions of *t*-BuHgX with 4-vinylpyridine[a]

	equivalents				
X	*t*-BuHgX	KI	other	time (h)	**2** (%)[b,c]
Cl	4	4		7	20
Cl	4	4	$K_2S_2O_8$ (2)	3	25
Cl	4	4	PTSA (4)	0.75	65
Cl	4	4	TMSI (2)	1	52[c]
I[d]	3	3		1	25
I[d]	3	3	PTSA (3)	0.05[e]	~16
I[d]	3	3	PTSA (3)	0.2	96

[a] 0.05 M 4-vinylpyridine in Me_2SO or at 35 °C with irradiation from a 275-W sunlamp. [b] ^1H NMR yield after workup with aqueous $Na_2S_2O_3$; $PhCH_3$ as an internal standard. [c] 25% of 2-(1,1-dimethylethyl)-4-(3,3-dimethylbutyl)pyridine was also formed. [d] 0.17 M 4-vinylpyridine. [e] In room light.

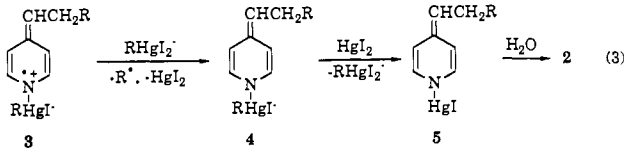


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Table II lists typical yields observed. The results of Table II suggest that Me_3Si can take the place of the proton in Scheme II with hydrolysis occurring during workup to yield **2**.

(b) Acridine. Photolysis of a 4:1 mixture of *t*-BuHgCl and acridine in the presence of KI in Me_2SO slowly forms 9-*tert*-butyl-9,10-dihydroacridine (**6a**) isolated after aqueous $Na_2S_2O_3$ workup. The presence of PTSA greatly accelerates this reductive alkylation (Table III). Although preformed *N*-methylacridinium ion is readily alkylated to form **6b** by *t*-BuHgCl/KI, the addition of MeI to acridine/*t*-BuHgCl/KI does not lead to *N*-methylation but does increase the rate of the alkylation significantly. The addition of Me_3SiI has a similar effect. Presumably MeI or Me_3SiI exchanges I^- for Cl^- and increases the concentrations of *t*-BuHgI and/or *t*-$BuHgI_2^-$. In the presence of KI and $K_2S_2O_8$ the reductive *tert*-butylation of acridine occurs in the dark. It

(11) The absolute rate constant for *t*-Bu• addition to CH_2=CHP(O)$(OEt)_2$ at 233 K has been measured as 5.9 × 10^4 M^{-1} s^{-1}: Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1981**, 161. Using E_a = 4 kcal/mol yields 4.8 × 10^5 M^{-1} s^{-1} at 35 °C.

(12) Rate constants have been reported at 57 °C in H_2O for attack of Bu• and *t*-Bu• upon PyH^+ as 4.4 × 10^4 and 3.3 × 10^4 M^{-1} s^{-1}, respectively: Citterio, A.; Minisci, F.; Franchi, V. *J. Org. Chem.* **1980**, *45*, 4752. Attack of 5-hexenyl radicals upon 4-$MeC_6H_4NH^+$ has been recalculated as 9.5 × 10^4 M^{-1} s^{-1} at 79 °C (Lorand, J. P. *Landolt-Börnstein, New Series* **1984**, *11/13a*, 165) on the basis of the data of: Citterio, A.; Minisci, F.; Porta, O.; Sesana, G. *J. Am. Chem. Soc.* **1977**, *99*, 7960. Competition at 57 °C indicated that 4-$MeC_6H_4NH^+$ is 0.3 times as reactive as PyH^+ toward Bu•.

Table III. Photostimulated Reactions of *t*-BuHgCl with Acridine in Me_2SO at 35–40 °C[a]

equivalents				
t-BuHgCl	KI	other	time (h)	**6a** (%)[b]
4	0	PTSA (4)	5	0
4	0	DABCO (4)	20	6
4	4	none	4	40
4	4	TMSI (2)	2	92
4	4	MeI (4)	4.5	90
4	4	PTSA (4)	1	100
4	4	DABCO (4)	24	95
4	4	$K_2S_2O_8$ (2)	20	94
4	4	$K_2S_2O_8$ (2)[c]	17	85
4	4		1	84[d]

[a] 0.05 M acridine; irradiation by a 275-W fluorescent sunlamp. [b] ^1H NMR yield with $PhCH_3$ as an internal standard after workup with aqueous $Na_2S_2O_3$. [c] Dark reaction. [d] Reaction of the *N*-methylacridinium ion to form **6b**.

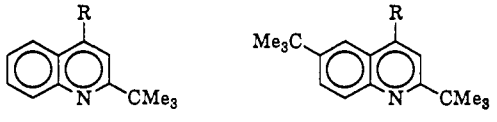
is known that the system *t*-BuHgCl/KI/$K_2S_2O_8$ rapidly forms *t*-Bu• by the displacement of *t*-Bu• from *t*-BuHgX by I•.[13]

6 **7**

a, R = H
b, R = Me
c, R = *t*-BuHgI
d, R = HgI

Since the reductive alkylation product is formed in the presence of acid or base (DABCO), it appears that the adduct radicals **7** do not readily lose the proton from C-9 because of an unfavorable peri-interaction upon deprotonation. In the absence of PTSA it seems reasonable that the adduct radical **7c** might undergo internal electron transfer to form *t*-Bu• and **6d**. However, the faster alkylations observed in the presence of KI suggest that **7c** prefers to undergo intermolecular electron transfer with I^-, *t*-$BuHgI_2^-$, or *t*-BuHg(I)/DABCO$^-$ to form **6c** (analogous to reaction 3). Further exchange reactions with HgI_2 may form **6d**. In the presence of KI, reductions of the adduct radical cations **7a** or **7b** generate **6a** or **6b** by reaction 2a without the formation of significant amounts of Hg^0.

Oxidative and Reductive *tert*-Butylations of Quinolines. 4-Substituted quinolines such as 4-chloro- or 4-methylquinoline (lepidine) undergo only substitutive alkylation to form **8** and **9** upon



8 **9**

a, R = H
b, R = Me
c, R = Cl
d, R = *t*-Bu

photolysis with *t*-BuHgCl. With 2-chloro-, 2-methyl-, or 2-*tert*-butylquinoline, reductive alkylation (at C-4) occurs in the presence of KI. With quinoline itself attack of *t*-Bu• at C-2 leads to the substitution product **8a** but attack at C-4 leads mainly to a reduced quinoline derivative.

(a) 4-Substituted Quinolines. Table IV presents pertinent results. Lepidine was converted to **8b**, which was further alkylated to **9b**. The reactions were not particularly promoted by PTSA but the addition of KI led to an appreciable rate acceleration, presumably because of the increased rate of radical formation.

(13) Russell, G. A.; Guo, D.; Baik, W.; Herron, S. J. *Heterocycles* **1989**, *28*, 143.

Table IV. Formation of **8** and **9** from 4-Chloro- and 4-Methylquinoline upon Photolysis with *t*-BuHgCl in Me_2SO at 35–40 °C[a]

	equivalents				percent yield[b]	
substituent	*t*-BuHgCl	KI	PTSA	time (h)	**8**	**9**
4-Cl	4	0	0	2	16	
4-Cl	4	0	0	22	48	
4-Cl	4	4	0	2	68	
4-Cl	4	4	0	4	89	
4-Cl	4	8	0	2	87	
4-Cl	4	0	4	4	tr	
4-Cl	4	4	4	2	80	tr
4-Me	4	0	0	2	71	tr[c]
4-Me	4	0	0	4	89	tr
4-Me	4	0	0	10	55	25
4-Me	4	4	0	2	75	16
4-Me	4	8	0	2	77	16[d]
4-Me	4	0	4	4	94	tr
4-Me	4	0	4	10	45	35
4-Me	4	4	4	2	62	26
4-Me	4	4	4	10	tr	70
4-Me	4	8	4	2	59	30

[a] 0.05 M substrate irradiated by a 275-W fluorescent sunlamp. [b] By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$. [c] In the presence of MeI (10 vol %), 72% of **8b** and 9% of **9b** were observed in a 2.5-h reaction. [d] In the presence of MeI (10 vol %), 48% of **8b** and 34% of **9b** were observed in a 2.5-h reaction.

Table V. Conversion of 2-Chloroquinone to **10** and **11** upon Photolysis with *t*-BuHgCl in Me_2SO at 35–40 °C[a]

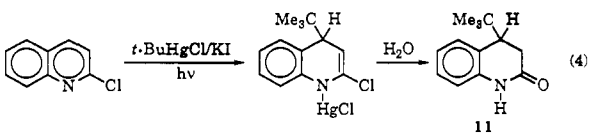
equivalents				percent yield[b]	
t-BuHgCl	KI	PTSA	time (h)	**10**	**11**
4	0	0	10	4	0
4	8	0	2	tr	26
4	8	0	2[c]	tr	45
4	8	0	3.5[d]	tr	69
4	0	4	22	49	7
4	8	4	22	tr	78

[a],[b] See Table IV. [c] DMF solvent. [d] 10 vol % MeI.

Substitution occurring via the intermediacy of a first formed dihydro intermediate can be excluded by the stoichiometry. Thus, the photolysis of 0.1 M lepidine with 4 equiv of *t*-BuHgCl and 4 equiv of KI for 83 min in Me_2SO-d_6 formed by ^1H NMR **8b** (0.74 equiv), $Me_2C{=}CH_2$ (0.43 equiv), and Me_3CH (0.62 equiv). There is only 0.19 equiv of Me_3CH formed over the 1:1 ratio of $Me_2C{=}CH_2$ and Me_3CH expected from *t*-Bu• disproportionation. Dehydrogenation of a dihydro intermediate would be expected to form 1 equiv of Me_3CH per equiv of **8b**.

4-Chloroquinoline yielded **8c** upon photolysis with *t*-BuHgCl. Only traces of **9c** were observed even with added KI and PTSA. The formation of **8c** showed little yield enhancement upon the addition of PTSA although KI showed a strong promoting effect.

(b) 2-Substituted Quinolines. Photolysis of *t*-BuHgCl with 2-chloroquinoline in Me_2SO gives little reaction. Upon the addition of PTSA the substitution product, 2-chloro-4-*tert*-butylquinoline (**10**) is formed while the addition of KI gives rise to a reductive alkylation product, the amide **11** (Table V). Competition between the reductive and oxidative alkylation pathways apparently occurs according to Scheme I with hydrolysis during workup to yield **11** (reaction 4). The addition of MeI



(4)

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increases the yield of **11** at a given *t*-BuHgCl/KI concentration by exchanging I^- for Cl^- and increasing the rate of the reductive electron transfer step (reaction 2a).

Scheme III. (R= *t*-Bu). Products Formed in the Reaction of Quinaldine with *t*-BuHgCl/KI/*hν*

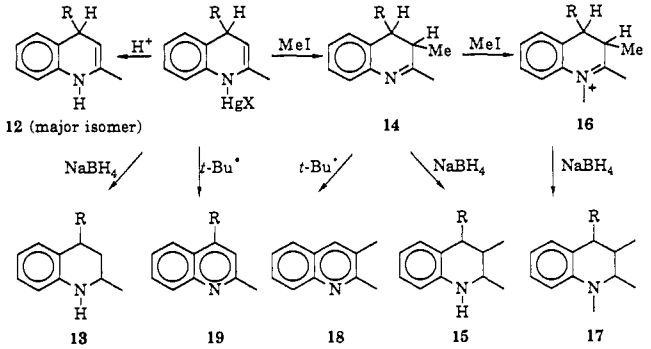
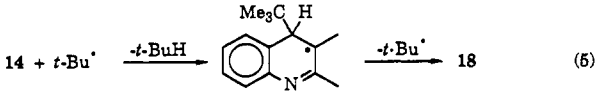


Table VI. Photolysis of *t*-BuHgCl/KI with Quinaldine in Me_2SO at 35–40 °C[a]

equivalents				percent yield[b]						
t-BuHgCl	KI	other	time (h)	12	13	14	15	17	18	19
4	0	none	20							55
4	0	PTSA (1)	20							76[c]
4	4	none	4	45						15
4	4	none	8	5						45
4	4	none	5[d]		50					34
4	4	$K_2S_2O_8$ (2)	5							60[e]
4	4	$K_2S_2O_8$ (2)	22							27[f]
4	4	PTSA (4)	2	25						47
4	4	PTSA (4)	2[d]		33					52
4	4	MeI[g]	2			60				
4	4	MeI[g]	2.5[d]				56	28		
4	4	MeI[g]	18			1			36	2
4	0	MeI[g]	22						30	4

[a] 0.05 M quinaldine irradiated with a 275-W fluorescent sunlamp. [b] By ^1H NMR using CH_2I_2 as an internal standard after workup with aqueous $Na_2S_2O_3$. [c] 8% of 4,6-di-*tert*-butyl-2-methylquinoline. [d] Workup with $NaBH_4$/MeOH. [e] 15% of 4,6-di-*tert*-butyl-2-methylquinoline. [f] 56% of 4,6-di-*tert*-butyl-2-methylquinoline. [g] 10 vol %.

Quinaldine reacted with *t*-BuHgCl/KI upon photolysis to form dihydroquinolines (predominately 4-*tert*-butyl-1,4-dihydro-2-methylquinoline (**12**)) (Scheme III and Table VI). The dihydroquinoline could be isolated, reduced by $NaBH_4$/MeOH on workup to the tetrahydroquinoline **13**, or methylated by MeI during the *tert*-butylation to form **14** as a single isomer, presumably trans. Workup with $NaBH_4$/MeOH converted the imine **14** to the tetrahydroquinoline **15**. The imine **14** was slowly methylated by MeI in Me_2SO to form **16**, which was lost on hydrolytic workup but could be converted to **17** upon workup with $NaBH_4$/MeOH. Long reaction times also converted the imine **14** into **18**, apparently via the β-elimination process of reaction 5. Long reaction times in the absence of MeI aromatized



(5)

the initially formed dihydroquinoline into the oxidative alkylation product **19** (Scheme III). The absence of **19** in reactions performed in the presence of MeI is taken as evidence that the adduct radical formed by addition of *t*-Bu• at C-4 of quinaldine has little tendency to lose a proton in reaction 1a and instead is reduced by I^- to yield only the dihydroquinoline.

Photolysis of 2-*tert*-butylquinoline with *t*-BuHgCl in the absence of KI yields 2,4-di-*tert*-butylquinoline (**8d**) or at longer reaction times 2,4,6-tri-*tert*-butylquinoline (**9d**). In the presence of KI at short reaction times the 1,4-dihydroquinoline analogous to **12** is the major product. The dihydroquinoline is slowly converted to **8d**/**9d** at long reaction times, see Table VII. Workup with $NaBH_4$/MeOH converts the dihydroquinoline into the

Table VII. Photochemical Reaction of 2-*tert*-Butylquinoline with *t*-BuHgCl in Me_2SO at 35–40 °C[a]

equivalents				percent yield[b]		
t-BuHgCl	KI	PTSA	time (h)	8d	9d	21
4	0	0	4	58	tr	tr
4	0	0	10	72	18	tr
4	4	0	4	38	15	22
4	4	0	10	52	15	tr
4	8	0	4	7	tr	70
4	8	4	0.5	17	tr	60[c]
4	8	4	1.5	72	13	
4	8	4	4	51	30	

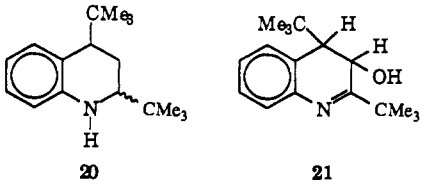
[a,b] See Table IV. [c] Workup with $NaBH_4$/MeOH gave a 34% yield of *cis*-**20** and 16% of **21**.

Table VIII. Photolysis of *t*-BuHgCl with Quinoline in Me_2SO at 35–40 °C[a]

equivalents				percent yield[b]			
t-BuHgCl	KI	PTSA	time (h)	8a	8d	9d	20
4	0	4	4	54	4		0[c]
4	8	0	4	35	11		44
4	8	4	4	tr	33	12	42
4	8	4	24		32	13	42

[a,b] See Table IV. [c] ~4% of 4-*tert*-butylquinoline was detected by GCMS.

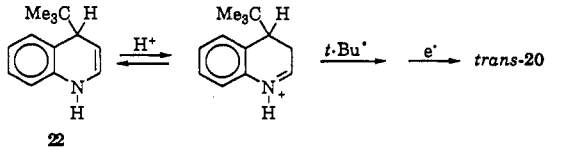
tetrahydroquinoline *cis*-**20** while workup in air with either aqueous



20 **21**

$Na_2S_2O_3$ or Na_2CO_3 leads to the surprisingly stable hydrate **21**. Enamines are known to readily undergo autoxidation involving the radical cation as an intermediate.[14] In the present case possibly the intermediate hydroperoxide is reduced by I^- to **21** instead of undergoing a base-catalyzed elimination of H_2O to form the 3-(4*H*)-quinolinone.

(c) Quinoline. Photolysis of *t*-BuHgCl with quinoline/PTSA yielded the 2-*tert*-butylated (**8a**), the 2,4-di-*tert*-butylated (**8d**), and the 2,4,6-tri-*tert*-butylated (**9d**) derivatives and only traces of 4-*tert*-butylquinoline. Surprisingly, in the presence of KI a major product was *trans*-**20** formed as a single geometric isomer (by GC or NMR) (Table VIII). Apparently attack of *t*-Bu• upon C-4 of quinoline leads to a reaction product only in the presence of KI. In the presence of KI and a proton donor (including the quinolinium ion formed by substitutive alkylation), the C-4 adduct radical cation can be reduced to the 1,4-dihydroquinoline **22**, which can be subsequently protonated to form an iminium ion that readily adds *t*-Bu• to yield *trans*-**20** (reaction 6).[15] Formation of the tetrahydroquinoline analogous to **20** was not observed with quinaldine, presumably because of steric restraint in the attack of *t*-Bu• upon the required iminium ion.



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(14) Malhotra, S. K.; Hostynek, J. J.; Lundin, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 6565.

(15) Russell, G. A.; Yao, C.-F.; Rajaratnam, R.; Kim, B. H. *J. Am. Chem. Soc.* **1991**, *113*, 373.

Scheme IV. (R = *t*-Bu). Products Formed in the Reaction of t-BuHgCl/KI with *N*-Methylquinaldinium Iodide

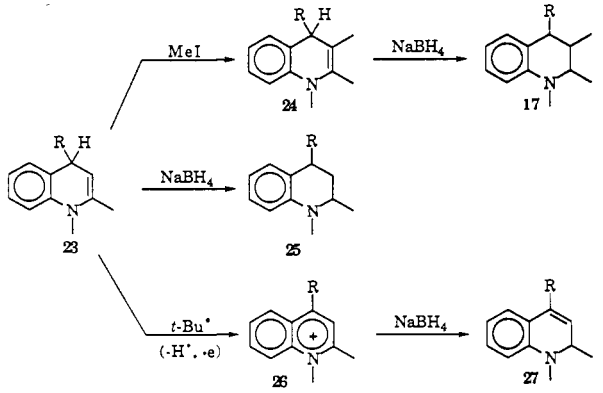


Table IX. Photolysis of *t*-BuHgCl/KI with *N*-Methylquinaldine Iodide in Me_2SO at 35–40 °C[a]

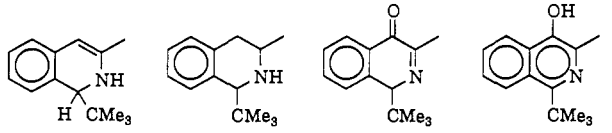
equivalents				percent yield[b]				
t-BuHgCl	KI	MeI	time (h)	23	24	25	17	27
4	4	0	1.5	90				
4	4	0	1.5[c]			90		
4	0	0	5[c]			52		12
4	0	0	18[c]			22		63
4	4	10 vol %	1		81			
4	4	10 vol %	1[c]			25	69	

[a,b] See Table VI. [c] Workup with $NaBH_4$/MeOH.

Although essentially only products derived from initial addition of *t*-Bu• at C-2 of the quinolinium ion (**8a, 8d, 9d**) are observed in the absence of a reducing agent,[16] *t*-Bu• addition must occur about equally at C-2 and C-4, since in the presence of KI the ratio of products derived from 2-attack (**8a, 8d, 9d**) to 4-attack (*trans*-**20**) is ~1.

(d) *N*-Methylquinaldinium Iodide. Preformed *N*-methylquinaldinium iodide reacts with *t*-BuHgCl with or without added KI to form the 1,4-dihydroquinoline **23** (Scheme IV and Table IX), which could be methylated in situ by MeI to form **24**, reduced by $NaBH_4$ workup to form **25**, or aromatized by long reaction times to form **26**. Both **24** and **26** could be reduced by $NaBH_4$ workup to form **17** and **27**, respectively.

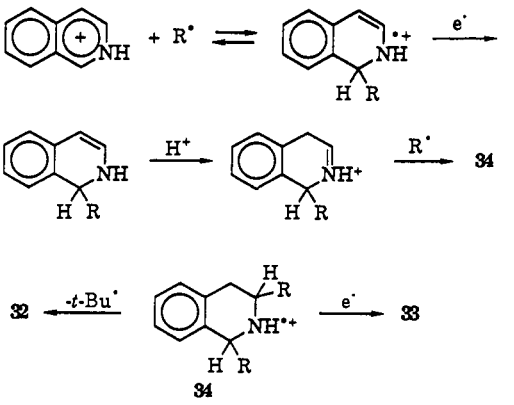
(e) Isoquinolines. Radicals are known to add preferentially to C-1 in isoquinoline.[17] Photolysis of 3-methylisoquinoline with 4 equiv each of *t*-BuHgCl, KI, and PTSA in Me_2SO yields the dihydro derivative **28**, which upon workup with $NaBH_4$/MeOH forms **29** in 74% yield. In the absence of a reducing workup, the enamine **28** is oxidized by air to give **30** (68% overall yield), which slowly isomerizes to **31** after isolation.

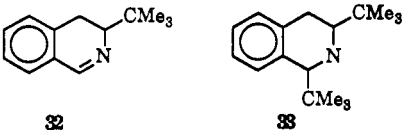


28 **29** **30** **31**

The reaction of isoquinoline itself with *t*-BuHgCl/KI/hν yields a variety of products in low yields. Addition of PTSA gives in a 2.5-h photolysis a modest yield (35%) of 3-*tert*-butyl-3,4-dihydroisoquinoline (**32**), a completely unexpected product. With 4 equiv each of *t*-BuHgI, KI, and PTSA (a better reducing system) a 3-h photolysis gave 2% of **32** and 31% of the di-*tert*-butylated tetrahydroisoquinoline **33**. Scheme V presents an explanation for the conversion of isoquinoline to an enamine that after protonation can be attacked by *t*-Bu• to yield the intermediate radical cation **34**, which may be reduced to **33** or undergo β-elimination of *t*-Bu• to form **32**.

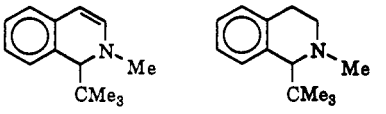
Scheme V. (R = *t*-Bu)





32 **33**

Photolysis of isoquinoline with *t*-BuHgCl/KI in the presence of MeI yields the same *tert*-butylation product as that from the preformed *N*-methylisoquinolinium iodide, where a rapid reductive alkylation occurs to form **35** in high yield (85% in 1.5 h). Workup with $NaBH_4$/MeOH yields the expected 1-*tert*-butyl-2-methyltetrahydroisoquinoline (**36**).



35 **36**

A photostimulated competitive reaction of a 1:1 mixture of 0.02 M 3-methylisoquinoline and quinaldine with *t*-BuHgCl/KI/PTSA (8 equiv each) in Me_2SO for 20 min followed by $NaBH_4$ workup yielded the *tert*-butylated tetrahydro derivatives **29** (40%) and **13** (23%) by ^1H NMR analysis. Under these reductive alkylation conditions the isoquinoline is attacked by *t*-Bu• at C-1 more than 1.5 times as readily as the quinoline is attacked at C-4.[18] (Previously it was demonstrated that the quinolinium ion is attacked about equally at C-2 and C-4.)

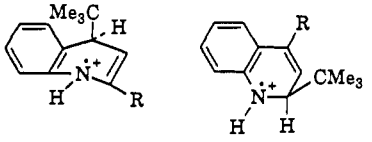
Conclusions

Reversibility in radical addition to pyridinium, quinolinium, or isoquinolinium ions is a function of the ease with which the adduct radicals are converted to stable products, e.g., by loss of a proton to form the easily oxidized pyridinyl radicals (reaction 1a) or by reduction to form a dihydropyridine (reaction 2a). With quinolines the adduct radicals at C-4 (**37**) are more resistant to deprotonation than the adducts at C-2 (**38**). This results in 4-attack by *t*-Bu•, leading initially to reductive alkylation in the presence of KI (R = H, Cl, Me, *t*-Bu), whereas 2-attack leads

(16) Citterio, Minisci, and Franchi[12] report that whereas *n*-Bu• attacks quinoline in acid solution about equally at C-2 and C-4, *tert*-butylation yields only 2-*tert*-butylquinoline. An explanation based on steric hindrance is advanced. It is also reported that, toward *t*-Bu•, lepidine is >100 times as reactive as quinaldine in oxidative *tert*-butylation in acid solution, although a reversal in selectivity was noted for *i*-Pr•, $PhCH_2$•, or α-THF•.[5] Photolysis of lepidine and quinaldine in a 1:1 ratio with excess *t*-BuHgCl/KI/PTSA in Me_2SO at 35 °C gave a mixture (by ^1H NMR) of **8b, 9b, 12,** and **19**. A 20-min reaction gave 26% lepidine (**8b, 9b**) and 13% quinaldine (**12, 19**) derived products while after 1 h the yields increased to 87 and 45%, respectively. Lepidine is attacked only about twice as readily as quinaldine by *t*-Bu•.

(17) Minisci, F.; Bernardi, R.; Bertini, F.; Galli, R.; Perchinummo, M. *Tetrahedron* **1971**, *27*, 3575.

(18) *Tert*-butylation of a 1:1 mixture of quinoline and isoquinoline in H_2O/H_2SO_4 at 70 °C by the procedure of Minisci (*t*-$BuCO_2H$, $AgNO_3$, $(NH_4)_2S_2O_8$) formed 2-*tert*-butylquinoline and 1-*tert*-butylisoquinoline in a ratio of >5:1, a reversal in selectivity from that observed under reductive conditions.



37 38

to substitutive alkylation. The radical cation **37** most likely has the *t*-Bu group in a quasi-axial position which places the proton at C-4 in the plane of the C-2–C-3 double bond. For this stereoelectronic reason, deprotonation of **37** occurs slowly and reduction is observed in the presence of KI. Apparently **38** loses the C-2 proton readily since only substitutive alkylation is observed.[19]

With quinoline itself substitutive alkylation at C-4 is a minor process upon photolysis with *t*-BuHgCl/PTSA. Because of reversibility in the addition of *t*-Bu•, and because the 2-adduct is more readily converted to the substitution product, essentially only 2-*tert*-butylquinoline is observed. In the presence of KI, where the adduct radical cation **37** (R = H) can be reduced to give eventually the tetrahydroquinoline *trans*-**20**, 4-attack is observed to be about as important as 2-attack. Because of the reversibility in radical addition and the rate differences with which the ortho and para adducts lose a proton, substitutive product ratios can give a misleading indication of the regio- or chemoselectivity for the radical additions to azaaromatics.

Experimental Section

Pyridine (0.2–1.0 mmol), *t*-BuHgI or *t*-BuHgCl (1–5 mmol), and KI (2–10 mmol) with or without added PTSA were placed in a pyrex test tube, and 2–10 mL of deoxygenated Me_2SO or DMF was added under nitrogen. With stirring the solution was irradiated with a 275-W General Electric fluorescent sunlamp ca. 25 cm from the reaction tube. The reaction mixture was poured into 50 mL of saturated aqueous $Na_2S_2O_3$ solution, neutralized if required, and extracted with CH_2Cl_2. The extract was washed with saturated aqueous $Na_2S_2O_3$ (3 × 50 mL) and saturated brine (50 mL), dried over anhydrous Na_2SO_4 or $MgSO_4$, and concentrated under vacuum. Products were isolated by flash column chromatography using 230–240 mesh, grade 60 Merck silica gel (Aldrich Chemical Co.) with hexane/ethyl acetate as the eluent.

Analytical gas chromatography was performed using a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator using $PhCH_3$ or PhPh as internal standards and predetermined response factors. NMR spectra were recorded by a Nicolet NT 300 spectrometer with TMS as the internal standard (300 MHz for ^1H, 75.4 MHz for ^{13}C). Yields were measured by ^1H NMR from integrations with a known amont of $PhCH_3$ as an internal standard. MS were recorded in the GC mode (CI or EI) with a Finnegan 4000 spectrometer. HRMS were recorded with a Kratos MS-50 spectrometer. Infrared spectra were obtained in the FT mode with an IBM IR 98 spectrometer. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

Me_2SO was distilled from CaH_2 under vacuum. Me_2SO-d_6 (Cambridge Isotope Laboratories) was dried over 4A molecular sieves. *t*-BuHgCl was prepared from *t*-BuLi and $HgCl_2$ in THF: mp 110–113 °C dec (lit.[20] 117–119 °C, dec); ^1H NMR ($CDCl_3$) δ 1.512 (s). *t*-BuHgI was prepared from *t*-BuHgCl and 2 equiv of KI in Me_2SO and crystallized from CH_2Cl_2 after an aqueous workup. The material decomposed upon heating: ^1H NMR ($CDCl_3$) δ 1.534 (s). 2-*tert*-Butylquinoline was prepared by the Minisci alkylation technique.[17] 4-*tert*-Butylquinoline was identified by GCMS only: *m/z* (relative intensity) 185 (M^+, 49), 186 (8), 170 (100), 154 (23), 143 (10), 77 (14), 57 (4).

The *N*-methyl iodide salts were prepared from 2,6-lutidine, 2-methylquinoline, isoquinoline, 3-methylisoquinoline, and acridine by reaction of the bases with excess MeI at room temperature for 24 h in a sealed tube.[21] Unreacted MeI was evaporated, and the solid residues were washed with hexane.

2-(1,1-Dimethylethyl)pyridine.[12] The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.372 (s, 9H), 7.078 (ddd, 1H, J = 0.6, 4.8, 7.2 Hz), 7.335 (d, 1H, J = 7.8 Hz), 7.602 (dt, 1H, J = 1.8, 7.8 Hz), 8.562 (d, 1H, J=4.8Hz); ^{13}C NMR ($CDCl_3$) δ 30.184 (q), 37.366 (s), 119.059 (d), 120.580 (d), 136.110 (d), 148.501 (d), 169.207 (s); GCMS *m/z* (relative intensity) 136 (M^+ + 1, 3), 135 (25), 134 (29), 120 (100), 104 (6), 93 (33), 79 (21), 51 (15); HRMS *m/z* 134.0985 [calcd for $C_9H_{12}N$ (M^+ – 1) 134.0970].

4-(1,1-Dimethylethyl)pyridine.[12] The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.315 (s, 9H), 7.275 (dd, 2H, J = 1.5, 4.5 Hz), 8.506 (dd, 2H, J = 1.5, 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 30.475 (q), 34.616 (s), 120.677 (d), 149.504 (d), 159.922 (s); GCMS *m/z* (relative intensity) 136 (M^+ + 1, 6), 135 (43), 120 (100), 104 (3.6), 92 (46), 51 (17); HRMS *m/z* 135.1052 (calcd for $C_9H_{13}N$ 135.1048).

4-(1,1-Dimethylethyl)-2,6-dimethylpyridine. The compound was isolated as a yellow solid: mp 56–58 °C; ^1H NMR ($CDCl_3$) δ 1.288 (s, 9H), 2.521 (s, 6H), 6.949 (s, 2H); GCMS *m/z* (relative intensity) 163 (M^+, 34), 149 (11), 148 (100), 146 (5), 121 (4), 120 (18), 91 (9), 77 (8), 57 (1.6); HRMS *m/z* 163.1363 (calcd for $C_{11}H_{17}N$ 163.1361).

4-(1,1-Dimethylethyl)-1,2,6-trimethylpyridinium Iodide. The salt had ^1H NMR ($CDCl_3$) δ 1.347 (s, 9H), 2.826 (s, 6H), 4.029 (s, 3H), 7.946 (s, 2H), 8.850 (broad s, 1H).

***tert*-Butylation of Pyridine-3,4-dicarboximide.** Photolysis with *t*-BuHgCl formed a mixture of the C-2 and C-6 substitution products. 2-(1,1-Dimethylethyl)-3,4-pyridinedicarboximide was isolated as a white solid; mp 180–182 °C; ^1H NMR ($CDCl_3$) δ 1.533 (s, 9H), 7.844 (d, J = 4.8 Hz, 1H), 7.890 (broad s, 1H), 8.956 (d, J = 4.8 Hz, 1H); GCMS *m/z* (relative intensity) 204 (M^+, 18), 205 (2.4), 203 (4), 190 (13), 189 (100), 162 (9), 161 (12), 143 (5), 117 (10), 77 (9), 76 (11), 57 (4); HRMS *m/z* 204.0900 (calcd for $C_{11}H_{12}N_2O_2$ 204.0899).

6-(1,1-Dimethylethyl)-3,4-pyridinedicarboximide was isolated as a white solid: mp 151–153 °C; ^1H NMR ($CDCl_3$) δ 1.446 (s, 9H), 7.834 (d, J = 1.2 Hz, 1H), 9.098 (d, J = 0.9 Hz, 1H); GCMS *m/z* (relative intensity) 204 (M^+, 12), 203 (8), 190 (11), 189 (100), 162 (11), 118 (8.6); HRMS *m/z* 204.0894 (calcd for $C_{11}H_{12}N_2O_2$ 204.0899).

Photostimulated *tert*-butylation with *t*-BuHgCl in the presence of MeI formed 6-(1,1-dimethylethyl)-1,6-dihydro-1-methylpyridine-3,4-dicarboximide (**1**) and its 1,4-dihydro isomer. Compound **1** was isolated as a pale yellow solid: mp 190–192 °C; ^1H NMR ($CDCl_3$) δ 0.863 (s, 9H), 3.178 (s, 3H), 5.096 (d, J = 7.2 Hz, 1 H), 6.11 (dd, J = 7.2, 0.8 Hz, 1H), 7.142 (d, J = 0.9 Hz, 1H), 7.819 (broad s, 1H); GCMS *m/z* (relative intensity) 220 (M^+, 4), 177 (10), 164 (16), 163 (100), 125 (4), 119 (6), 105 (17), 99 (5), 97 (7), 92 (14), 85 (14), 84 (14), 71 (17), 57 (28); HRMS 220.1206 (calcd for $C_{12}H_{16}N_2O_2$ 220.1212). 6-(1,1-Dimethylethyl)-1,4-dihydro-1-methyl-3,4-pyridinedicarboximide was isolated as a yellow solid: mp 182–184 °C; ^1H NMR ($CDCl_3$) δ 0.979 (s, 9H), 3.230 (s, 3H), 3.952 (dd, J = 5.4, 0.6 Hz, 1 H), 5.866 (d, J = 5.4 Hz, 1H), 7.297 (s, 1H), 7.915 (broad s, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.843 (q), 41.543 (s), 46.321 (q), 70.816 (d), 98.467 (s), 111.054 (d), 130.285 (s), 143.039 (d), 165.922 (s), 166.613 (s); GCMS *m/z* (relative intensity) 220 (M^+, 1.4), 164 (4), 163 (27), 86 (60), 84 (77), 57 (5), 51 (38), 49 (100), 40 (78); HRMS *m/z* 220.1207 (calcd for $C_{12}H_{16}N_2O_2$ 220.1212).

4-(3,3-Dimethylbutyl)pyridine (2).[2] This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.966 (s, 9H), 1.462–1.531 (m, 2H), 2.53–2.587 (m, 2H), 7.110 (d, J = 5.4 Hz, 2H), 8.469 (d, J = 5.7 Hz, 2H); GCMS *m/z* (relative intensity) 163 (M^+, 31), 148 (25), 118 (3.5), 1.8 (6), 107 (61), 106 (74), 93 (12), 92 (16), 65 (18), 57 (100); HRMS *m/z* 163.1362 (calcd for $C_{11}H_{17}N$ 163.1361).

9-(1,1-Dimethylethyl)-9,10-dihydroacridine (6a).[22] This compound was isolated as a white solid: mp 190–195 °C (lit.[22a] 189–192 °C dec, lit.[22b] 227–230 °C dec with sintering at 190 °C); ^1H NMR ($CDCl_3$) δ 0.806

(19) The rates of proton transfer from cation radicals are often poorly or even inversely correlated with the pK_a of the cation radical. Charge distribution in the radical cation often seems to play a dominant role: Parker, V. D.; Chao, Y.; Reitstöen, B. *J. Am. Chem. Soc.* **1991**, *113*, 2336. It is difficult to separate charge distribution and stereoelectronic effects on the rates of proton transfer from the radical cations obtained by *t*-Bu• addition at C-2 and C-4 of the quinolinium ion. In Me_2SO the adduct radical cations formed by *t*-Bu• addition at either C-2 or C-4 (major) of the *N*-methoxypyridinium ion undergo electron transfer with I^-/t-$BuHgI_2^-$ in preference to proton loss. It is not clear whether this reflects a slower rate of proton loss (relative to the case of the adduct radical cations formed from the pyridinium ion) or a faster rate of electron transfer to what should be a more stable cation radical. For examples of stereochemical control in the deprotonation of ketones or iminium ions, see: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, U.K., **1983**; pp 274–284. Stereoelectronic effects in the α-deprotonation of trialkylamine or tetraalkylhydrazine radical cations are recognized: Nelsen, S. F. In *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B., Takeuchi, Y., Eds.; VCH: New York, 1992; Chapter 7.

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(s, 9H), 3.627 (s, 1H), 5.981 (s, 1H), 6.750 (d, J = 8.1 Hz, 2H), 6.897 (t, J = 7.5 Hz, 2H), 7.106–7.153 (m, 4H); GCMS m/z (relative intensity) 237 (M^+, 2.5), 180 (100), 179 (9.5), 178 (4.6), 152 (4.6), 90 (1.3), 77 (1.2), 57 (1.3); HRMS m/z 237.15151 (calcd for $C_{17}H_{19}N$ 237.15175); FTIR ($CDCl_3$) 3375 (100), 2922 (83), 1653 (44), 1481 (48) cm^{-1}.

9-(1,1-Dimethylethyl)-9,10-dihydro-10-methylacridine (6b). Isolated material had mp 178–181 °C; ^1H NMR ($CDCl_3$) δ 0.772 (s, 9H), 3.339 (s, 3H), 6.923 (m, 4H), 7.118 (dd, J = 7.5, 1.2 Hz, 2H), 7.216 (td, J = 7.8, 1.8 Hz, 2H); GCMS m/z (relative intensity) 251 (M^+, 2.6), 195 (15), 194 (100), 180 (2.5), 179 (17), 152 (2.3), 97 (2.5), 57 (1.6); HRMS m/z 251.1678 (calcd for $C_{18}H_{21}N$ 251.1676).

2-(1,1-Dimethylethyl)-4-methylquinoline (8b).[23] The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.453 (s, 9H), 2.663 (s, 3H), 7.335 (s, 1H), 7.492–7.437 (m, 1H), 7.663–7.608 (m, 1H), 7.908 (d, J = 8.1 Hz, 1H), 8.053 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.934 (q), 30.124 (q), 37.893 (s), 118.822 (d), 123.309 (d), 125.312 (d), 126.468 (s), 128.611 (d), 129.911 (d), 143.528 (s), 147.253 (s), 168.819 (s); GCMS m/z (relative intensity) 199 (M^+, 33), 184 (100), 157 (50), 143 (29), 115 (27), 77 (10); HRMS m/z 199.1359 (calcd for $C_{14}H_{17}N$ 199.1361).

4-Chloro-2-(1,1-dimethylethyl)quinoline (8c). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.450 (s, 9H), 7.575–7.521 (m, 1H), 7.592 (s, 1H), 7.729–7.674 (m, 1H), 8.060 (broad d, J = 8.1 Hz, 1H), 8.153 (dd, J = 8.4, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.970 (q), 38.213 (s), 118.374 (d), 123.620 (d), 124.562 (s), 126.531 (d), 129.663 (d), 129.835 (d), 142.196 (s), 148.232 (s), 169.229 (s); GCMS m/z (relative intensity) 219 (M^+, 28), 220 (11), 222 (10), 204 (100); HRMS m/z 219.0811 (calcd for $C_{13}H_{14}NCl$ 219.0815).

2,4-Bis(1,1-dimethylethyl)quinoline (8d). The compound was identified by ^1H NMR and MS: ^1H NMR ($CDCl_3$) δ 1.465 (s, 9H), 1.605 (s, 9H), 7.457–7.401 (m, 1H), 7.471 (s, 1H), 7.618–7.563 (m, 1H), 8.096 (dd, J = 8.4, 1.2 Hz, 1H), 8.327 (dd, J = 8.4, 1.2 Hz, 1H); GCMS m/z (relative intensity) 241 (M^+, 44), 242 (8), 226 (100), 199 (65), 185 (13), 128 (7), 77 (6), 57 (9).

2,6-Bis(1,1-dimethylethyl)-4-methylquinoline (9b). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.428 (s, 9H), 1.454 (s, 9H), 2.645 (d, J = 0.6 Hz, 3H), 7.286 (d, J = 0.6 Hz, 1H), 7.565 (dd, J = 8.7, 1.8 Hz, 1H), 7.858 (d, J = 8.7 Hz, 1H), 8.009 (d, J=2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.830 (q), 30.188 (q), 31.221 (q), 34.972 (s), 37.861 (s), 118.290 (d), 122.957 (d), 124.134 (d), 124.398 (s), 125.172 (d), 143.163 (s), 147.401 (s), 151.801 (s), 168.888 (s); GCMS m/z (relative intensity) 255 (M^+, 37), 240 (100), 224 (27), 213 (84), 199 (19), 99 (74), 77 (7), 57 (8); HRMS m/z 255.1981 (calcd for $C_{18}H_{25}N$ 255.1987).

2,4,6-Tris(1,1-dimethylethyl)quinoline (9d). The compound was identified by ^1H NMR and GCMS: ^1H NMR ($CDCl_3$) δ 1.433 (s, 9H), 1.463 (s, 9H), 1.597 (s, 9H), 7.413 (s, 1H), 7.525 (dd, J = 9.0, 2.1 Hz, 1H), 8.034 (d, J = 2.1 Hz, 1H), 8.268 (d, J = 9.0 Hz, 1H); GCMS m/z (relative intensity) 297 (M^+, 58), 298 (12), 282 (100), 255 (86), 241 (12), 134 (11), 120 (23), 57 (26), 41 (29).

2-Chloro-4-(1,1-dimethylethyl)quinoline (10). The product was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.607 (s, 9H), 7.332 (s, 1H), 7.556–7.500 (m, 1H), 7.699–7.644 (m, 1H), 8.050 (dd, J = 8.1, 1.2 Hz, 1H), 8.371 (dd, J = 8.7, 1.2 Hz, 1H); GCMS m/z (relative intensity) 219 (M^+, 78), 220 (11), 221 (24), 204 (100), 184 (94), 168 (34), 77 (22), 57 (29), 41 (49).

4-(1,1-Dimethylethyl)-3,4-dihydro-2(1*H*)-quinolinone (11). The compound was isolated as a solid: mp 116–117 °C; ^1H NMR ($CDCl_3$) δ 0.910 (s, 9H), 2.700-2.609 (m, 2H), 2.869–2.789 (m, 1H), 6.866 (dd, J = 7.8, 1.2 Hz, 1H), 6.942 (td, J = 7.5, 1.2 Hz, 1H), 7.101 (dd, J = 7.8, 1.8 Hz, 1H), 7.157 (td, J = 7.5, 1.5 Hz, 1H), 9.657 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.554 (q), 32.721 (t), 35.263 (s), 46.567 (d), 115.913 (d), 122.016 (d), 124.144 (s), 127.620 (d), 130.904 (d), 137.616 (s), 172.831 (s); GCMS m/z (relative intensity) 203.0 (M^+, 18), 204 (3), 205 (0.2), 164 (10), 146 (100), 128 (27), 77 (9), 57 (32); HRMS m/z 203.1314 (calcd for $C_{13}H_{17}NO$ 203.1310); FTIR ($CDCl_3$) 3208, 1684 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.79; H, 8.76; N, 6.78.

4-(1,1-Dimethylethyl)-1,4-dihydro-2-methylquinoline (12). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.868 (s, 9H), 1.795 (s, 1H), 2.334 (s, 3H), 2.779 (s, 1H), 4.620 (d, J = 0.9 Hz, 1H), 7.041–7.153 (m, 4H). GCMS indicated a mixture of three isomers of $C_{14}H_{19}N$, one of which (presumably 1,4-dihydro) greatly predominated. Upon storage of the material isolated by column chromatography, additional ^1H NMR signals appeared consistent with the isomerization of the 1,4-dihydro to the less stable 1,2- and 3,4-dihydro isomers. On the basis of ^1H NMR the initially isolated material was >95% of the 1,4-isomer with isomerization occurring under GC conditions. The isolated material also readily underwent oxidation to yield 4-(1,1-dimethylethyl)-2-methyl-3(4*H*)-quinolinone: MS m/z 215.1311 (calcd for $C_{14}H_{17}NO$ 215.1310), 200 (100%), 159, 146, 91, 57.

4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-2-methylquinoline (13). The compound was isolated as a white solid: mp 36–38 °C; ^1H NMR ($CDCl_3$) δ 0.920 (s, 9H), 1.195 (d, J = 6.0 Hz, 3H), 1.549–1.659 (m, 1H), 2.008–2.096 (m, 1H), 2.730 (t, J = 9.0 Hz, 1H), 2.952–3.063 (m, 1H), 6.550 (dd, J = 7.8, 0.9 Hz, 1H), 6.672 (td, J = 7.5, 1.2 Hz, 1H), 6.973 (td, J=7.5, 1.2 Hz, 1H), 7.174 (d, J=7.8 Hz, 1H); GCMS m/z (relative intensity) 204 (1.5), 203 (M^+, 10), 188 (1.8), 146 (100), 147 (11), 130 (14), 118 (5), 77 (6), 57 (2.5); HRMS m/z 203.1670 (calcd for $C_{14}H_{21}N$ 203.1674); FTIR ($CDCl_3$) 1477, 3359 cm^{-1}.

4-(1,1-Dimethylethyl)-3,4-dihydro-2,3-dimethylquinoline (14). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.829 (s, 9H), 0.924 (d, J = 7.2 Hz, 3H), 2.190 (s, 1H), 2.222 (s, 3H), 2.643 (q, J = 7.2 Hz, 1H), 7.059–7.150 (m, 2H), 7.224–7.291 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.054 (q), 26.193 (q), 27.739 (q) 34.478 (d), 34.812 (d), 52.599 (d), 125.491 (d), 125.676 (s), 125.719 (d), 127.485 (d), 131.716 (d), 143.669 (s), 174.983 (s); GCMS m/z (relative intensity) 216 (2), 215 (M^+, 11), 158 (94), 159 (16), 144 (100), 115 (23), 91 (11), 77 (7), 57 (19); HRMS m/z 215.1670 (calcd for $C_{15}H_{21}N$ 215.1674); IR $CDCl_3$ 1477, 1604, 1641, 3067 cm^{-1}.

4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-2,3-dimethylquinoline (15). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.858 (s, 9H), 1.046 (d, J = 6.9 Hz, 3H), 1.118 (d, J = 3.6 Hz, 1H), 1.248 (d, J = 6.3 Hz, 3H), 1.834–1.947 (m, 1H), 2.502–2.596 (m, 1H), 3.250 (m, 1H), 6.582 (dd, J = 8.4, 1.2 Hz, 1H), 6.701 (td, J=7.2, 1.2 Hz, 1H), 6.968–7.0179 (m, 2H); GCMS m/z (relative intensity) 218 (1.6), 217 (M^+, 10), 203 (3), 160 (100), 161 (11), 146 (24), 144 (14), 130 (10), 118 (12), 77 (4), 57 (2.5); HRMS m/z 217.18295 (calcd for $C_{15}H_{23}N$ 217.18305); FTIR ($CDCl_3$) 754, 1477, 1607, 2955, 3355 cm^{-1}.

4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-1,2,3-trimethylquinoline (17). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.840 (s, 9H), 1.020 (d, J = 6.6 Hz, 3H), 1.272 (d, J = 6.3 Hz, 3H), 1.973–2.071 (m, 1H), 2.089 (d, J = 2.7 Hz, 1H), 2.152–2.244 (m, 1H), 2.623 (s, 3H), 6.729 (tt, J = 7.8, 0.9 Hz, 2H), 6.974 (dd, J = 8.7, 1.2 Hz, 1H), 7.119 (td, J = 7.8, 1.5 Hz, 1H); GCMS m/z (relative intensity) 232 (1.7), 231 (M^+, 11), 174 (100), 175 (11), 158 (11), 159 (6), 144 (12), 132 (10), 118 (5), 77 (2), 57 (2); HRMS m/z 231.1981 (calcd for $C_{16}H_{25}N$ 231.1987).

2,3-Dimethylquinoline (18).[24] The compound was isolated as a white solid: mp 68–69 °C (lit.[24] 67–69 °C); ^1H NMR ($CDCl_3$) δ 2.454 (s, 3H), 2.695 (s, 3H), 7.449 (td, J = 8.1, 0.9 Hz, 1H), 7.613 (td, J = 8.4, 1.5 Hz, 1H), 7.706 (d, J = 8.1 Hz, 1H), 7.840 (s, 1H), 7.999 (d, J=8.4 Hz, 1H); GCMS m/z (relative intensity) 158 (12), 157 (M^+, 100), 142 (15), 115 (40), 89 (18), 77 (8), 63 (20), 51 (17), 50 (13); HRMS m/z 157.0893 (calcd for $C_{11}H_{11}N$ 157.0892).

4-(1,1-Dimethylethyl)-2-methylquinoline (19). The compound was isolated as a yellow liquid: ^1H NMR ($CDCl_3$) δ 1.605 (s, 9H), 2.718 (s, 3H), 7.232 (s, 1H), 7.454 (td, J = 7.2, 1.8 Hz, 1H), 7.620 (td, J = 8.1, 1.2 Hz, 1H), 8.054 (dd, J = 9.6, 1.2 Hz, 1H), 8.353 (dd, J=8.4, 0.9 Hz, 1H); GCMS m/z (relative intensity) 200 (10), 199 (M^+, 63), 184 (100), 168 (27), 157 (10), 144 (11), 128 (14), 57 (5); HRMS m/z 199.1359 (calcd for $C_{14}H_{17}N$ 199.1361).

4,6-Bis(1,1-dimethylethyl)-2-methylquinoline. The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.425 (s, 9H), 1.595 (s, 9H), 2.708 (s, 3H), 7.177 (s, 1H), 7.541 (dd, J = 9.4, 1.2 Hz, 1H), 8.022 (d, J = 2.4 Hz, 1H), 8.285 (d, J = 9.3 Hz, 1H); GCMS m/z (relative intensity) 256 (7), 255 (M^+, 35), 241 (19), 240 (100), 184 (23), 144 (32); HRMS m/z 255.1985 (calcd for $C_{18}H_{25}N$ 255.1987).

***trans*-2,4-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydroquinoline (20).** The trans isomer formed in the *tert*-butylation of quinoline was isolated as a solid: mp 60–61 °C; ^1H NMR ($CDCl_3$) δ 0.932 (s, 9H), 0.950 (s, 9H), 1.418 (td, J = 13.5, 5.1 Hz, H-3a), 2.112 (ddd, J = 13.5, 4.2, 2.1 Hz, H-3e), 2.490 (dd, J = 5.1, 2.1 Hz, H-4e), 3.211 (dd, J = 12.9, 4.2 Hz, H-2a), 3.857 (s, NH), 6.460 (dd, J = 7.8, 0.6 Hz, 1H), 6.520 (td, J = 7.2, 0.9 Hz, 1H), 7.011–6.947 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.405 (q), 25.810 (q), 29.220 (d), 34.353 (s), 34.940 (s), 45.659 (d), 57.317 (d), 113.106 (d), 114.799 (d), 122.489 (s), 127.041 (d), 130.515 (d), 145.104 (s); GCMS m/z (relative intensity) 245 (M^+, 10), 188 (100), 132 (13), 130 (24), 91 (2), 77 (5), 57 (12); HRMS m/z 245.2141 (calcd for $C_{17}H_{27}N$

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245.2144); FTIR ($CDCl_3$) 3450 cm^{-1}. Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.41; H, 11.32; N, 5.67.

***cis*-2,4-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydroquinoline (20).** Reduction of the *tert*-butylation reaction products from **8a** in the presence of KI by $NaBH_4$/MeOH yielded the title compound: mp 44.0–44.5 °C; ^1H NMR ($CDCl_3$) δ 0.935 (s, 9H), 0.974 (s, 9H), 1.669 (ddd, J = 13.2, 12.0, 7.8 Hz, H-3a), 2.036 (ddd, J = 13.2, 9.3, 3.6 Hz, H-3e), 2.647 (dd, J = 12.0, 3.6 Hz, H-4a), 2.703 (~t, J = 8.7 Hz, H-2a), 3.505 (broad s, NH), 6.578 (dd, J = 7.8, 1.2 Hz, 1H), 6.664 (td, J = 7.5, 1.2 Hz, 1H), 6.982 (td, J = 7.5, 1.5 Hz, 1H), 7.182 (broad d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.29 (q), 28.15 (t), 28.76 (q), 33.39 (s), 36.00 (s), 45.64 (d), 63.19 (d), 115.37 (d), 117.34 (d), 126.09 (d), 126.35 (s), 130.65 (d), 149.72 (s); GCMS m/z (relative intensity) 345 (M^+, 10), 246 (2), 188 (100), 130 (33), 57 (17); HRMS m/z 245.2144 (calcd for $C_{17}H_{27}N$ 245.2144). Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.71; H, 11.46; N, 5.66.

2,4-Bis(1,1-dimethylethyl)-3,4-dihydro-3-hydroxyquinoline (21). The compound was isolated as a solid: mp 124–125 °C; FTIR 1614, 3281 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 9H), 1.35 (s, 9H), 1.65 (d, J = 9.6 Hz, 1H), 2.68 (d, J = 1.2 Hz, 1H), 4.52 (dd, J = 9.3, 1.2 Hz, 1H), 7.16–7.42 (m, 4H); ^1H NMR ($CDCl_3$ plus D_2O) δ 0.88 (s, 9H), 1.35 (s, 9H), 2.67 (s, 1H), 4.51 (s, 1H), 7.16–7.42 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.0 (q), 28.6 (q), 33.9 (s), 39.2 (s), 54.5 (d), 61.3 (d), 125.1 (s), 126.1 (d), 127.1 (d), 127.8 (d), 131.8 (d), 143.6 (s), 176.8 (s); GC and HRMS m/z (relative intensity) 259.1929 (M^+, 40, calcd for $C_{17}H_{25}NO$ 259.1936), 244 (96), 217 (5), 202 (31), 186 (100), 170 (28), 146 (54), 118 (21), 91 (9), 77 (3), 57 (48); GCMS (CI, NH_3) m/z (relative intensity) 260 (M^+ + 1, 100), 186 (3). Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40. Found: C, 78.36; H, 9.45; N, 5.33.

4-(1,1-Dimethylethyl)-1,4-dihydro-1,2-dimethylquinoline (23). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.767 (s, 9H), 2.005 (s, 3H), 2.986 (d, J = 6.0 Hz, 1H), 3.127 (s, 3H), 4.559 (d, J = 6.0 Hz, 1H), 6.790 (d, J = 8.1 Hz, 1H), 6.856 (t, J = 7.5 Hz, 1H), 6.980 (d, J = 6.3 Hz, 1H), 7.154 (t, J = 7.2 Hz, 1H); GCMS m/z (relative intensity) 215 (M^+, 3.4), 200 (1.6), 159 (12), 158 (100), 143 (8), 115 (5); HRMS m/z 215.1676 (calcd for $C_{15}H_{21}N$ 215.1674).

4-(1,1-Dimethylethyl)-1,4-dihydro-1,2,3-trimethylquinoline (24). The compound was isolated as a white solid: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 0.738 (s, 9H), 1.845 (s, 3H), 1.938 (s, 3H), 2.862 (s, 1H), 3.147 (s, 3H), 6.792 (d, J = 8.4 Hz, 1H), 6.854 (td, J = 7.2, 0.9 Hz, 1H), 6.945 (dd, J = 7.5, 1.5 Hz, 1H), 7.144 (td, J = 7.5, 1.8 Hz, 1H); GCMS m/z (relative intensity) 230 (3), 229 (M^+, 20), 172 (100), 173 (12), 157 (21), 115 (5); HRMS m/z 229.1827 (calcd for $C_{16}H_{23}N$ 229.1831).

4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-1,2-dimethylquinoline (25). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.982 (s, 9H), 1.179 (d, J = 6.3 Hz, 3H), 1.502–1.640 (m, 1H), 2.151–2.240 (m, 1H), 2.538–2.591 (m, 1H), 2.727 (s, 3H), 2.908–2.983 (m, 1H), 6.681–6.729 (m, 2H), 7.104 (t, J = 7.8 Hz, 1H), 7.191 (d, J = 7.2 Hz, 1H); GCMS m/z (relative intensity) 218 (2), 217 (M^+, 13), 160 (100), 144 (12), 131 (5), 77 (3), 57 (1); HRMS m/z 217.1834 (calcd for $C_{15}H_{23}N$ 217.1831).

4-(1,1-Dimethylethyl)-1,2-dihydro-1,2-dimethylquinoline (27). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.975 (d, J = 6.3 Hz, 3H), 1.335 (s, 9H), 2.848 (s, 3H), 3.919 (pentet, J = 6.3 Hz, 1H), 5.738 (d, J = 6.6 Hz, 1H), 6.541 (d, J = 8.4 Hz, 1H), 6.679 (td, J = 7.1, 0.9 Hz, 1H), 7.100 (td, J = 8.1, 0.9 Hz, 1H), 7.533 (dd, J = 7.8, 0.9 Hz, 1H); GCMS m/z (relative intensity) 215 (M^+, 11), 201 (15), 200 (100), 185 (16), 184 (17), 170 (9), 158 (24), 115 (3), 57 (1.5); HRMS m/z 215.1672 (calcd for $C_{15}H_{21}N$ 215.1674).

1-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-3-methylisoquinoline (29). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.975 (s, 9H), 1.574 (d, J = 6.0 Hz, 3H), 2.612 (dd, J = 15.9, 3.9 Hz, 1H), 2.740 (t, J = 15.6 Hz, 1H), 2.900 (m, 1H), 2.194 (broad s, 1H), 4.161 (d, J = 1.2 Hz, 1H), 7.09–7.125 (m, 2H), 7.179–7.241 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.958 (q), 27.477 (q), 37.035 (s), 37.169 (t), 58.197 (d), 74.974 (d), 126.079 (d), 127.572 (d), 127.573 (d), 130.595 (d), 131.745 (s), 135.396 (s); GCMS m/z (relative intensity) 203 (M^+, 0.03), 202 (0.18), 147 (12), 146 (100), 129 (6), 77 (2), 57 (1); GCMS (CI, ammonia) m/z (relative intensity) 204 (100), 146 (18); HRMS m/z 202.1596 (calcd for $C_{14}H_{20}N$ 202.1596).

1-(1,1-Dimethylethyl)-3-methyl-4(1*H*)-isoquinolinone (30). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.901 (s, 9H), 2.400 (d, J = 0.9 Hz, 3H), 4.992 (s, 1H), 7.368–7.546 (m, 3H), 8.041 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.128 (q), 27.186 (q), 39.164 (s), 70.578 (d), 126.300 (d), 127.577 (d), 128.007 (d), 130.811 (s), 131.295 (d), 145.089 (s), 165.239 (s), 176.310 (s); GCMS m/z (relative intensity) 215 (M^+, 30), 214 (40), 200 (40), 174 (11), 173 (100), 159 (14), 144 (3), 130 (10), 92 (14), 77 (8), 57 (1.8); GCMS (CI, ammonia) 216 (M^+ + 1, 100), 160 (14); HRMS m/z 215.1307 (calcd for $C_{14}H_{17}NO$ 215.1310); FTIR ($CDCl_3$) 1205, 1365, 1637, 1677, 2964 cm^{-1}.

1-(1,1-Dimethylethyl)-4-hydroxy-3-methylisoquinoline (31). ^1H NMR ($CDCl_3$) δ 1.605 (s, 9H), 2.589 (s, 3H), 7.435 (td, J = 7, 1.5 Hz, 1H), 7.538 (td, J = 8.4, 1.2 Hz, 1H), 8.223 (d, J = 7.8 Hz, 1H), 8.396 (d, J = 8.7 Hz, 1H).

3-(1,1-Dimethylethyl)-3,4-dihydroisoquinoline (32). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.065 (s, 9H), 2.576 (t, J = 15.3 Hz, 1H), 2.725 (dd, J = 15.4, 5.4 Hz, 1H), 3.089 (ddd, J = 15.3, 5.4, 3 Hz, 1H), 7.146–7.390 (m, 4H), 8.370 (d, J = 3.3 Hz, 1H); GCMS m/z (relative intensity) 187 (M^+, 1.3), 172 (6), 131 (37), 130 (100), 103 (7), 77 (10), 57 (15); HRMS m/z 187.1359 (calcd for $C_{13}H_{17}N$ 187.1361).

1,3-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydroisoquinoline (33). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.959 (s, 9H), 1.026 (s, 9H), 1.729 (broad s, 1H), 2.601 (dd, J = 16.8, 10.5 Hz, 1H), 2.760 (dd, J = 17.1, 6 Hz, 1H), 3.143 (dd, J = 10.2, 5.7 Hz, 1H), 3.660 (s, 1H), 7.029–7.177 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.072 (q), 29.534 (q and t), 34.383 (s), 37.662 (s), 56.261 (d), 64.056 (d), 124.227 (d), 126.051 (d), 127.984 (d), 129.289 (d), 136.367 (s), 137.622 (s); GCMS m/z (relative intensity) 245 (M^+, 0.04), 189 (15), 188 (100), 171 (1.5), 156 (3), 130 (18), 115 (3), 57 (6.7); GCMS (CI, ammonia) m/z (relative intensity) 247 (18.9), 246 (M+1, 100), 188 (20), 130 (4); HRMS m/z 244.2063 (calcd for $C_{17}H_{27}N$ 244.2065); FTIR ($CDCl_3$) 1477, 2950, 3436 cm^{-1}.

1-(1,1-Dimethylethyl)-1,2-dihydro-2-methylisoquinoline (35).[25] The compound was isolated as a purple solid: mp 46–47 °C; ^1H NMR ($CDCl_3$) δ 0.862 (s, 9H), 2.995 (s, 3H), 3.930 (d, J = 0.6 Hz, 1H), 5.277 (d, J = 7.2 Hz, 1H), 6.176 (dd, J = 6.9, 1.2 Hz, 1H), 6.842 (dd, J = 7.2, 0.6 Hz, 1H), 6.903 (dd, J = 7.5, 1.2 Hz, 1H), 7.016 (td, J = 7.5, 1.2 Hz, 1H), 7.133 (td, J = 7.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.502 (q), 41.625 (s), 44.877 (q), 71.351 (d), 98.386 (s), 122.102 (d), 123.604 (d), 124.368 (s), 126.872 (d), 128.483 (d), 134.520 (s), 137.523 (d); GCMS m/z (relative intensity) 201 (M^+, 2.5), 145 (13.4), 144 (100), 129 (7), 103 (11), 77 (5), 57 (1.4); HRMS m/z 201.1514 (calcd for $C_{14}H_{19}N$ 201.1518).

1-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-2-methylisoquinoline (36). The compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.877 (s, 9H), 2.306–2.391 (m, 1H), 2.506 (m, 3H), 2.520–2.598 (m, 1H), 2.843–2.939 (m, 1H), 3.204 (s, 1H), 3.205–3.266 (m, 1H), 7.010–7.158 (m, 4H); GCMS m/z (relative intensity) 203 (M^+, 0.05), 188 (2.5), 146 (100), 131 (4), 103 (2), 91 (1), 77 (2.5), 57 (0.62); GCMS (CI, ammonia) m/z (relative intensity) 204 (M^+ + 1, 100), 221 (10); HRMS m/z 202.1597 (calcd for $C_{14}H_{20}N$ 202.1596).

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