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Photostimulated tert-butylation of quinolines, quinolinium salts, quinoline N-oxides, N-benzylideneanilines, and azobenzenes

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Photostimulated *tert*-butylation of quinolines, quinolinium salts, quinoline *N*-oxides, *N*-benzylideneanilines, and azobenzenes

By

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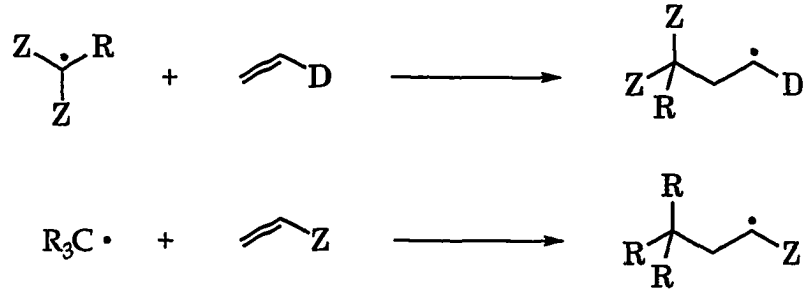
GENERAL INTRODUCTION

Free radicals are species with at least one unpaired electron. Although they are neutral species, their chemical reactivity is dominated by the nature of the atom containing the unpaired electron. Accordingly, they may be endowed with either electrophilic or nucleophilic character. The electrophilic or nucleophilic character is also influenced by the nature of the substituents attached to the radical center containing the unpaired electron. The case of carbon centered radicals is particularly important since a fundamental appreciation of their differing types and behavior lies at the very heart of organic synthesis in terms of carbon-carbon bond formation.[1,2] Alkyl radicals, substituted with electron-releasing groups (e.g., alkyl, alkoxy, amino, etc.), act as nucleophiles and react very fast with alkenes substituted by electron-withdrawing substituents (nitrile, ketone, ester, etc.).[3-5] On the other hand, radicals with electron-withdrawing substituents (e.g., CN, F, etc.) act as electrophiles and react fast with electron-rich alkenes.[3,6,7] These considerations are summarized as in Scheme I.

Scheme I. The Chemoselective Character of Substituted Alkyl Radicals.



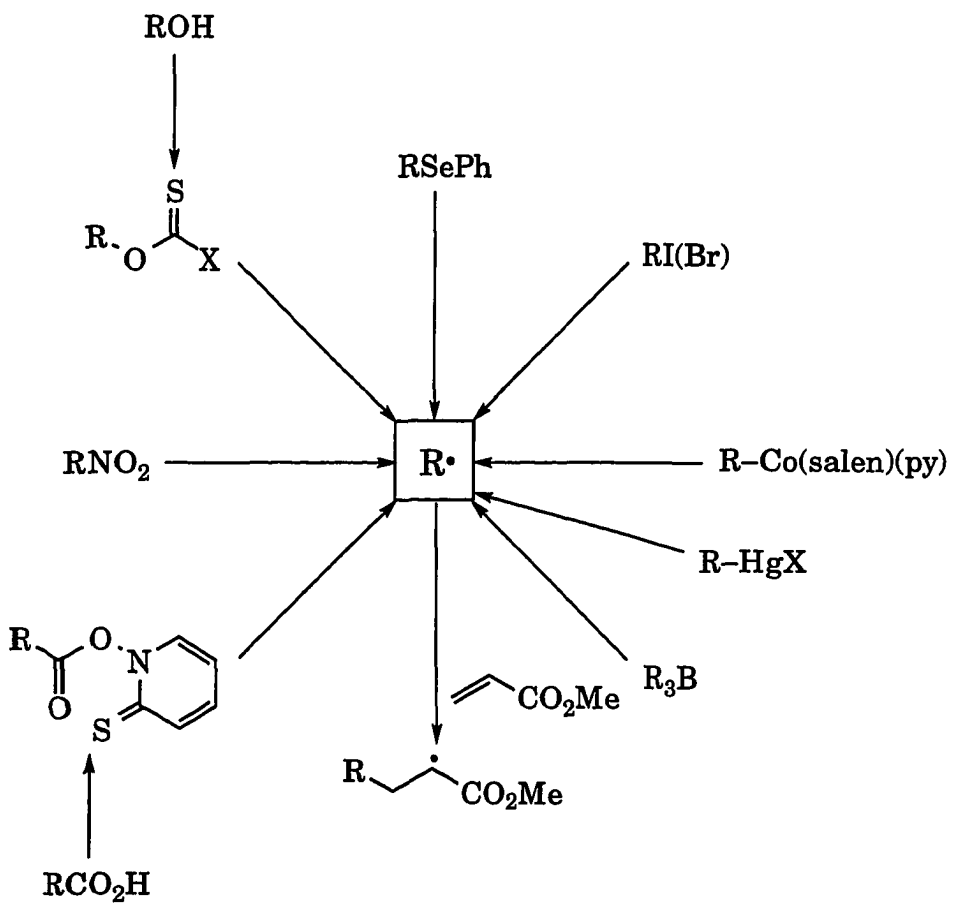
Z = electron-withdrawing group, e.g., CN, COOMe, SO_2Ar, etc.

D = electron-releasing group, e.g., NR_2, OR.

R = alkyl group

Some recent methods used for the generation of a carbon centered radical are illustrated in Scheme II.[1]

Scheme II. Some Recent Radical Triggers used for Carbon-Carbon Bond Formation.



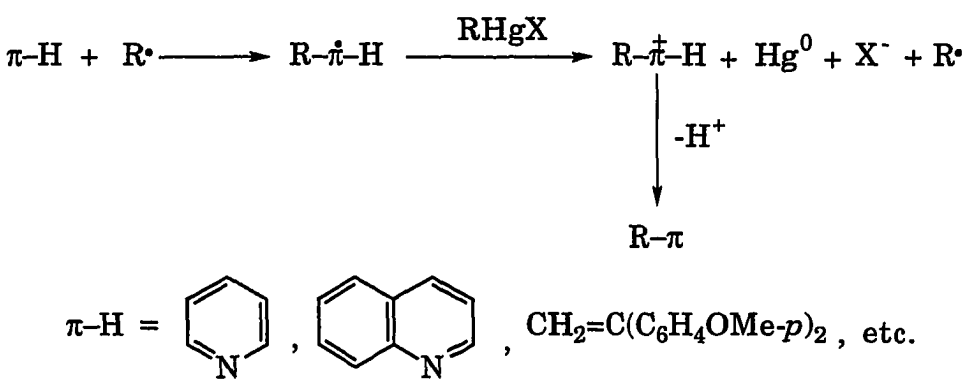
Alkylmercurials are readily available organometallic reagents possessing moderate reactivity in electrophilic attack at carbon.[8] During the past several years, Russell has developed a series of free radical reactions in which alkylmercury halides or dialkylmercurials participate in the propagation step of a chain process.[9-30] Alkylmercury halides have proven to be a convenient source of alkyl radicals in these photostimulated chain reactions.

Basically, there are two types of reactions in which loss of a proton or addition of a proton can be involved in the electron transfer processes of alkylmercury halides.

1. Oxidative (or substitutive) alkylation.[8,15,17,31]

Alkylmercury halides are readily attacked in a chain propagation reaction by donor radicals (Scheme III). Chain reactions occur when the alkyl

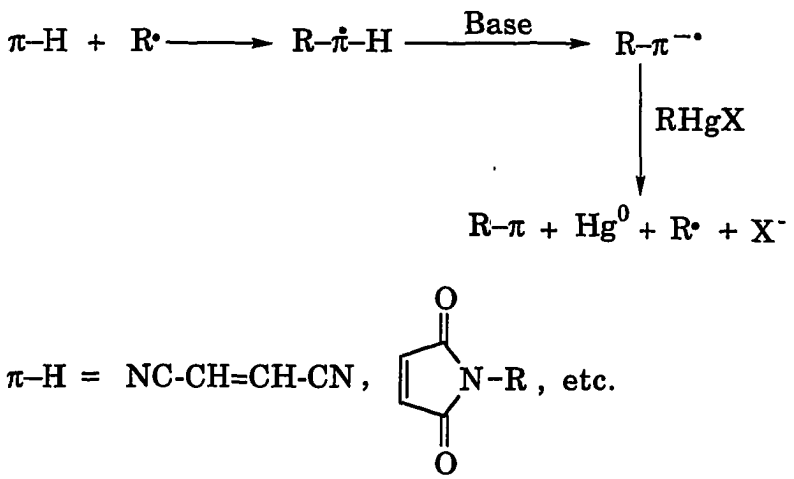
Scheme III. Oxidative Alkylation.



radicals can be recycled to generate donor radicals. Loss of a proton from the carbonium cation yields the substitutive product.

The reaction can be promoted by bases (Scheme IV)[32]. The R-π-H· radical, generated from the attack of π-H by R· radical, loses the acidic proton to form the radical anion in the presence of a base. The radical anion yields the oxidative alkylation product upon electron transfer to the alkylmercury halide.

Scheme IV. Oxidative Alkylation Promoted by Base.



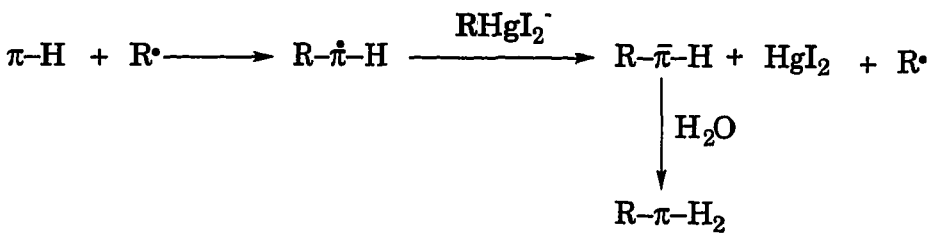
2. Reductive (additive) alkylation.[31-33]

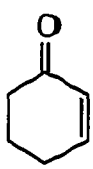
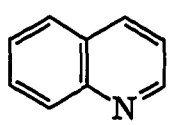
Photostimulated chain reactions of alkylmercury chlorides with many α,β-unsaturated ketones, esters, lactones, and amides occur readily in the presence of iodide ion. Enolyl radicals can be reduced to the enolate anion (I^- or $RHgI_2^-$ may be the reducing agent) and the chain reaction propagated (Scheme V).

Reductive alkylation can be promoted by acid (SchemeVI)[32-34]. In the presence of an acid, the yield and the rate of formation of the reductive

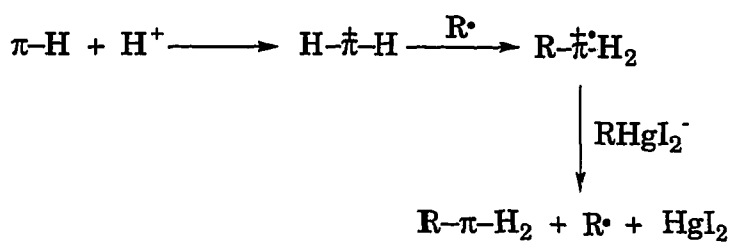
alkylation product increase. It suggests that the protonation step precedes the radical addition step. The radical cation formed is reduced by I^- and/or $RHgI_2^-$ by electron transfer.

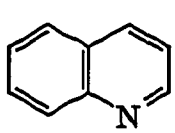
Scheme V. Reductive Alkylation.



π–H = H-C≡C-COOEt,  ,  , etc.

Scheme VI. Acid-promoted Reductive Alkylation



π–H = Ph-CH=N-Ph ,  , etc.

CHAPTER I. OXIDATIVE AND REDUCTIVE ALKYLATION OF QUINOLINES BY *tert*-BUTYLMERCURY HALIDES

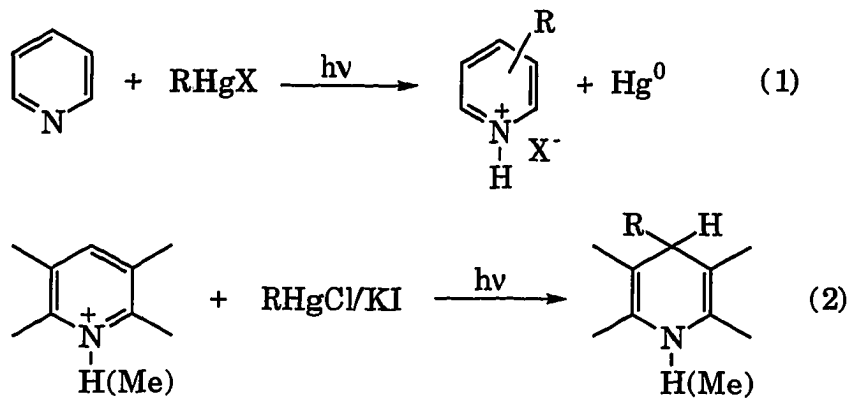
Introduction

The Friedel-Crafts reaction is important for introducing alkyl groups onto an aromatic ring. An electron-rich aromatic ring is required for this type of reaction. Heteroaromatic bases, such as pyridines and quinolines, are electron-deficient aromatic compounds and cannot undergo the Friedel-Crafts reaction. The substitution of heteroaromatic bases by nucleophilic carbon-centered radicals has been developed as one of the most important general reactions in the heteroaromatic series,[35-39] due to the high regio- and chemoselectivity, the availability of numerous and inexpensive radical sources, which can be successfully applied and the simple experimental conditions. It reproduces most of the numerous aspects of the Friedel-Crafts aromatic substitutions, but with opposite reactivity and selectivity.

Thermal and photochemical decomposition of organomercury compounds has been used to produce alkyl radicals for the homolytic alkylation of heteroaromatics. Photolysis of alkylmercury chlorides in pyridine solution forms the 2- and 4-alkylpyridines and free mercury in high yield.[18] With the photochemically more labile *t*-BuHgI,[29] or a mixture of *t*-BuHgCl and KI, the reaction proceeds more readily. Alkylation may involve the attack of *t*-Bu· upon the free pyridine, upon a complex of the pyridine with *t*-BuHgX,[40] or upon the pyridinium ion formed as the substitution reaction 1 proceeds.

Reductive alkylation is observed with some pyridine derivatives,

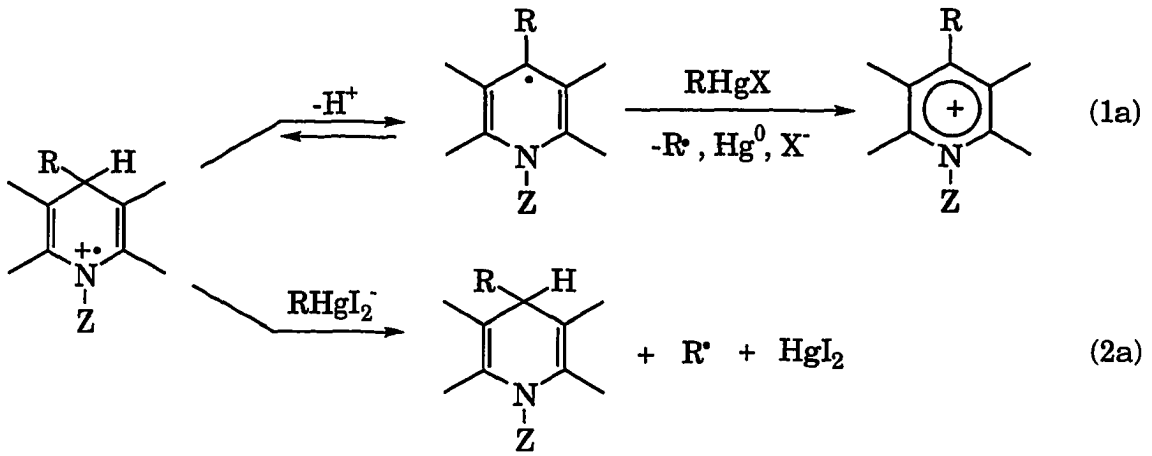
particularly in the presence of *p*-toluenesulfonic acid (PTSA) and KI.[33] For example, reductive alkylation of 4-vinylpyridine yields 4-(3,3-dimethylbutyl)pyridine. Similar reductive alkylations are observed for the N-methylpyridinium ions derived from acridine or quinaldine (reaction 2).[33]



Protonation of heteroaromatics is known to activate them toward radical additions.[41] Complexion 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 apparent only in the initial stages of the reaction.

The system RHgCl/KI is a unique one because of the presence of both the mild oxidizing agent required for reaction 1 (RHgX) and the reducing agent (I^- or $RHgI_2^-$)[18] required for reaction 2. The competition between oxidative and reductive alkylation is apparently controlled by the rate of proton removal from the initial adduct radical (Scheme VII).

Scheme VII. Oxidative and Reductive Alkylation.



Reaction 1a greatly predominates for simple pyridines, but when the proton in the adduct radical is not easily lost because of steric or steroelectronic reasons, reaction 2a predominates.

Results and Discussion

Photostimulated *tert*-Butylation of 4-Substituted Quinolines by *tert*-Butylmercury Halides

Photostimulated *tert*-butylation of 4-methylquinoline (lepidine) and 4-chloroquinoline by *tert*-butylmercury halides produced exclusively the substitutive (oxidative) products. Lepidine was converted to 2-*tert*-butyl-4-methylquinoline **1**, which was further alkylated to 2,6-di-*tert*-butyl-4-methylquinoline **2**. The reaction was 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. The addition of MeI to the mixture of lepidine/*t*-BuHgCl/KI in Me_2SO appears to speed up the reaction by exchanging I^- for Cl^- (Table I).

Attack of the *tert*-butyl radical at C-2 position of the quinolinium cation gives the *N*-centered radical cation **3**, which loses a proton to give an easily oxidizable quinolinyl radical **4**. An electron is transferred from **4** to *t*-BuHgX to form the quinolinium salt **5**, and a *t*-Bu· that continues the chain (Scheme VIII).

Kurosawa[43,44] has reported that 1,4-dihydropyridines can be oxidized to 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. In our case, 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 **1** (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*-

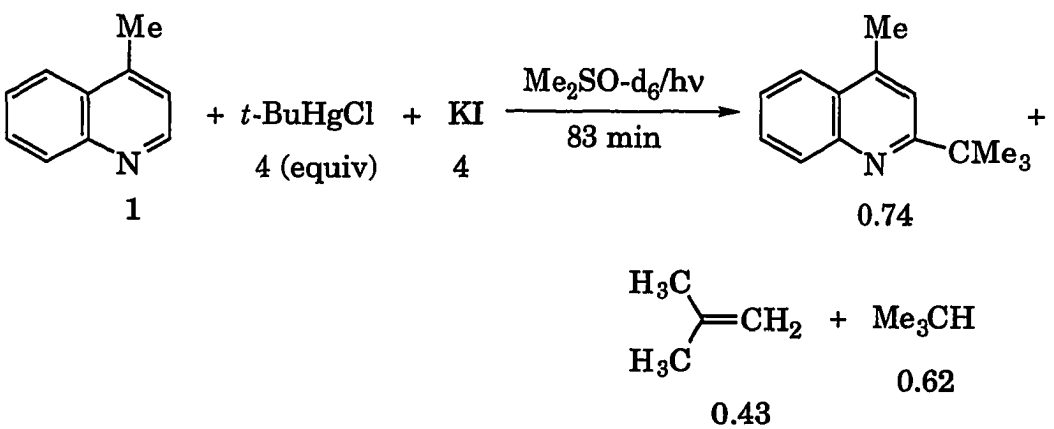
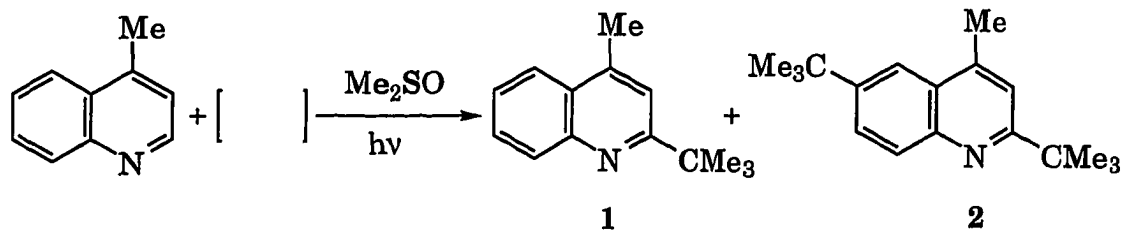


Table I. Photostimulated *tert*-Butylation of Lepidine by *t*-BuHgX in Me_2SO at 35–40 °C.[a]



1 **2**

equivalents				yield (%)[b]	
t-BuHgCl	KI	PTSA	time (h)	1	2
4	0	0	2[c]	71	tr
4	0	0	4	89	tr
4	0	0	10	55	25
4	4	0	2	75	16
4	4	0	4	61	22
4	8	0	2[d]	77	16
4	8	0	4	60	24
4	0	4	4	94	tr
4	0	4	10	45	35
4	4	4	2	62	26
4	4	4	10	tr	70
4	8	4	2	59	30
4	8	4	10	tr	73

[a] 0.05 M 4-methylquinoline irradiated by a 275 W fluorescent sunlamp.

b By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

Table I. (continued)

[c] In the presence of MeI (10 vol %), 72% of **1** and 9% of **2** were observed in a 2.5 h reaction.

[d] In the presence of MeI (10 vol %), 48% of **1** and 34% of **2** were observed in a 2.5 h reaction.

butyl radical disproportionation. Dehydrogenation of a dihydro intermediate would be expected to form 1 equiv of Me_3CH per equiv of **1**. Thus, substitution occurring via the intermediacy of a first formed dihydro intermediate can be excluded by the stoichiometry.

4-Chloroquinoline yielded 2-*tert*-butyl-4-chloroquinoline **6** upon photolysis with *t*-BuHgCl. Only traces of 2,6-di-*tert*-butyl-4-chloroquinoline **7** were observed even with added KI and PTSA. The formation of **6** showed little yield enhancement upon the addition of PTSA, although KI showed a strong promoting effect (Table II).

Photostimulated *tert*-Butylation of 2-Substituted Quinolines by *tert*-Butylmercury Halides

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 **8** is formed, while addition of KI gives rise to a reductive alkylation product, the amide **9** (Table III).

Competition between the reductive and oxidative alkylation pathways is shown in Scheme IX.

Scheme VIII. Photostimulated *tert*-Butylation of 4-Methylquinoline by *tert*-Butylmercury Halides.

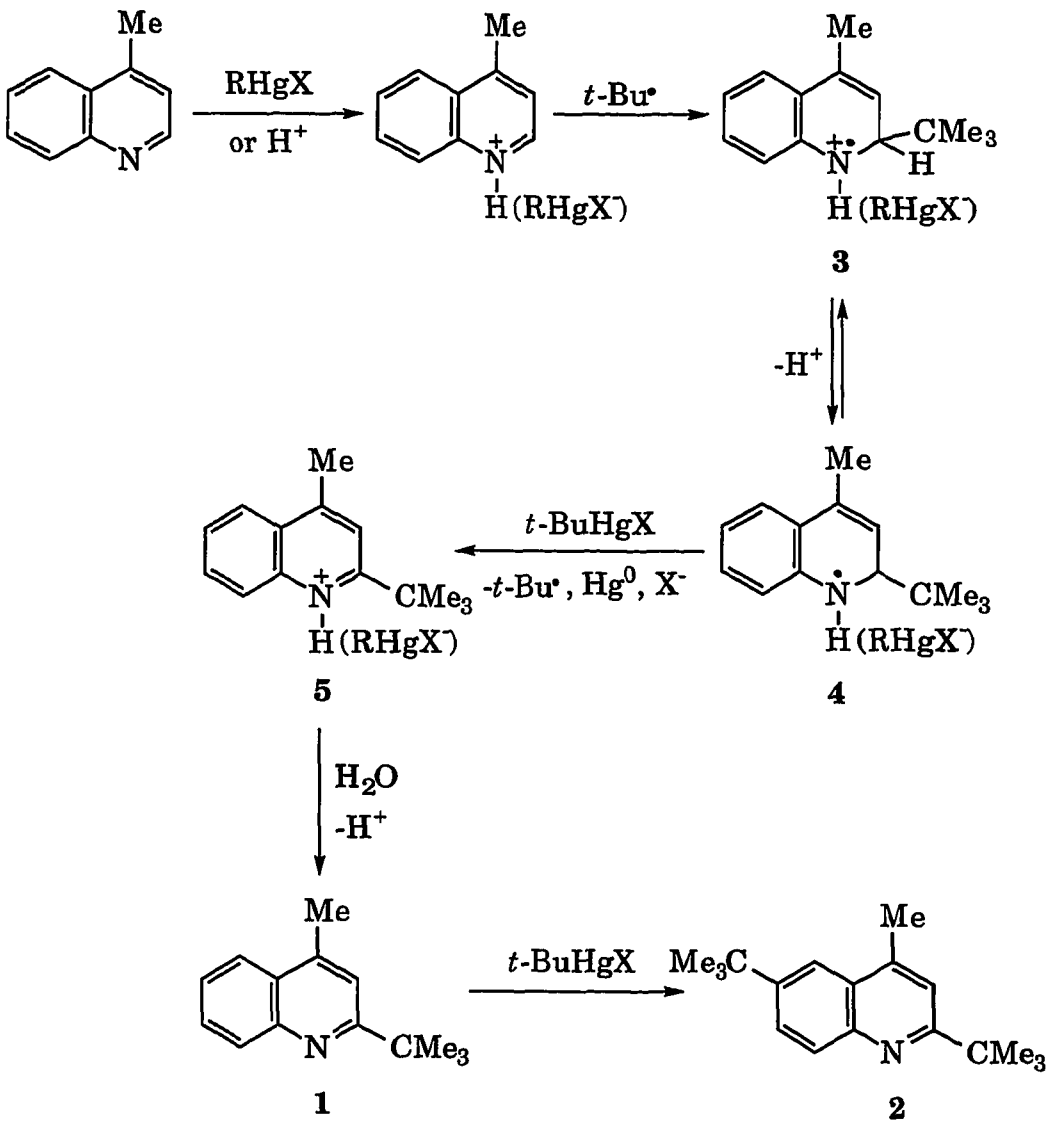
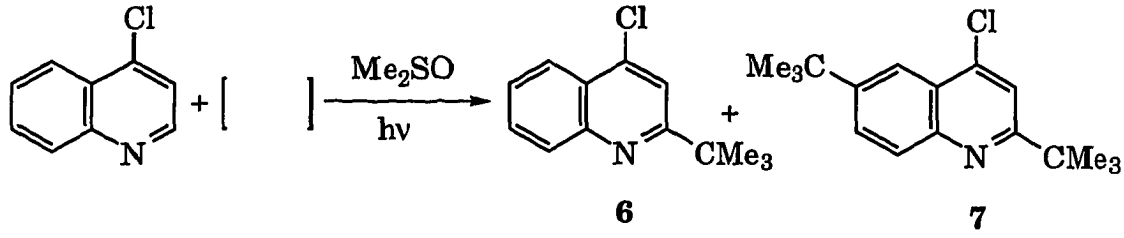


Table II. Photostimulated *tert*-Butylation of 4-Chloroquinoline by *t*-BuHgX in Me_2SO at 35–40 °C.[a]



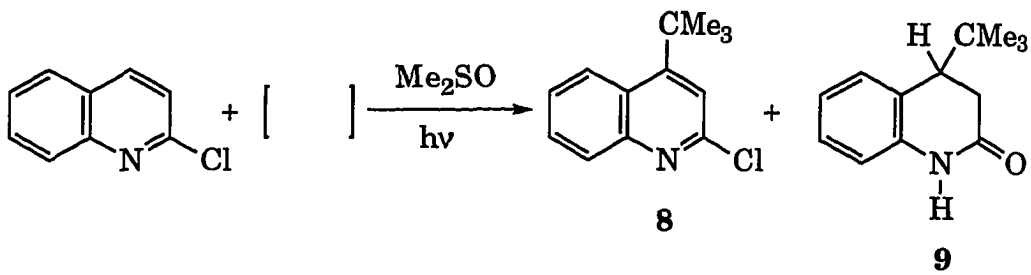
6 **7**

equivalents				yield (%)[b]	
t-BuHgCl	KI	PTSA	time (h)	**6**	**7**
4	0	0	2	16	0
4	0	0	4	24	0
4	0	0	22	48	0
4	4	0	2	68	0
4	4	0	4	90	0
4	8	0	2	87	0
4	4	4	2	80	3
4	8	4	2	69	5

[a] 0.05 M 4-chloroquinoline irradiated by a 275 W fluorescent sunlamp.

[b] By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

Table III. Photostimulated *tert*-Butylation of 2-Chloroquinoline by *t*-BuHgX in Me_2SO at 35–40 °C.[a]



8 **9**

equivalents				yield (%)[b]	
t-BuHgCl	KI	PTSA	time (h)	**8**	**9**
4	0	0	10	4	0
4	4	0	2	0	22
4	8	0	2	0	26
4	0	4	4	20	3
4	0	4	22	49	7
4	8	4	22	tr	78
4	8	0	3.5[c]	tr	69
4	8	0	2[d]	0	45

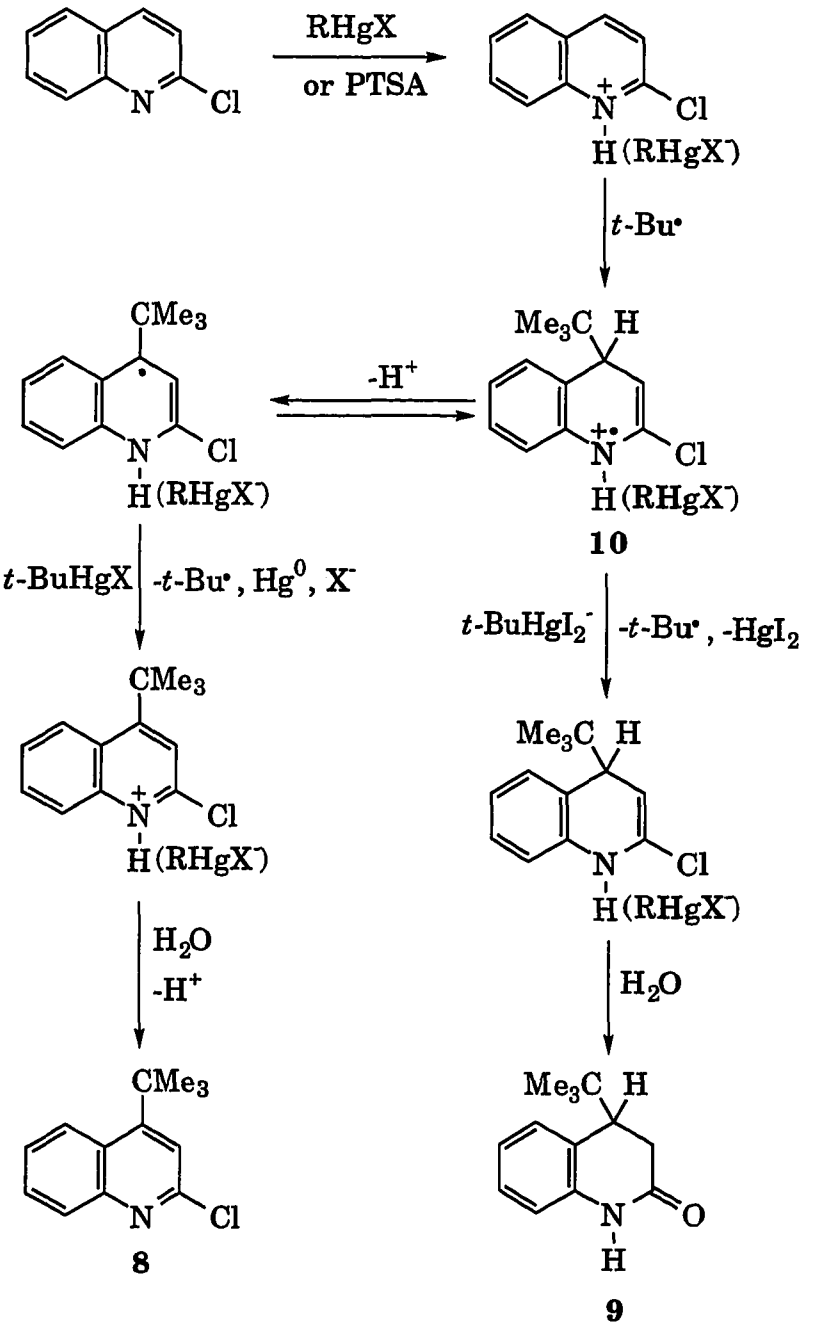
[a] 0.05 M 2-chloroquinoline irradiated by a 275 W fluorescent sunlamp.

[b] By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] 10 vol % MeI.

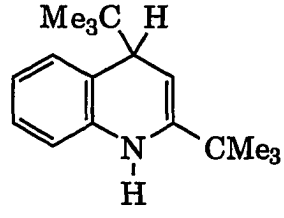
[d] DMF solvent.

Scheme IX. Photostimulated *tert*-Butylation of 2-Chloroquinoline by *tert*-Butylmercury Halides.



The addition of MeI increases the yield of **9** at a given *t*-BuHgCl/KI concentration by exchanging I^- for Cl^- and increasing the rate of the reductive electron transfer step.

Photolysis of 2-*tert*-butylquinoline with *t*-BuHgCl in the absent of KI yields 2,4-di-*tert*-butylquinoline **12**. At longer reaction times, **12** can be further alkylated to 2,4,6-tri-*tert*-butylquinoline **13**. In the presence of KI at short reaction times, a dihydroquinoline derivative is the major product. The dihydroquinoline is slowly converted to **12** at long reaction times (Table IV). We originally believed the dihydroquinoline to be **14**.

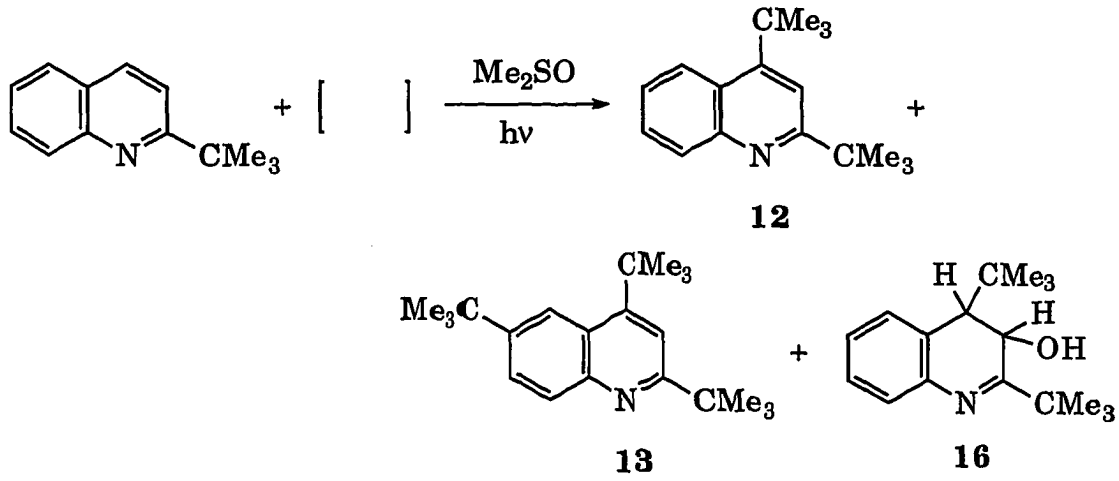


14

Workup with $NaBH_4$/MeOH converts the dihydroquinoline into the tetrahydroquinoline **15**, which is assigned to the *cis*-isomer according to ^1H NMR spectroscopy (see p. 35). Workup with either aqueous $Na_2S_2O_3$ or Na_2CO_3 solution leads to the surprisingly stable hydrate **16** (Scheme X). No evidence for **14** has been obtained. Furthermore, it was found that **16** was reduced to **15** by $NaBH_4$. Apparently **16** and not **14** is the initial dihydroquinoline formed.

With the 4-*tert*-butylquinolinium adduct radical cation **17**, the reduction to **14** does not occur readily because the reductive electron transfer to **17** is apparently sterically hindered. Hydration of the radical cation becomes important leading to the stable 2,4-di-*tert*-butylquinoline hydrate **16** (Scheme

Table IV. Photostimulated *tert*-Butylation of 2-*tert*-Butylquinoline by *t*-BuHgX in Me_2SO at 35–40 °C.[a]



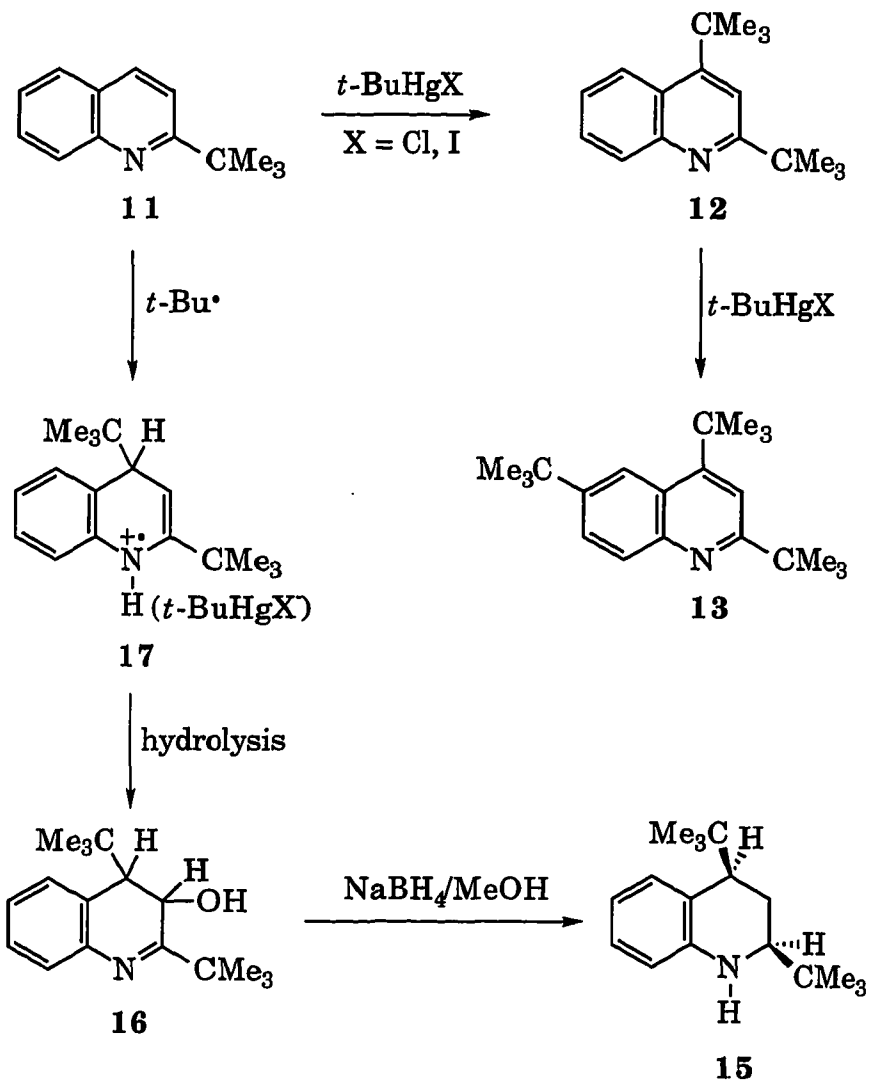
equivalents				yield (%)[b]		
t-BuHgCl	KI	PTSA	time (h)	**12**	**13**	**16**
4	0	0	4	58	tr	tr
4	0	0	10	72	18	tr
4	4	0	4	38	15	22
4	4	0	10	52	15	tr
4	8	0	4	7	tr	70
4	8	4	0.5[c]	17	tr	60
4	8	4	1.5	72	13	–
4	8	4	4	51	30	–

[a] 0.05 M 2-chloroquinoline irradiated by a 275 W fluorescent sunlamp.

[b] By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

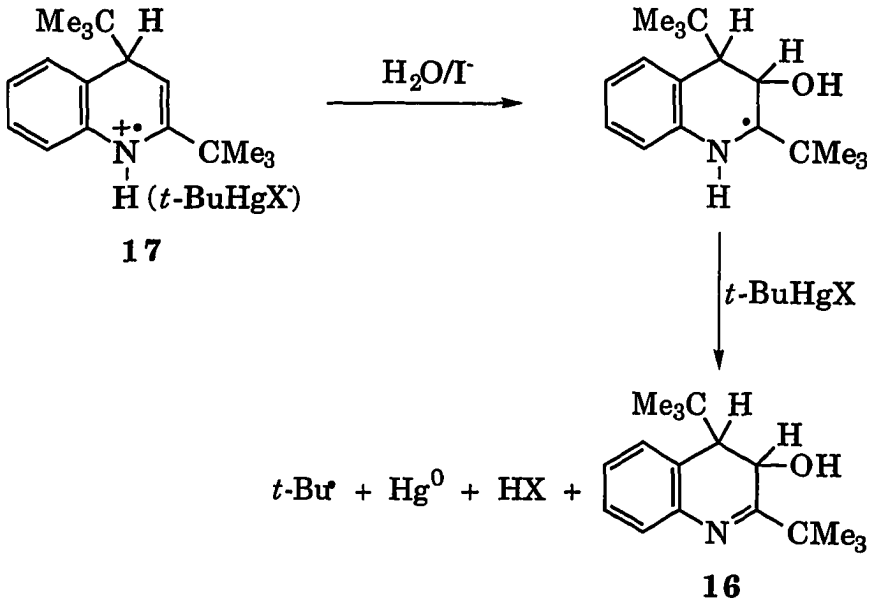
[c] Workup with $NaBH_4$/MeOH gave a 34% yield of **15** and 16% of **16**.

Scheme X. Photostimulated *tert*-Butylation of 2-*tert*-Butylquinoline by *tert*-Butylmercury Halides.



XI). However, the effect of I^- which increases the yield of **16** is puzzling. Perhaps the radical cation **17** forms an unstable iodide which is oxidized and hydrolyzed to **16**.

Scheme XI. Hydration of the Radical Cation **17**



In Chapter II the formation of **16** from reaction of *t*-BuHgCl/KI with quinoline N-oxide will be discussed. These results will demonstrate that the reaction proceeds by deoxygenation to form quinoline and that the yield of **16** formed from quinoline is increased by the addition of H_2O and is not increased by the presence of O_2. These results indicate that the major reaction pathway of **17** in the presence of I^- appears to be hydration by trace of H_2O to yield **16** (Scheme XI). However, **16** can undergo dehydration under the reaction conditions, particularly in the presence of PTSA, so that a relatively fast *tert*-butylation reaction is required for the detection of **16** as a reaction product. One effect of added I^- is to increase the rate of the reaction so that an appreciable conversion of 2-*tert*-butylquinoline to products is observed in a short period of time. Another possible effect of I^- is in the oxidation step of Scheme XI where the hydrated radical cation is connected to **16**. Possibly *t*-BuHgI is a better

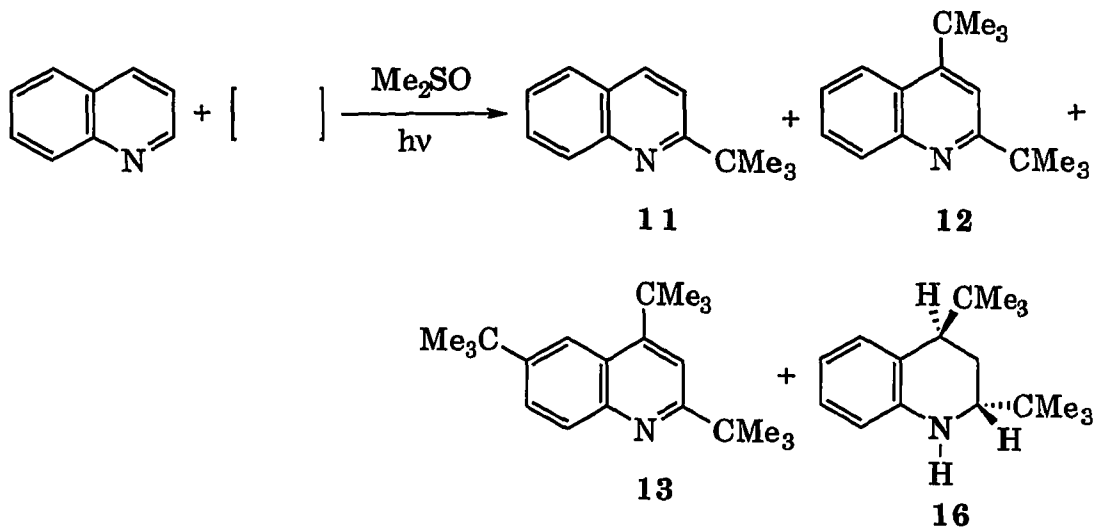
electron acceptor than *t*-BuHgCl in this step. Although I^- functions as a reducing agent in the conversion of **10** to **9**, the less readily reduced **17** appears to react by the hydration-oxidation steps of Scheme XI.

Photostimulated *tert*-Butylation of Quinoline by *tert*-Butylmercury Halides

Photolysis of *t*-BuHgCl with quinoline yielded 2-*tert*-butylquinoline **11** slowly, which could be further alkylated to 2,4-di-*tert*-butylquinoline **12** and 2,4,6-tri-*tert*-butylquinoline **13**. Only traces of 4-*tert*-butylquinoline were observed by GCMS. Surprisingly, in the presence of KI, a major product was *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline **18** formed as a single geometric isomer observed by ^1H NMR spectroscopy (see p. 36) and GCMS (Table V).

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 **19**, which can be subsequently protonated to form an iminium ion **20** that can readily add *t*-Bu· to yield **18** (Scheme XII).[34] The hydrate **16** might have been expected to form from **11** in the presence of I^-. However with a reaction time of 4 h in the presence of PTSA, **16** would have been dehydrated to give **12** (see Table IV). Formation of the tetrahydroquinoline analogous to **18** was not observed with quinaldine,[33] presumably because of steric restraint in the attack of *t*-Bu· upon the required iminium ion. It has been reported that whereas *n*-Bu· attacks quinoline in acid solution about equally at C-2 and C-4, *tert*-butylation

Table V. Photostimulated *tert*-Butylation of Quinoline by *t*-BuHgX in Me_2SO at 35–40 °C.[a]



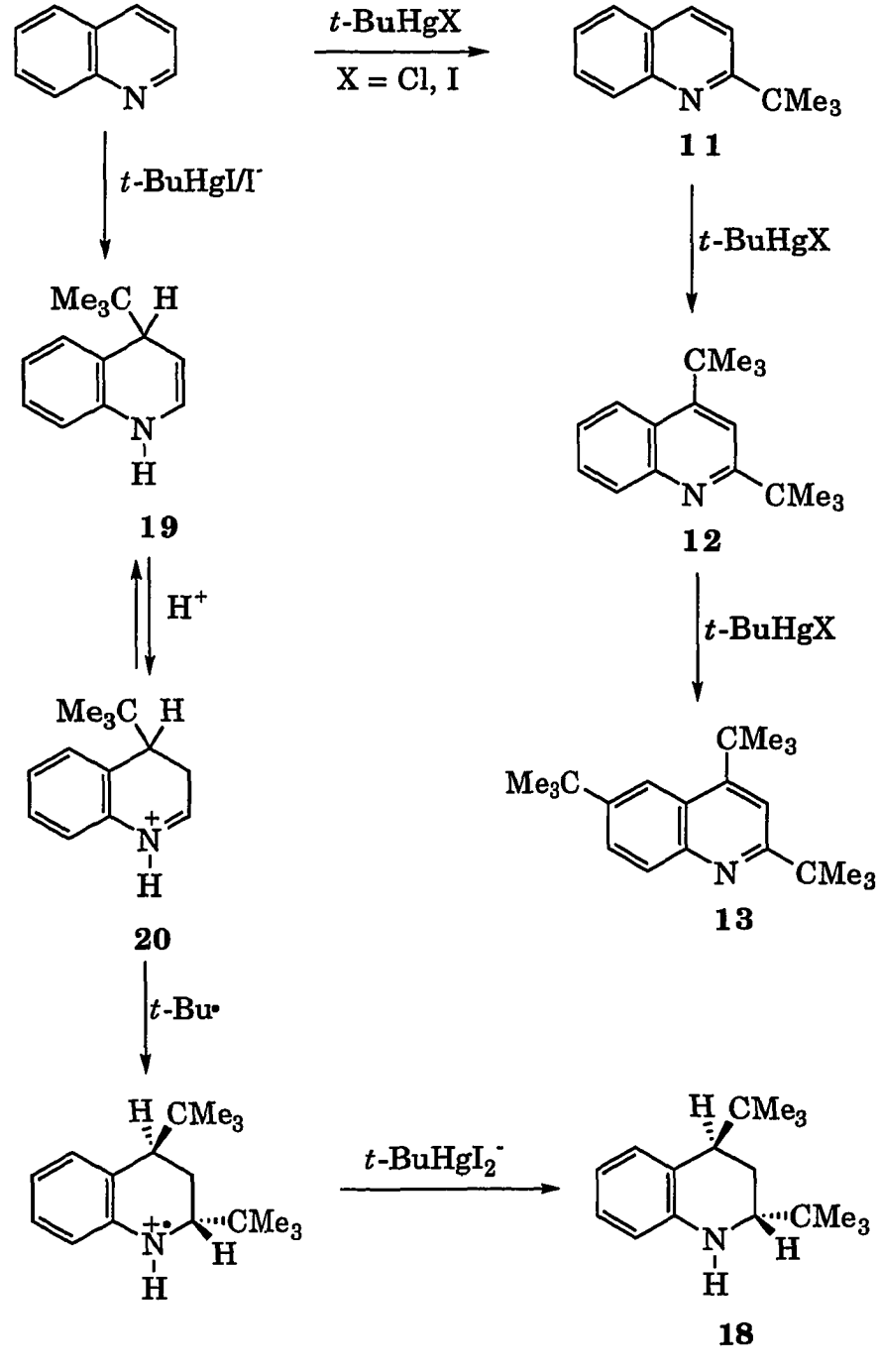
equivalents				yield (%)[b]			
t-BuHgCl	KI	PTSA	time (h)	**11**	**12**	**13**	**18**
4	0	0	9.5[c]	46	7	0	0
4	0	0	24[c]	40	45	tr	0
4	0	4	4[c]	54	4	0	0
4	8	0	4	35	11	0	44
4	4	4	9.5	0	30	10	44
4	8	4	4	tr	33	12	42
4	8	4	24	0	32	13	42

[a] 0.05 M quinoline irradiated by a 275 W fluorescent sunlamp.

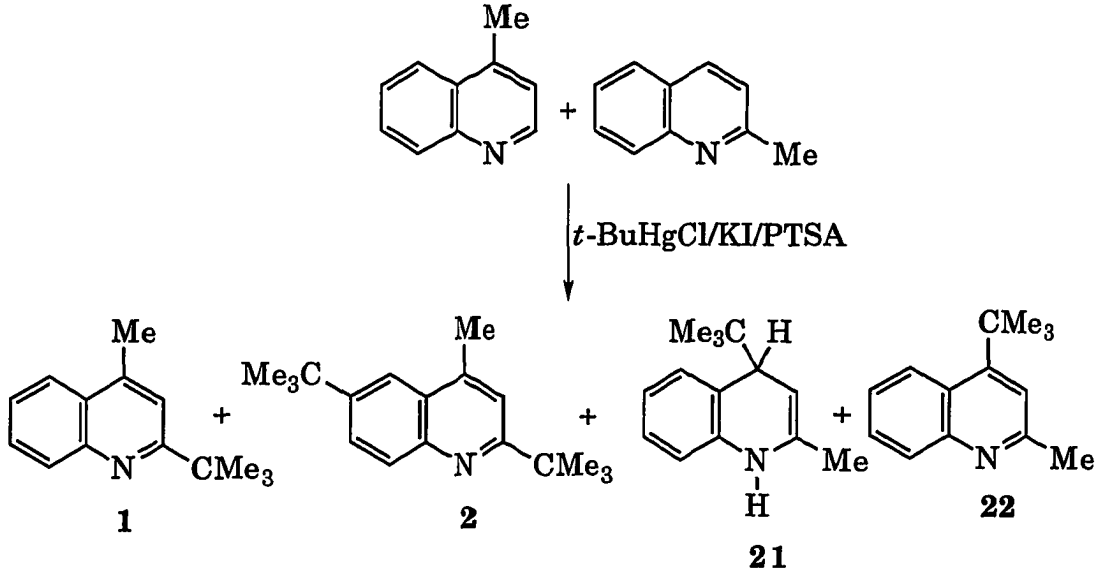
[b] By ^1H NMR with $PhCH_3$ as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] ~ 3% 4-*tert*-Butylquinoline detected by GCMS.

Scheme XII. Photostimulated *tert*-Butylation of Quinoline by *tert*-Butylmercury Halides.

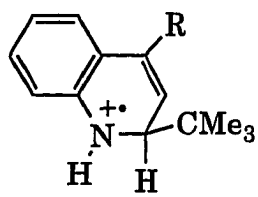


yields only 2-*tert*-butylquinoline.[45] An explanation based on steric hindrance was advanced[45]. It was also reported that, towards *t*-Bu·, lepidine is > 100 times as reactive as quinaldine in oxidative *tert*-butylation in acid solution.[41] Photolysis of lepidine and quinaldine in a 1:1 ratio with excess *t*-BuHgCl/KI/PTSA in Me_2SO at 35°C gave a mixture of **1**, **2**, 4-*tert*-butyl-1,4 -dihydro-2-methylquinoline **21**, and 4-*tert*-butyl-2-methylquinoline **22** as

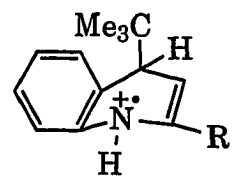


determined by ^{1}HNMR spectroscopy. A 20 min reaction gave 26% lepidine (**1**, **2**) and 13% quinaldine (**21**,**22**) derived products while after 1 hour, the yields increased to 87 and 45%, respectively. Lepidine attack is only about twice as readily as quinaldine by *t*-Bu·. Although essentially only products derived from initial addition of *t*-Bu· at C-2 of the quinolinium ion (**11**,**12**, **13**) are observed in the absence of a reducing agent, *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 (**11**, **12**, **13**) to 4-attack (**18**) is about 1.

The above observation may be interpreted in terms of the rate of proton loss from **23** or **24**. Compound **24** exists in a conformation that places H(4) in a quasi-equatorial position in the plane of the π-system of the radical cation. For steric and stereoelectronic reasons, this proton is lost slowly. On the other hand, Compound **23** would be expected to have a conformation with H(2) in a quasi-axial position. A large dihedral angle between the C(2)-H bond and the plane of the amine radical cation favors rapid proton loss. However, another



23



24

explanation can be advanced. In compound **24**, there would not be much hindrance to the approach of *t*-$BuHgI_2^-$ to the amine radical cation center and electron transfer would be expected to be fast. In compound **23**, this approach might be sterically hindered. Since **23** might not be readily reduced, proton loss could occur leading to the observed substitution product. On the other hand, compound **23** is a more localized radical cation than compound **24**. If steric effects are not important in the reduction, one might expert compound **23** to be more readily reduced.

Conclusion

Photolysis of *tert*-butylmercury halides with quinolines leads to alkylation products. With 4-methylquinoline and 4-chloroquinoline, only

substitutive products are observed. The reactions are not particularly promoted by PTSA, but the addition of KI and MeI lead to rate acceleration. With 2-substituted quinolines, both oxidative and reductive alkylation products are observed. The oxidative alkylation is promoted by PTSA, while the addition of KI gives rise to the reductive alkylation products. Hydration of the radical cation from the photolysis of *tert*-butylmercury halides with 2-*tert*-butylquinoline is important and the stable hydration product 2,4-di-*tert*-butyl-3,4-dihydro-3-hydroxyquinoline is obtained. 4-*tert*-Butyl-2-chloro-1,4-dihydroquinoline is readily hydrolyzed to form the amide. With quinoline itself, substitutive alkylation at C-4 is a minor process upon photolysis with *t*-BuHgCl/PTSA. Essentially, only 2-*tert*-butylquinoline is observed. In the presence of KI, *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline is obtained. 4-Attack is observed to be about as important as 2-attack.

Experimental Section

General Consideration

Analytical gas chromatography (GC) was performed on a Perkin-Elmer 3920 gas chromatography equipped with a Hitachi D-2500 Chromato-integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT 300 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane (300 MHz for ^{1}H NMR) or for ^{13}C NMR measured relative to the central line of internal $CDCl_3$ at 77.000 ppm (75.4 MHz for ^{13}C NMR). GCMS were recorded on a Finnegan 4000 spectrometer with Incos data system

and high resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Infrared spectra (IR) were recorded on an IBM IR-98 FT spectrometer or Digital FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

The products were isolated by flash column chromatography on silica gel (Kiesel gel, 230-400 mesh ATSM, purchased from EM Reagents Co.) with mixed solvents (hexane/ethyl acetate) as eluents. GC yields were determined by using an internal standard (toluene). ^{1}H NMR spectroscopy yields were determined by integration with a known amount of an internal standard (toluene or diiodomethane).

Solvents and Reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride and stored over 4 Å molecular sieves under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium metal. Other solvents were purchased and used without further purification.

Chemical reagents in high purity grades were purchased mostly from Aldrich Chemical Co. In most cases, the reagents were used without further purification.

Preparation of *tert*-Butylmercury Chloride

tert-Butylmercury chloride was prepared from mercuric chloride and *tert*-butyllithium by a modified literature method.[46] A solution containing mercuric chloride (0.18 mol) in dry ether (500 ml) was stirred in an ice bath under nitrogen and *tert*-butyllithium (0.17 mol, 1.7 M solution in pentane) was added dropwise. After the addition, the mixture was stirred for at least 4 hours at room temperature. The mixture was then poured into water and extracted 3 times with ether (500 ml each). The combined ether layer was washed with brine solution three times and dried over anhydrous magnesium sulfate. The solution was filtered through a celite-filled sintered glass funnel and the solvent was evaporated. The white precipitate was recrystallized from hexane/ether solution. The white needles melted at 110–113 °C (lit.[46] 123 °C); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H).

In an alternative method of preparation, a solution containing mercuric chloride (0.18 mol) in dry THF (200 ml) was stirred in an ice bath under nitrogen and *tert*-butyllithium (0.17 mol, 1.7 M solution in pentane) was added dropwise. After the addition, the mixture was stirred for 2 hours at room temperature. The solution was filtered through a celite-filled sintered glass funnel and the solvent was evaporated. The white precipitate was dissolved in 1500 ml of ether and washed three times with brine solution. Drying with anhydrous $MgSO_4$, evaporation, and two recrystallizations gave the white needles of *tert*-butylmercury chloride.

Materials

2-*tert*-Butylquinoline was prepared by the Minisci alkylation technique.[47] To a solution of quinoline (0.01 mol) and $AgNO_3$ (0.1 mol per mole of added peroxydisulphate) in 10% H_2SO_4 (0.01 mol) and trimethylacetic acid (0.05 mol), heated at 70 °C, was added, under stirring in about 10 min to a solution of $(NH_4)_2S_2O_8$ (0.02 mol) in H_2O (0.01 mol of peroxydisulphate was dissolved in 5 mL of H_2O), between 70 and 90 °C. After the emission of CO_2 stopped, stirring and heating were continued for 20 min. The solution was poured into ice and NH_3 aqueous solution, extracted with $CHCl_3$, the organic layer washed with 5% NaOH and H_2O, dried with $CaCl_2$, and the solvent evaporated. The product was isolated by column chromatography and identified by ^1H NMR ($CDCl_3$) δ 8.05 (d, J = 8.7 Hz, 2 H), 7.75 (dd, J = 8.1, 0.9 Hz, 1 H), 7.65 (ddd, J = 8.1 , 6.9, 1.2 Hz, 1 H), 7.51 (d, J = 8.7 Hz, 1 H), 7.48–7.43 (m, 1 H), 1.47 (s, 9 H) (lit.[47] 1.47 (s, 9 H), 7.2–8.2 (m, 6 H)).

General Procedure for the Photostimulated Reactions

The substrate (0.2–1.0 mmol), *t*-BuHgCl (0.2–4.0 mmol), and KI (0–8 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 x 50

mL) and saturated brine (50 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. Products were isolated by flash column chromatography with hexane/ethyl acetate as the eluent. All solids were recrystallized from hexane/ethyl acetate.

Photostimulated *tert*-Butylation Reactions of Quinolines Followed by $NaBH_4$ Reduction

A dry Pyrex tube containing substrate and coreactants dissolved in 2–10 mL of deoxygenated Me_2SO was equipped with a rubber septum. The solution was irradiated under N_2 atmosphere by a 275 W General Electric florescence sunlamp ca. 25 cm from the reaction tube. After the reaction, the solution was cooled and 1 mL MeOH of was added. Excess $NaBH_4$ was added in small portions over a period of 10 min until gas emission stopped. Water (25 mL) was added to the reaction mixture followed by extraction with three 15 mL portions of CH_2Cl_2. The combined CH_2Cl_2 extract was washed with water three times (50 mL each) and dried over $MgSO_4$. The solvent was evaporated and the NMR yield was determined with a known amount of internal standard. The mixture was analyzed by GC and each compound was isolated by flash column chromatography using hexane/ethyl acetate as eluents.

Photostimulated *tert*-Butylation Reactions of Quinolines with Added MeI

A dry Pyrex tube containing substrate and coreactants dissolved in 2–10 mL of deoxygenated Me_2SO was equipped with a rubber septum. MeI was then added by a syringe through the septum. The solution was irradiated under N_2

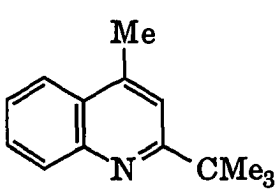
atmosphere by a 275 W General Electric florescence sunlamp ca. 25 cm from the reaction tube. The reaction mixture was poured into 50 mL of saturated aqueous $Na_2S_2O_3$ solution, neutralized if required, and extracted with CH_2Cl_2. The extract was washed with saturated aqueous $Na_2S_2O_3$ (3 x 50 mL) and saturated brine (50 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The NMR yield was determined with a known amount of internal standard. The mixture was analyzed by GC and each compound was isolated by flash column chromatography using hexane/ethyl acetate as eluents.

Purity of Products

Isolated products showed no significant impurities by GC and/or by ^1H NMR and are determined to be at least 97% pure.

Characterization of Products

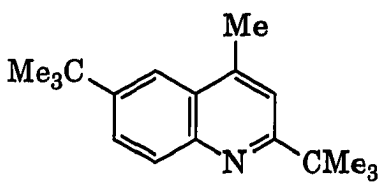
2-(1,1-Dimethyl)-4-methylquinoline (1)[48]



The compound was isolated as a liquid: ^1H NMR ($CDCL_3$) δ 8.05 (d, J = 8.1 Hz, 1 H), 7.91 (d, J = 8.1 Hz, 1 H), 7.66–7.61 (m, 1 H), 7.49–7.44 (m, 1 H), 7.34 (s, 1 H), 2.66 (s, 1 H), 1.45 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 168.82 (s), 147.25 (s), 143.53 (s), 129.91 (d), 128.61 (d), 126.47 (s), 125.31 (d), 123.31 (d), 118.82 (d), 37.89

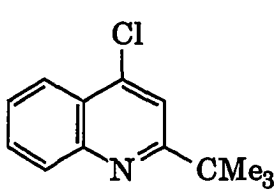
(s), 30.12 (q), 18.93 (q); GCMS m/z (relative intensity) 199 (M^+, 33), 184 (100), 157 (50), 143 (29), 115 (27), 77 (10); HRMS calcd for $C_{14}H_{17}N$ 199.1361, found 199.1359.

2,6-Bis(1,1-dimethylethyl)-4-methylquinoline (2)



This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 8.01 (d, J = 2.1 Hz, 1 H), 7.86 (d, J = 8.7 Hz, 1 H), 7.57 (dd, J = 8.7, 1.5 Hz, 1 H), 7.29 (d, J = 0.6 Hz, 1 H), 2.65 (d, J = 0.6 Hz, 3 H), 1.45 (s, 9 H), 1.43 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 168.89 (s), 151.80 (s), 147.40 (s), 143.16 (s), 125.17 (d), 124.40 (s), 124.13 (d), 122.96 (d), 118.29 (d), 37.86 (s), 34.97 (s), 31.22 (q), 30.19 (q), 18.83 (q); GCMS m/z (relative intensity) 255 (M^+, 37), 240 (100), 224 (27), 213 (84), 199 (19), 99 (74), 77 (7), 57 (8); HRMS calcd for $C_{18}H_{25}N$ 255.1987, found 255.1981.

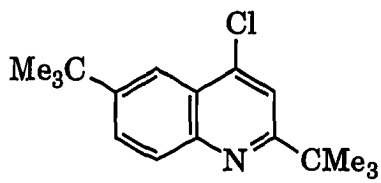
4-Chloro-2-(1,1-dimethylethyl)quinoline (6)



This compound was isolated as a liquid: ^1H NMR (CDCl3) δ 8.15 (dd, J = 8.4, 1.5 Hz, 1 H), 8.06 (br d, J = 8.1 Hz, 1 H), 7.73–7.67 (m, 1 H), 7.59 (s, 1 H),

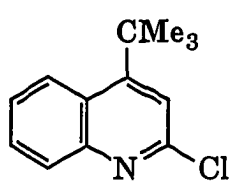
7.57–7.52 (m, 1 H), 1.45 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 169.23 (s), 148.23 (s), 142.20 (s), 129.84 (d), 129.66 (d), 126.53 (d), 124.56 (s), 123.62 (d), 118.37 (d), 38.21 (s), 29.97 (q); GCMS m/z (relative intensity) 222 (10), 220 (11), 219 (M^+, 28), 204 (100); HRMS calcd for $C_{13}H_{14}NCl$ 219.0815, found 219.0811.

4-Chloro-2,6-bis(1,1-dimethylethyl)quinoline (7)



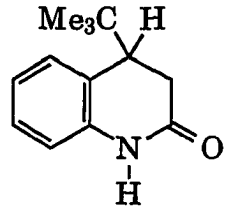
This compound was only detected by GCMS m/z (relative intensity) 277 (12), 275 (M^+, 33), 260 (100), 233 (57), 109 (15), 91 (10), 77 (6), 57 (11), 41 (35).

2-Cholo-4-(1,1-dimethylethyl)quinoline (8)



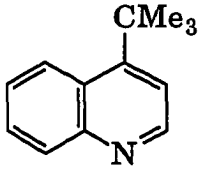
This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 8.37 (dd, J = 8.7, 1.2 Hz, 1H), 8.05 (dd, J = 8.1, 1.2 Hz, 1 H), 7.67–7.64 (m, 1 H), 7.56–7.50 (m, 1 H), 7.33 (s, 1 H), 1.61 (s, 9H); GCMS m/z (relative intensity) 221 (24), 220 (11), 219 (M^+, 78), 204 (100), 184 (94), 168 (34), 77 (22), 57 (29), 41 (49).

4-(1,1-Dimethylethyl)-3,4-dihydro-2(1H)-quinolinone (9)



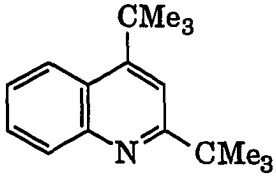
This compound was isolated as a solid: mp 116–117 °C; ^{1}H NMR ($CDCl_3$) δ 9.66 (s, 1H), 7.16 (td, J = 7.5, 1.2 Hz, 1H), 7.10 (dd, J = 7.8, 1.8 Hz, 1 H), 6.94 (dd, J = 7.5, 1.2 Hz, 1 H), 6.87 (dd, J = 7.8, 1.2 Hz, 1 H), 2.87–2.79 (m, 1 H), 2.70–2.61 (m, 2 H), 0.91 (s, 9 H); ^{13}C NMR ($CDCl_3$), δ 172.83 (s), 137.62 (s), 130.90 (d), 127.62 (d), 124.14 (s), 122.02 (d), 115.91 (d), 46.57 (d), 35.26 (s), 32.72 (t), 27.55 (q); GCMS m/z (relative intensity) 205 (0.2), 204 (3), 203 (M^+, 18), 164 (10), 146 (100), 128 (27), 77 (9), 57 (32); HRMS calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1314; 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)quinoline



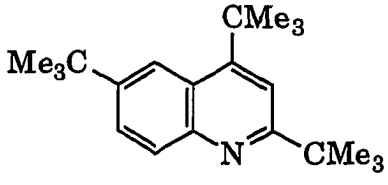
This compound was detected by GCMS only. GCMS m/z (relative intensity) 186 (8), 185 (M^+, 49), 170 (100), 154 (23), 143 (10), 77 (14), 57 (4).

2,4-Bis(1,1-dimethylethyl)quinoline (12)



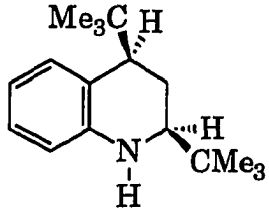
This compound was identified by ^{1}H NMR and GCMS: ^{1}H NMR ($CDCl_3$) δ 8.33 (dd, J = 8.4, 1.2 Hz, 1 H), 8.10 (dd, J = 8.4, 1.2 Hz, 1 H), 7.62–7.56 (m, 1 H), 7.47 (s, 1 H), 7.46–7.40 (m, 1 H), 1.61 (s, 9 H), 1.46 (s, 9 H); GCMS m/z (relative intensity) 242 (8), 241 (M^+, 44), 226 (100), 199 (65), 185 (13), 128 (7), 77 (6), 57 (9).

2,4,6-Tris(1,1-dimethylethyl)quinoline (13)



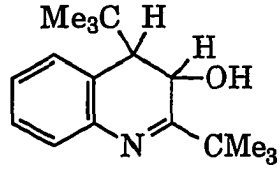
This compound was identified by ^{1}H NMR and GCMS: ^{1}H NMR ($CDCl_3$) δ 8.27 (d, J = 9.0 Hz, 1 H), 8.04 (d, J = 2.1 Hz, 1 H), 7.53 (dd, J = 9.0, 2.1 Hz, 1 H), 7.42 (s, 1 H), 1.60 (s, 9 H), 1.46 (s, 9H), 1.43 (s, 9H); GCMS m/z (relative intensity) 298 (12), 297 (M^+, 58), 282 (100), 255 (86), 241 (12), 134 (11), 120 (23), 57 (26), 41 (29).

cis-2,4-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydroquinoline (15)



Reduction of the *tert*-butylation reaction products from 2-*tert*-butylquinoline in the presence of KI by $NaBH_4$/MeOH yielded the title compound: mp 44.0–44.5 °C; ^1H NMR ($CDCl_3$) δ 7.18 (br d, J = 7.5 Hz, 1 H), 6.98 (td, J = 7.5, 1.5 Hz, 1 H), 6.66 (td, J = 7.5, 1.2 Hz, 1 H), 6.58 (dd, J = 7.8, 1.2 Hz, 1 H), 3.50 (br s, N-H), 2.70 (~ t, J = 8.7 Hz, H-2a), 2.65 (dd, J = 12.0, 3.6 Hz, H-4a), 2.04 (ddd, J = 13.2, 9.3, 3.6 Hz, H-3e), 1.67 (ddd, J = 13.2, 12.0, 7.8 Hz, H-3a), 0.97 (s, 9H), 0.94 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 149.72 (s), 130.65 (d), 126.35 (s), 126.09 (d), 117.34 (d), 115.37 (d), 63.19 (d), 45.64 (d), 36.00 (s), 33.39 (s), 28.76 (q), 28.14 (t), 26.29 (q); GCMS m/z (relative intensity) 246 (2), 245 (M^+, 10), 188 (100), 130 (33), 57 (17); HRMS calcd for $C_{17}H_{27}N$ 245.2144, found 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.

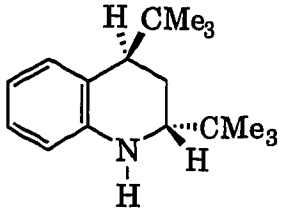
2,4-Bis(1,1-dimethylethyl)-3,4-dihydro-3-hydroxyquinoline (16)



This compound was isolated as a solid: mp 125–126 °C; ^1H NMR ($CDCl_3$) δ 7.16–7.42 (m, 4 H), 4.52 (dd, J = 9.3, 1.2 Hz, 1 H), 2.68 (d, J = 1.2 Hz, 1 H), 1.65

(d, J = 9.6 Hz, 1 H), 1.35 (s, 9 H), 0.88 (s, 9 H); ^{1}H NMR ($CDCl_3$ plus D_2O) δ 7.16–7.42 (m, 4 H), 4.51 (s, 1 H), 2.67 (s, 1 H), 1.35 (s, 9 H), 0.88 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 176.81 (s), 143.64 (s), 131.83 (d), 127.79 (d), 127.11 (d), 126.18 (d), 125.18 (s), 61.30 (d), 54.52 (d), 39.17 (s), 33.90 (s), 28.58 (q), 28.02 (q); GCMS m/z (relative intensity) 259 (M^+, 40), 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); HRMS Calcd for $C_{17}H_{25}NO$ 259.1936, found 259.1929; FTIR 1614, 3281 cm^{-1}; 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.

trans-**2,4-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydroquinoline (18)**



The *trans* isomer formed in the *tert*-butylation of quinoline was isolated as a solid: mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 7.01–6.95 (m, 2 H), 6.52 (td, J = 7.2, 0.9 Hz, 1 H), 6.46 (dd, J = 7.8, 0.6 Hz, 1 H), 3.86 (s, NH), 3.21 (dd, J = 12.9, 4.2 Hz, H-2a), 2.49 (dd, J = 5.1, 2.1 Hz, H-4e), 2.11 (ddd, J = 13.5, 4.2, 2.1 Hz, H-3e), 1.42 (td, J = 13.5, 5.1 Hz, H-3a), 0.95 (s, 9 H), 0.93 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 145.10 (s), 130.52 (d), 127.04 (d), 122.49 (s), 114.80 (d), 113.11 (d), 57.32 (d), 45.66 (d), 34.94 (s), 34.35 (s), 29.22 (d), 25.81 (q), 24.40 (q); GCMS m/z (relative intensity) 245 (M^+, 10), 188 (100), 132 (13), 130 (24), 91 (2), 77 (5), 57 (12); HRMS Calcd for

$C_{17}H_{27}N$ 245.2144, found 245.2141; 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.

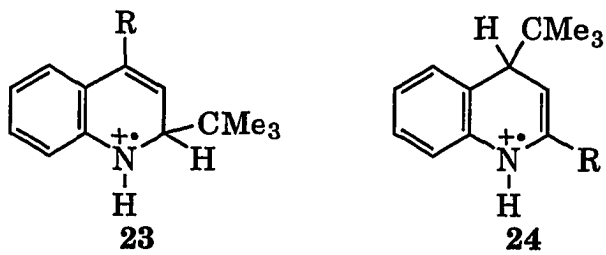
CHAPTER II. PHOTOSTIMULATED *tert*-BUTYLATION OF QUINOLINIUM CATIONS AND QUINOLINE *N*-OXIDES BY *tert*-BUTYLMERCURY HALIDES

Introduction

Quinoline *N*-oxides are characterized by the presence of a so-called "donative" (or "coordinative covalent") bond between nitrogen and oxygen, namely, of a covalent bond formed by the overlap of the nonbonding electron pair on the nitrogen with an empty orbital on the oxygen atom. They do not fit well into the normal classification of π-deficient and π-excessive heterocycles.[49-53] Like the parent heterocyclics, these compounds are electron-poor aromatics, and this leads to the expectation of easy nucleophilic substitution of substituents in α and γ to the *N*-oxide group. However, both electrophilic and nucleophilic aromatic substitutions occur on these compounds, and even in the latter class of reaction, the scope is remarkably different from the parent heterocycles.[49] Electrophilic attack at the oxygen atom is obviously facile, and the role of the quaternary salts is central in a great number of reactions leading in the end to functionalized heterocycles.

The system *t*-BuHgCl/KI is a unique one, because it not only generates *tert*-butyl radical upon photolysis in Me_2SO, but also serves as an oxidizing or reducing agent toward easily oxidizable or reducible radicals or radical ions. In the presence of *t*-BuHgCl/KI, the adduct radical cations formed by the addition of *t*-Bu· to a quinolinium cation can undergo either reduction or proton loss followed by oxidation. Previous work has demonstrated that the 2-

and 4-*tert*-butylquinolinium adduct radical cations **23** and **24** show quite different reactivities in the presence of *t*-BuHgI/KI in Me_2SO.[31] The adduct **23**

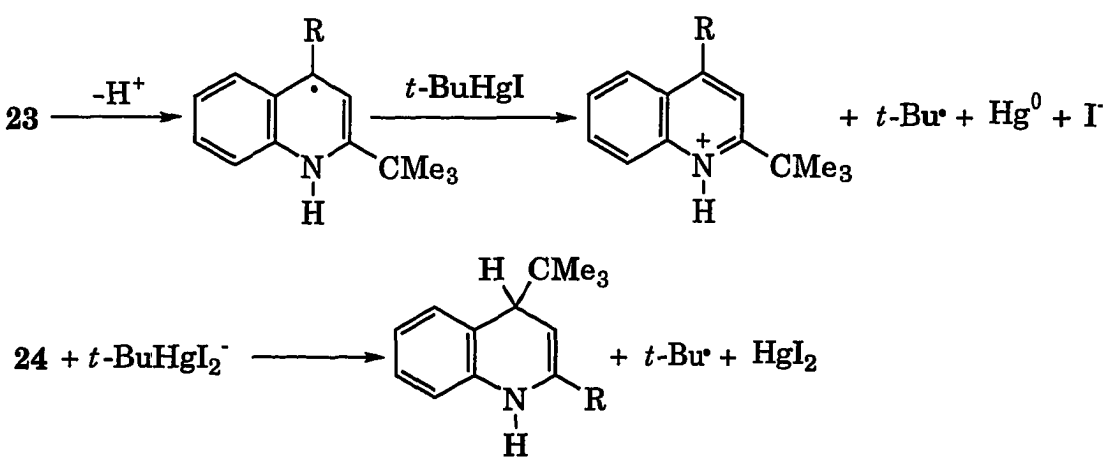


23 **24**

R = H, Me, Cl

loses a proton to form an easily oxidized quinolinyl radical, while the adduct **24** undergoes electron transfer with I^- or *t*-$BuHgI_2^-$ to form the 1,4-dihydroquinoline derivative (Scheme XIII). These observations are consistent with either **23** losing a proton more readily than **24** (for stereoelectronic

Scheme XIII. Oxidative and Reductive Reactions of Quinolinium Radical Cations.



reactions) or with **24** being more easily reduced than **23**, possibly for steric reactions.

In this chapter, photolysis of *tert*-butylmercury halides with quinoline derivatives, the *N*-methyl and *N*-methoxy quinolinium salts and quinoline *N*-oxides, has been studied. The results indicate that probably the ease of reduction of **23** and **24** is not important in determining whether an oxidative or reductive alkylation occurs. The case of proton loss appears to control the alkylation pathway.

Results and Discussion

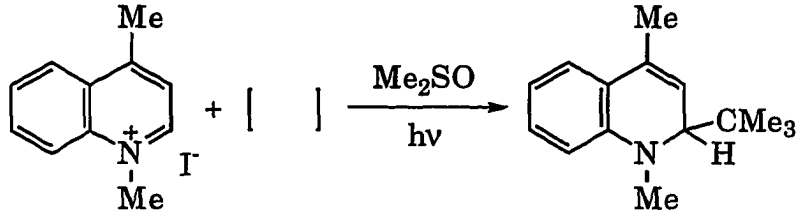
tert-Butylation of *N*-Methylquinolinium Salts

Photolysis of *N*-methyllepidinium iodide with 4 equiv of *t*-BuHgCl and 0–8 equiv of KI in Me_2SO for 2 hours produced the 1,2-dihydroquinoline derivative **25** in 85–90% yield (Table VI).

Attack of the *t*-butyl radical at C-2 position of the quinolinium cation gives the *N*-centered radical cation **26**, which is reduced by I^- and/or *t*-$BuHgI_2^-$ without loss of the proton at C-2. The low acidity of the adduct radical cation may be connected with an expected increase in strain from the vicinal *t*-Bu and Me interactions upon deprotonation (Scheme XIV).

Photolysis of 4-chloro-*N*-methylquinolinium iodide with 4 equiv of *t*-BuHgCl for 2 h produced only 7% of **27** and 37 % of the demethylated product, 2-*tert*-butyl-4-chloroquinoline **6**. Since **27** is relatively stable under the reaction conditions, the major reaction course yielding the product **6** was apparently

Table VI. Photostimulated Reaction of *t*-BuHgX with *N*-Methyllepidinium Iodide.[a]



25

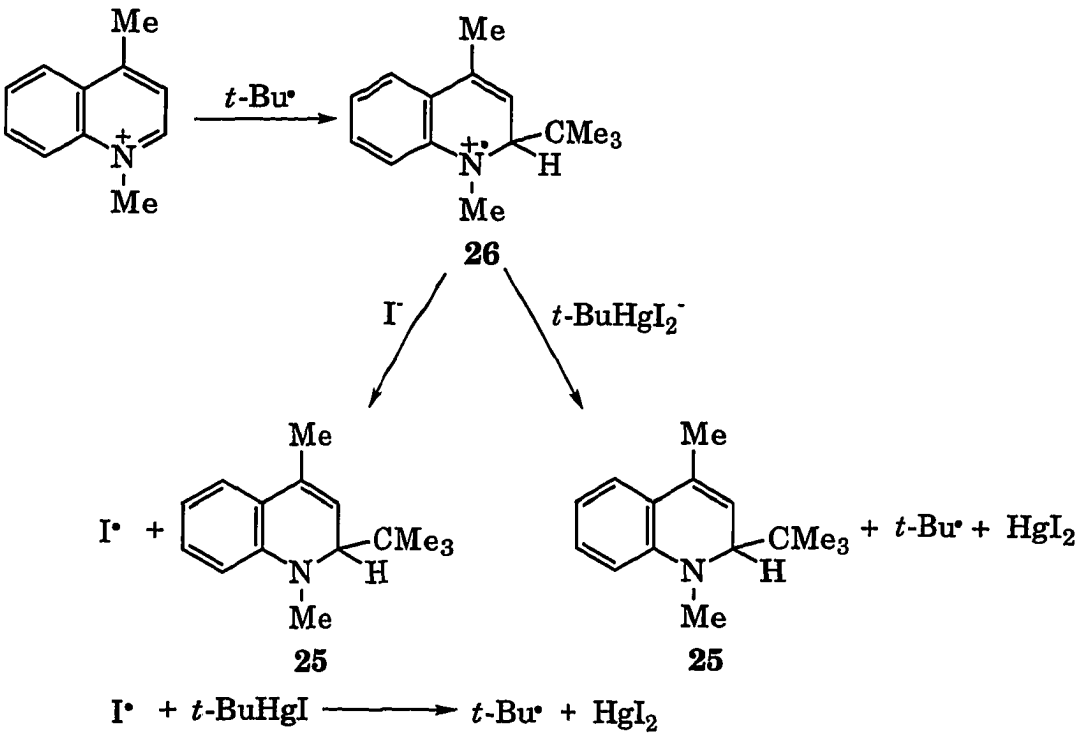
equivalents			yield(%)[b]
t-BuHgCl	KI	time (h)	**25**
4	0	2	85
4	4	2	90
4	8	2	90

[a] 0.5 mmol in 10 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

demethylation to form 4-chloroquinoline, followed by substitutive *tert*-butylation. In the presence of 8 equiv of KI, the yield of **27** increased to 89% with only 7% of the demethylated product **6**. The presence of I^- increases not only the reducing ability of *t*-BuHgCl but also the rate of photochemical formation of *t*-Bu·.[29] Thus, in the presence of KI, a fast free radical alkylation replaces the slow demethylation observed in its absence (Table VII and Scheme XV).

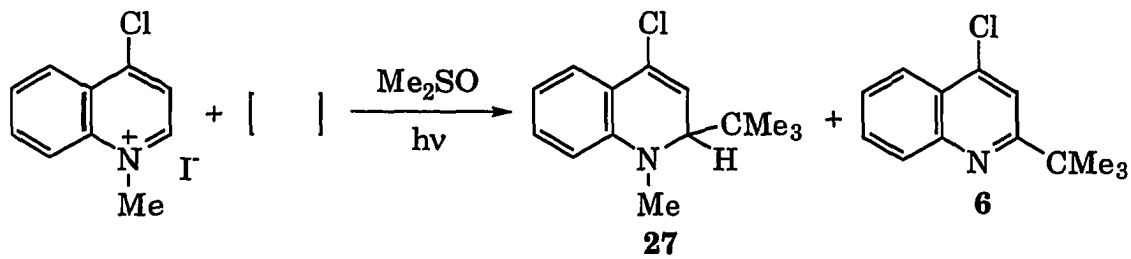
Scheme XIV. Photolysis of *t*-BuHgX with *N*-Methyllepidinium Iodide.



2-Chloro-*N*-methylquinolinium iodide when subjected to the workup conditions of $Na_2S_2O_3$ aqueous solution, underwent hydrolysis to form 1-methyl-2(1H)-quinolinone **28**.

Photolysis of *t*-BuHgX with 2-chloro-*N*-methylquinolinium iodide formed after workup 4-*tert*-butyl-3,4-dihydro-1-methyl-2(1H)-quinolinone **29** and 1-methyl-2(1H)-quinolinone **28**. With 4 equiv of *t*-BuHgCl and 8 equiv of KI for 2 hours, 44% of **29** and 30% of **28** were observed. Continuing the reaction for 16 hours did not increase the yield of **29**, but reduced the yield of **28** to 7% (Table VIII). The most reasonable interpretation for the formation of **29** is that the

Table VII. Photostimulated Reactions of *t*-BuHgX with 4-Chloro-*N*-methylquinolinium Iodide.[a]

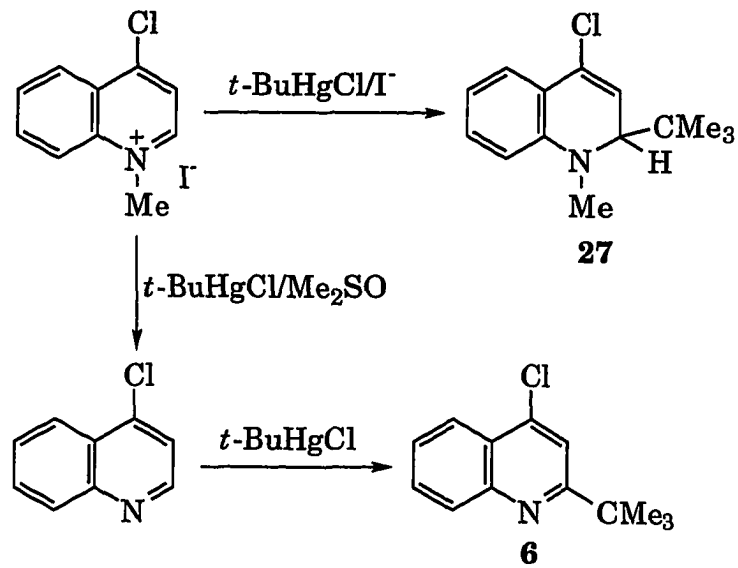


equivalents			yield (%)[b]	
t-BuHgCl	KI	time (h)	**27**	**6**
4	0	2	7	37
4	4	2	81	10
4	8	2	89	7

[a] 0.5 mmol in 10 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

Scheme XV. Photolysis of *t*-BuHgX with 4-Chloro-*N*-methylquinolinium Iodide.

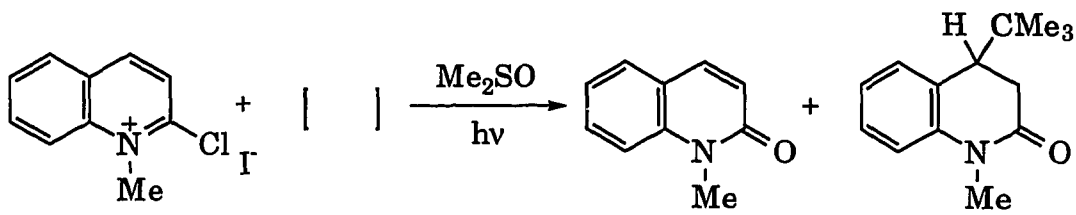


reaction with *t*-BuHgCl/KI forms 4-*tert*-butyl-2-chloro-1,4-dihydro-1-methylquinoline **30,** which is hydrolyzed to **29** upon workup (Scheme XVI).

N-Methylquinaldinium iodide yielded 4-*tert*-butyl-1,4-dihydro-1,2-dimethylquinoline in 90% yield upon photolysis with *t*-BuHgCl/KI in Me_2SO solution.[31] Attempts to make 2-*tert*-butyl-*N*-methylquinolinium iodide from 2-*tert*-butylquinoline were not successful, presumably because of the steric hindrance of the *tert*-butyl group at the C-2 position.

Photolysis of *t*-BuHgX with *N*-methylquinolinium iodide initially produces **31** (and possibly its 1,2-dihydro isomer). Further reaction converts **31** into a single stereoisomer **32** in a process that occurs more readily in the presence of PTSA (Table IX). For example, with 8 equiv of KI for 0.5 h, 81% of **31** and 12% of **32** were formed. At a longer reaction time (4 h), **31** was mostly

Table VIII. Photostimulated Reactions of *t*-BuHgX with 2-Chloro-*N*-methylquinolinium Iodide.[a]



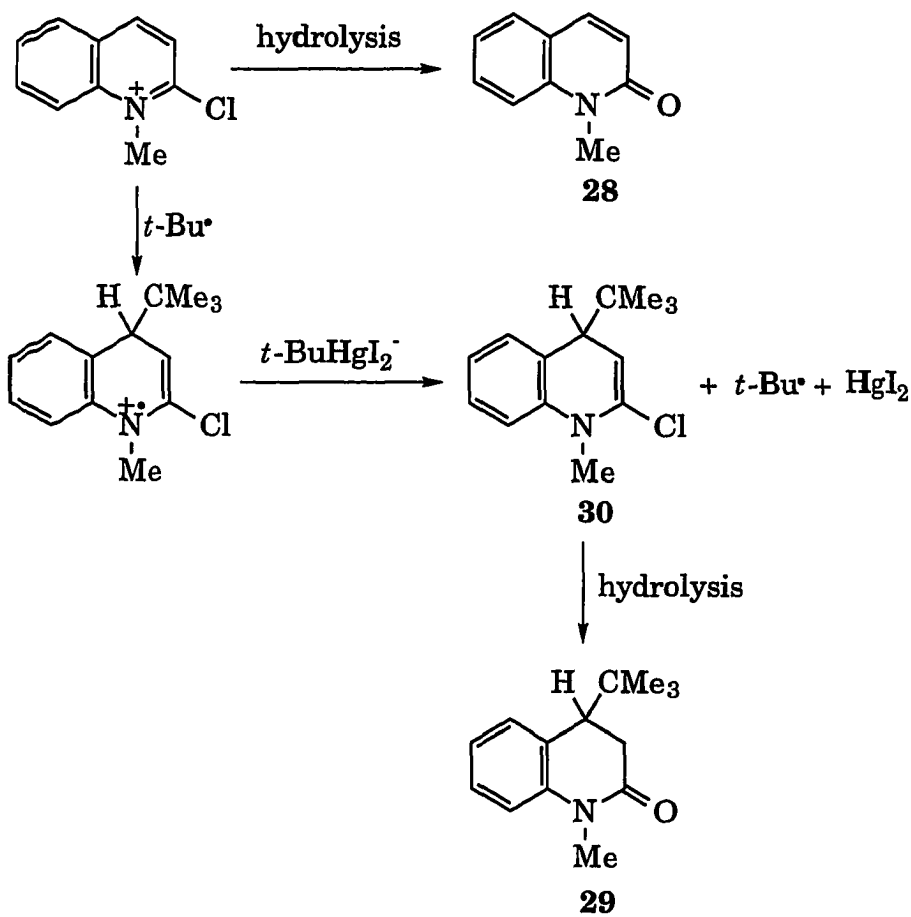
28 **29**

equivalents			yield (%)[b]	
t-BuHgCl	KI	time (h)	**28**	**29**
4	0	2	41	13
4	4	2	30	36
4	8	2	30	44
4	8	16	7	44

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

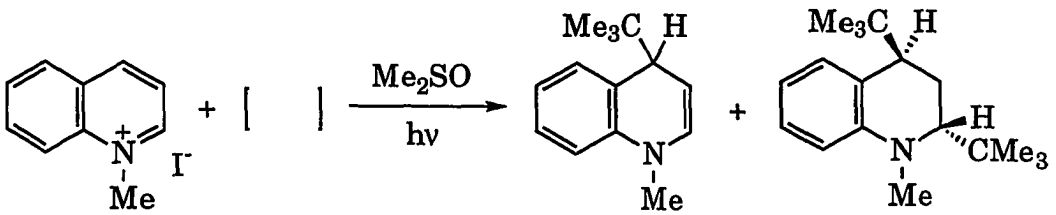
Scheme XVI. Photolysis of *t*-BuHgX with 2-Chloro-*N*-methylquinolinium Iodide.



converted to **32** since 82% of **32** and 7% of **31** were detected. PTSA dramatically increased the rate of the formation of compound **32,** since 84% of **32** was formed in 0.5 h in its presence.

Scheme XVII is apparently being followed. The attack of *t*-Bu· upon quinolinium ion is not selective and nearly equal amounts of attack occur at C-

Table IX. Photostimulate Reactions of *t*-BuHgX with *N*-Methylquinolinium Iodide.[a]



31 **32**

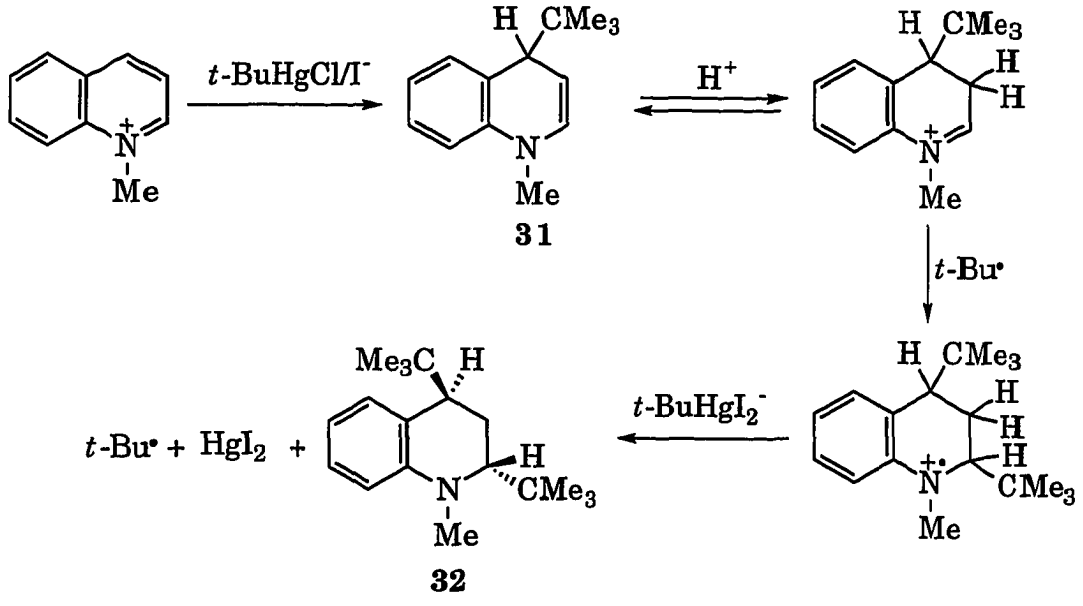
equivalents				yield (%)[b]	
t-BuHgCl	KI	PTSA	time (h)	**31**	**32**
4	0	0	2	10	tr
4	4	0	0.5	86[c]	8
4	4	0	4	10	80
4	8	0	0.5	81[c]	12
4	8	0	4	7	82
4	8	4	0.5	0	84

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] A mixture of two isomers in a 3.5:1 ratio.

Scheme XVII. Photolysis of *t*-BuHgX with *N*-Methylquinolinium Iodide *tert*-Butylation of *N*-Methoxyquinolinium Salts.



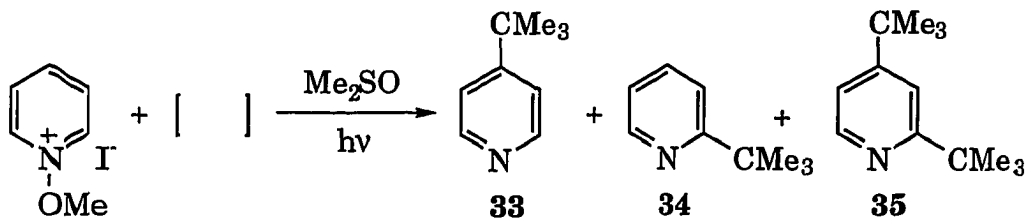
2 and C-4.[31] However, with the *N*-methyl derivative, attack occurs selectively at C-4, undoubtedly for steric reasons.

tert-Butylation of *N*-Methoxyquinolinium Salts

In most cases, photolysis of the perchlorate salts with *t*-BuHgCl/KI in Me_2SO gave demethoxylated alkylation products. In general, it appears that *tert*-butylation precedes demethoxylation. Photolysis of *t*-BuHgX with *N*-methoxypyridinium iodide forms 2- and 4-*tert*-butylpyridines with a para/ortho ratio greater than that observed from pyridine or pyridinium ion. Photolysis

with 4 equiv of *t*-BuHgCl for 2 hours produced 4-*tert*-butylpyridine **33** (71%) and 2-*tert*-butylpyridine **34** (23%) with a trace of 2,4-di-*tert*-butylpyridine **35**. With 4 equiv of KI added, similar yields were observed (*p/o* = 3.5) in 30 min of sunlamp photolysis (Table X). The *p/o* ratio observed with pyridinium ion itself depends

Table X. Photostimulated Reactions of *t*-BuHgX with *N*-Methoxypyridinium Iodide.[a]



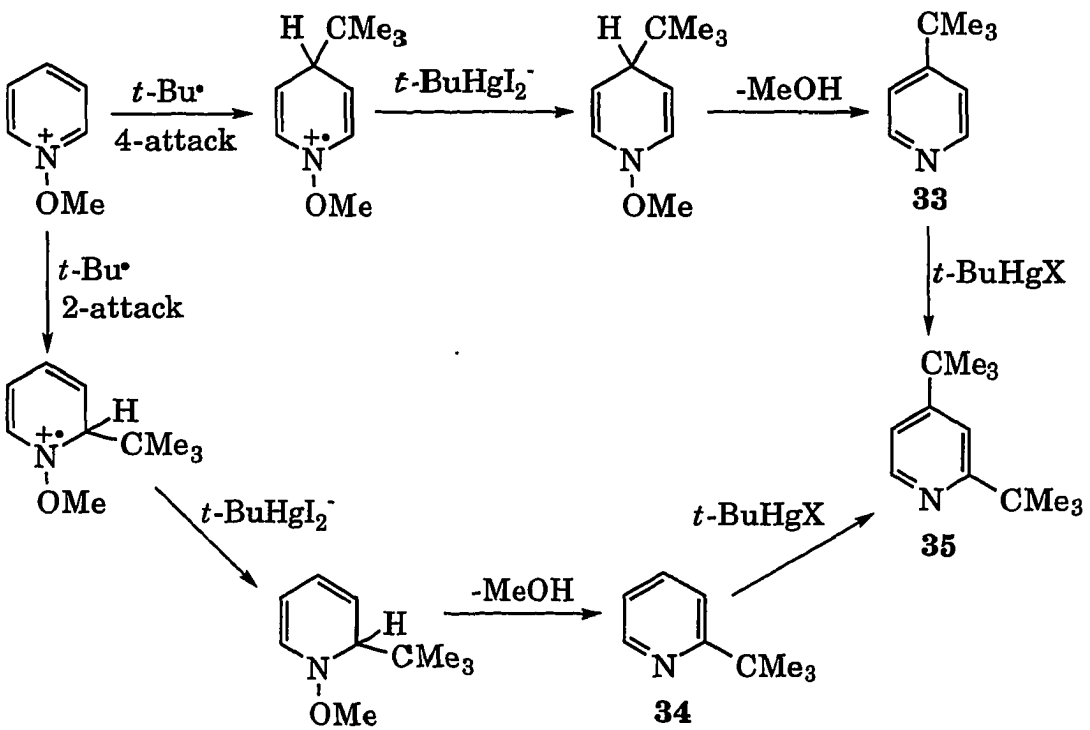
equivalents			yield (%)[b]		
t-BuHgCl	KI	time (h)	**33**	**34**	**35**
4	0	2	71	23	tr
4	0	24	5	–	73
4	4	2	56	20	12
4	8	0.5	70	21	tr
4	8	2	52	18	15

[a] 0.5 Mmol in 10 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

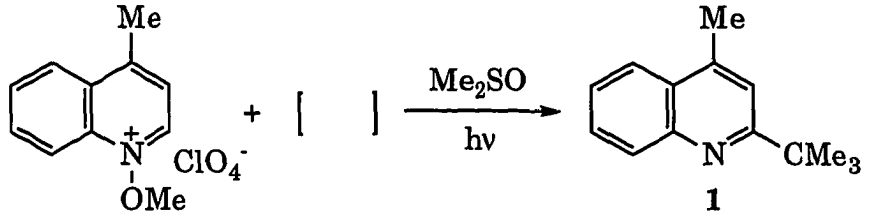
somewhat upon the reaction conditions, but is usually in the range of 1–2, while in the absence of a protonating agent pyridine initially gave a *p/o* ratio of ~0.5.[31] The higher selectivity observed for *N*-methoxypyridinium ion suggests that the reaction may involve 2- and 4-*tert*-butyl-*N*-methoxydihydropyridines that lose MeOH to form the observed products (Scheme XVIII).

Scheme XVIII. Photolysis of *t*-BuHgX with *N*-Methoxypyridinium Iodide.



Photolysis of *N*-methoxy-4-methylquinolinium perchlorate with *t*-BuHgCl with or without added KI rapidly forms 2-*tert*-butyl-4-methylquinoline **1**. With 4 equiv of *t*-BuHgCl and 4–8 equiv of KI, a yield of 90–93% was observed in 15–30 min (Table XI). In the absence of KI, 82% of 2-*tert*-butyllepidine was

Table XI. Photostimulated Reactions of *t*-BuHgX with *N*-Methoxy-4-methylquinolinium Perchlorate.[a]



equivalents			yield (%)[b]
t-BuHgCl	KI	time (h)	1
4	0	0.5	82
4	4	0.5	93
4	8	0.5	90
4	8	0.25[c]	89

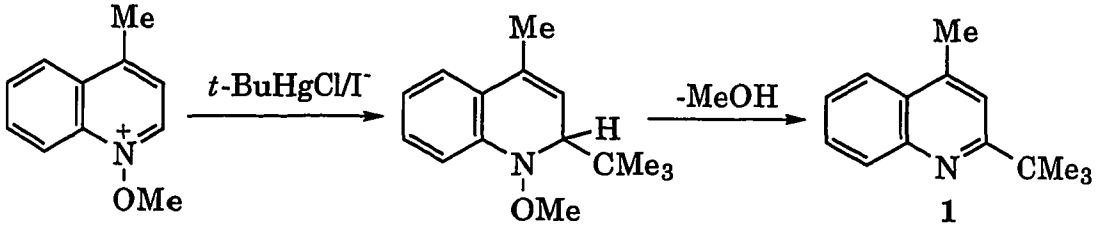
[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] Workup with $NaBH_4$/MeOH.

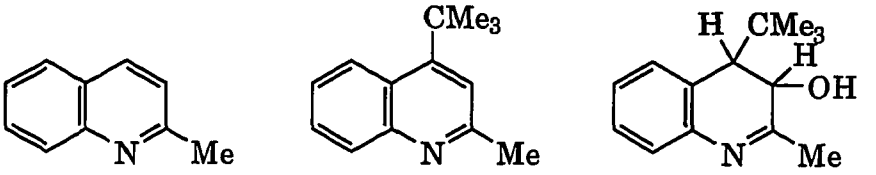
formed in 0.5 h while 71% of it was formed in 2 h for the *tert*-butylation of lepidine (see Chapter I). The reaction with *N*-methoxylepidinium salt is faster than with lepidine. This suggests that the reaction initially formed a reductive alkylation product **38**, followed by the loss of MeOH (Scheme XIX).

Scheme XIX. Photolysis of *t*-BuHgX with *N*-Methoxy-4-methylquinolinium Perchlorate.



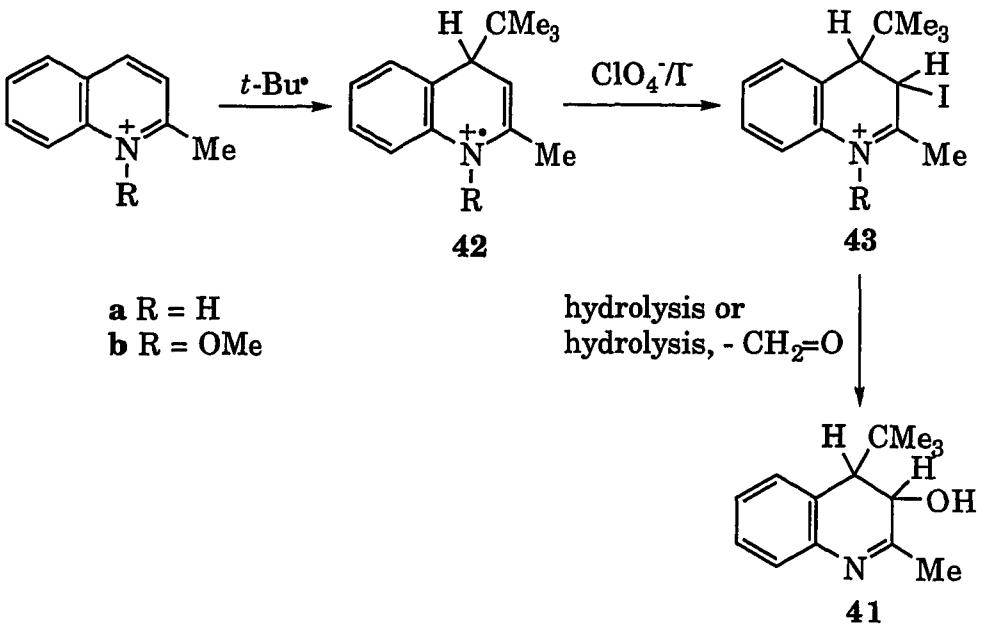
38 **1**

In the absence of added KI, photolysis of *N*-methoxy-2-methylquinolinium perchlorate forms quinaldine and its 4-*tert*-butyl derivative **40** (Table XII). Possibly the elimination of CH_2=O from the *N*-methoxy salt occurred prior to *tert*-butylation. The presence of perchlorate ion has a dramatic effect on the reaction since the hydrate **41** is not produced in the reaction of quinaldinium tosylate with *t*-BuHgCl/KI in Me_2SO, even in the presence of 1 equiv of H_2O.[31] The hydrate becomes the major product in the reaction of quinaldinium perchlorate with *t*-BuHgCl/KI. Apparently, the perchlorate yields a species which can trap the radical cation **42** with R = OMe or H. Molecular iodine is a likely possibility. Hydrolysis of **43a** or hydrolysis and elimination of CH_2=O from **43b** could lead to **41** (Scheme XX).



39 **40** **41**

Scheme XX. Photolysis of *t*-BuHgX with Quinaldinium and *N*-Methoxyquinaldinium Perchlorates.



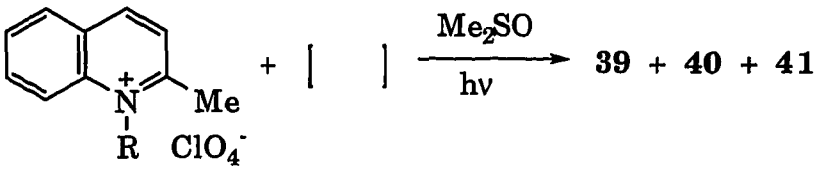
42 **43**

a R = H
b R = OMe

41

Qualitatively, the products formed from quinaldinium and *N*-methoxyquinaldinium perchlorates are similar although quantitative differences exist. As shown in Table XII, the reactions of the *N*-methoxy

Table XII. Reaction of Quinaldinium and *N*-Methoxyquinaldinium Perchlorates with *t*-BuHgCl in Me_2SO.[a]



R = H, OCH_3

	equivalents				yield (%)[b]	
R	*t*-BuHgCl	KI	time (h)	**39**	**40**	**41**
H	4	0	1	88	0	6
H	4	4	1	30	10	45
OCH_3	4	0	0.5	12	32	0
OCH_3	4	0	2	19	69	0
OCH_3	4	0	0.5[c]	38	37	0
OCH_3	4	4	0.5	9	14	26
OCH_3	4	8	0.25[d]	0	0	55
OCH_3	4	8	0.5	0	4	38

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] 4 Equiv of PTSA added.

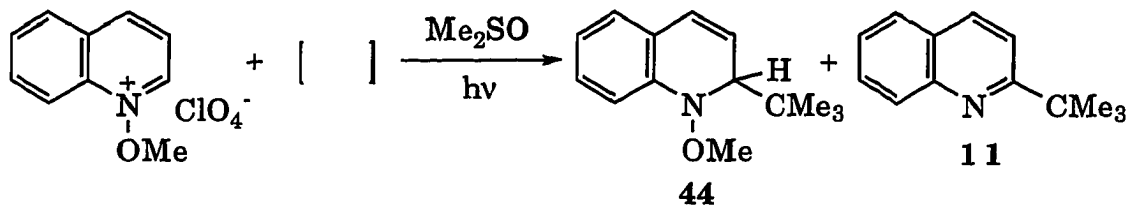
[d] Workup with $NaBH_4$/MeOH formed 4-*tert*-butyl-2-methyl-1,2,3,4-tetrahydroquinoline in 56% yield.

derivative are much faster than quinaldinium ion itself, suggesting that alkylation precedes demethoxylation.

Photolysis of *t*-BuHgCl/KI with *N*-methoxyquinolinium perchlorate yielded mainly the reductive alkylation product **44** (Table XIII). From steric considerations, *t*-Bu· should attack the *N*-methoxyquinolinium ion mainly at C-4 as observed for *N*-methylquinolinium cation. However, the experimental results show that at least 90% of the attack occurred at C-2 to form **45**. Moreover, **45** did not readily lose the proton from C-2 and in the presence of I^-, underwent reduction to form the 1,2-dihydroquinoline derivative **44** (Scheme XXI). Compound **44** was difficult to isolate by column chromatography, but treatment of the crude reaction product with either PTSA or NaOMe at 85 °C gave good yields of 2-*tert*-butylquinoline **11** (Table XIII). This result clearly demonstrates that with quinolinium ion itself, the formation of the substitutive (oxidative) alkylation product from C-2 attack but the additive (reductive) alkylation product from C-4 attack, can not be reasonably explained by postulating that electron transfer from I^- or *t*-$BuHgI_2^-$ to **23** does not occur readily because with **45**, reduction is the dominant reaction.

From Table XIII, it is clear that over 90% of the products formed result from *t*-Bu· addition to C-2 of *N*-methoxyquinolinium cation. The observation of the *N*-methoxy-*tert*-butyltetrahydroquinoline (~ 10%) upon $NaBH_4$ workup possibly indicated attack at C-4 with the formation of *N*-methoxy-4-*tert*-butyl-1,4-dihydroquinoline, a possible precursor to *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline **18** observed in the reaction performed in the presence of PTSA (Table XIII). Alternately, in the presence of PTSA, the formation of *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline (9%) could indicate that some

Table XIII. Photostimulated Reactions of *t*-BuHgX with *N*-Methoxy quinolinium Perchlorate in Me_2SO.[a]



44 11

equivalents				yield (%)[b]	
t-BuHgCl	KI	PTSA	workup	44	11
4	8	0	$Na_2S_2O_3$	70	20
4	8	0	NaOMe, 85 °C	0	72[c]
4	8	0	$NaBH_4$/MeOH	55	20[d]
4	8	4	$Na_2S_2O_3$	[e]	45[f]
4	8	0	PTSA, 85 °C	0	64[g]

[a] 0.1 Mmol in 2 mL Me_2SO irradiated with a 275 W fluorescent sunlamp for 10 min at 35–40 °C.

[b] By ^1H NMR with an internal standard.

[c] Also formed, 4-*tert*-butylquinoline (~ 3%), *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline (~ 7%).

[d] By GCMS, there was ~ 10% of *N*-methoxy-*tert*-butyltetrahydroquinoline, possibly the 4-*tert*-butyl isomer.

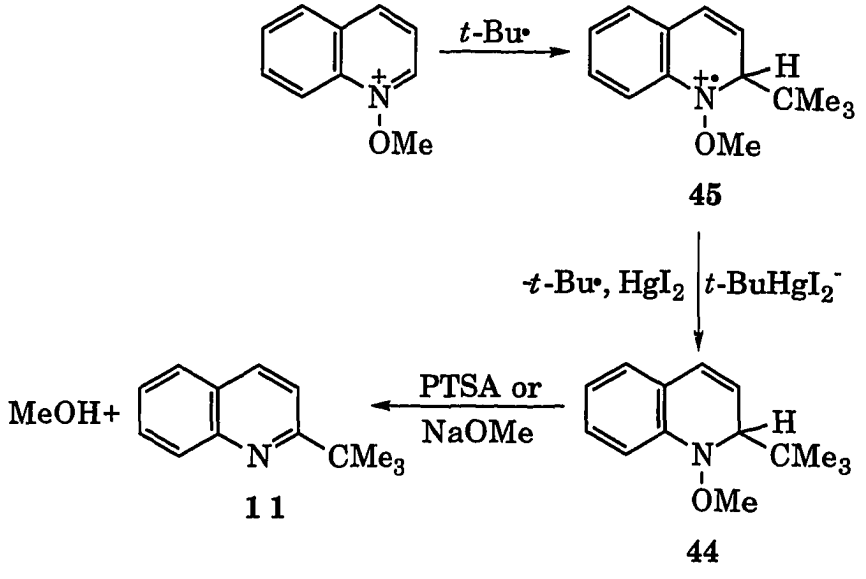
[e] 9% of **44** or possibly its 4-*tert*-butyl isomer.

[f] 20% of 2,4-di-*tert*-butylquinoline and 9% of *trans*-2,4-di-*tert*-1,2,3,4-tetrahydroquinoline also observed.

[g] 26% of 2,4-di-*tert*-butylquinoline formed.

of the reaction proceeded by demethoxylation to form quinolinium ion since **18** is a major product of the *tert*-butylation of quinolinium ion, but not of 2-*tert*-butylquinoline (see Chapter I).

Scheme XXI. Photolysis of *t*-BuHgX with Quinolinium Perchlorate.

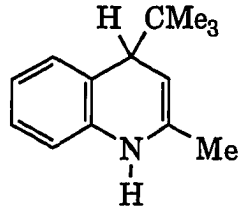


tert-Butylation of Quinoline *N*-Oxides

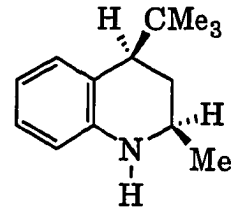
2-Substituted Quinoline *N*-Oxides

In the presence of 4 equiv of KI in Me_2SO in the dark, quinaldine *N*-oxide did not undergo any reaction in 20 h at 40 °C. However, with sunlamp irradiation, 74% yield of quinaldine was observed. Photolysis with 4 equiv of *t*-BuHgCl and 8 equiv of KI for 2 h produced 8% of quinaldine **39**, 6% of 4-*tert*-butyl-2-methylquinoline **40** and 15% of 4-*tert*-butyl-2-methyl-1,4-

dihydroquinoline **46**. After 8 h of photolysis, the yields were 46%, 12%, and 8%, respectively (Table XIV). Apparently, iodide ion promoted deoxygenation of the



46

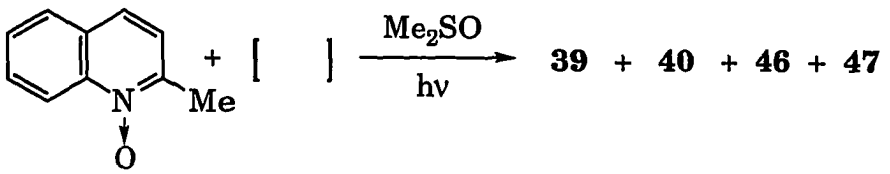


47

N-oxide is the first step in the reaction sequence. When worked up with $NaBH_4$/MeOH, the 1,4-dihydro compound **46** was reduced to 4-*tert*-butyl-2-methyl-1,2,3,4-tetrahydroquinoline **47** (Scheme XXII). A trace of 1,2,3,4-tetrahydroquinoline was detected by GCMS. In the presence of diazabicyclo[2.2.2]octane (DABCO), photolysis of *t*-BuHgCl/I^- with 2-methylquinoline *N*-oxide gave little reaction in 1 h. The only product detected was 2-methylquinoline. No detectable 4-*tert*-butyl-2-methylquinoline *N*-oxide was observed by GCMS.

Photolysis of *t*-BuHgCl with 2-chloroquinoline *N*-oxide produced the dimer **48**. With 4 equiv of *t*-BuHgCl, the yield of **48** after 2 h of photolysis increased from 8 to 46 to 56% in the presence of 0, 4, and 8 equiv of KI respectively (Table XV). Deoxygenation of the 2-chloroquinoline *N*-oxide did not occur. Scheme XXIII shows a possible mechanism for the reaction of 2-chloroquinoline *N*-oxide. The adduct radical **49** is a resonance stabilized

Table XIV. Photostimulated Reactions of *t*-BuHgCl with 2-Methylquinoline *N*-Oxide in Me_2SO.[a]



equivalents			yield (%)[b]			
t-BuHgCl	KI	time (h)	**39**	**40**	**46**	**47**
0	4	20[c,d]	–	–	–	–
0	4	20[d]	74	–	–	–
4	8	2	8	6	15	–
4	8	4	32	8	13	–
4	8	8	46	12	8	–
4	8	2[e]	9	7	–	18
4	8	4[e]	41	11	–	16
4	8	8[e]	53	14	–	13

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with CH_2I_2 as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] Wrapped with aluminium foil ca. 25 cm from sunlamp irradiation.

[d] 0.05 Mmol in 0.5 mL Me_2SO-d_6.

[e] Workup with $NaBH_4$/MeOH.

Scheme XXII. Photolysis of *t*-BuHgX with 2-Methylquinoline *N*-Oxide.

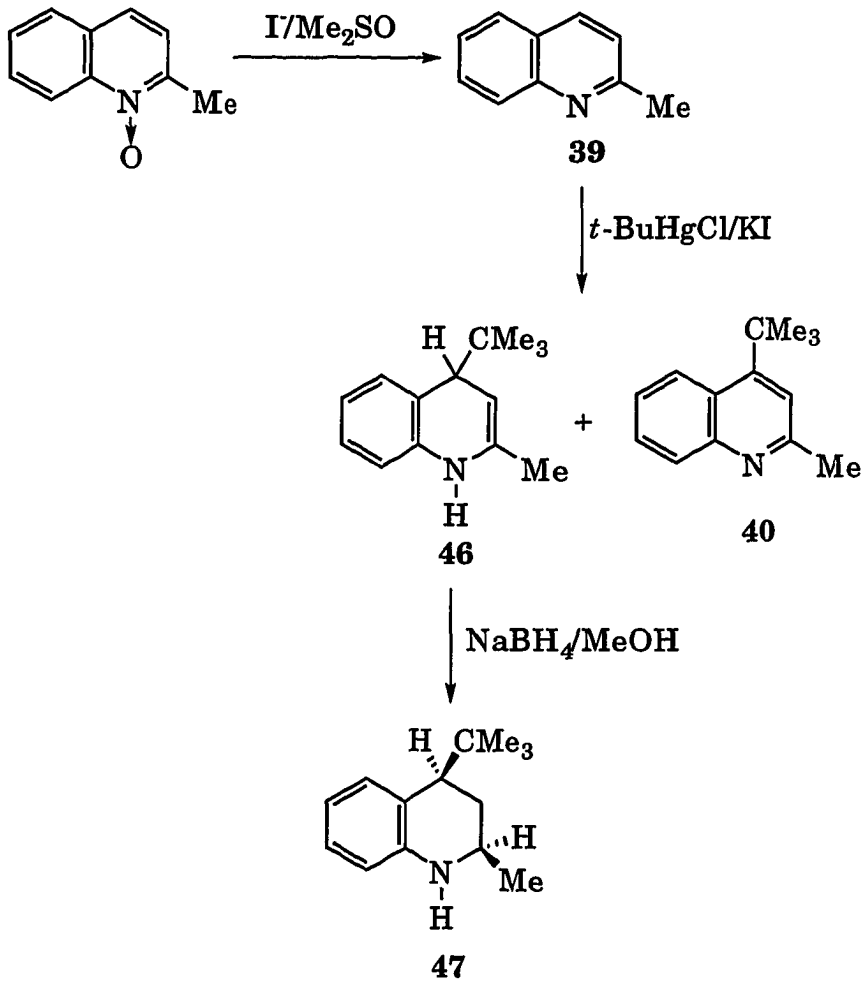
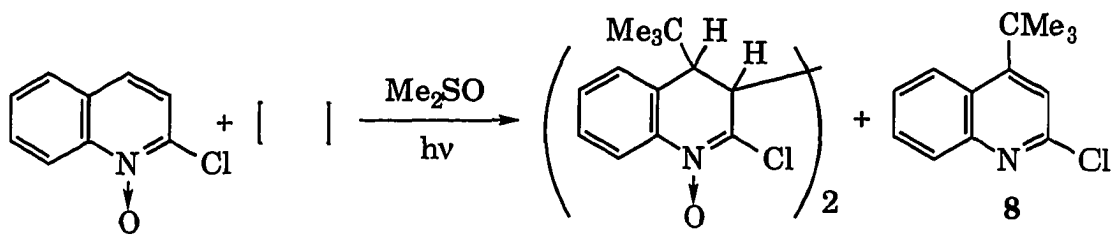


Table XV. Photostimulated Reactions of *t*-BuHgCl with 2-Chloroquinoline *N*-Oxide in Me_2SO.[a]



48

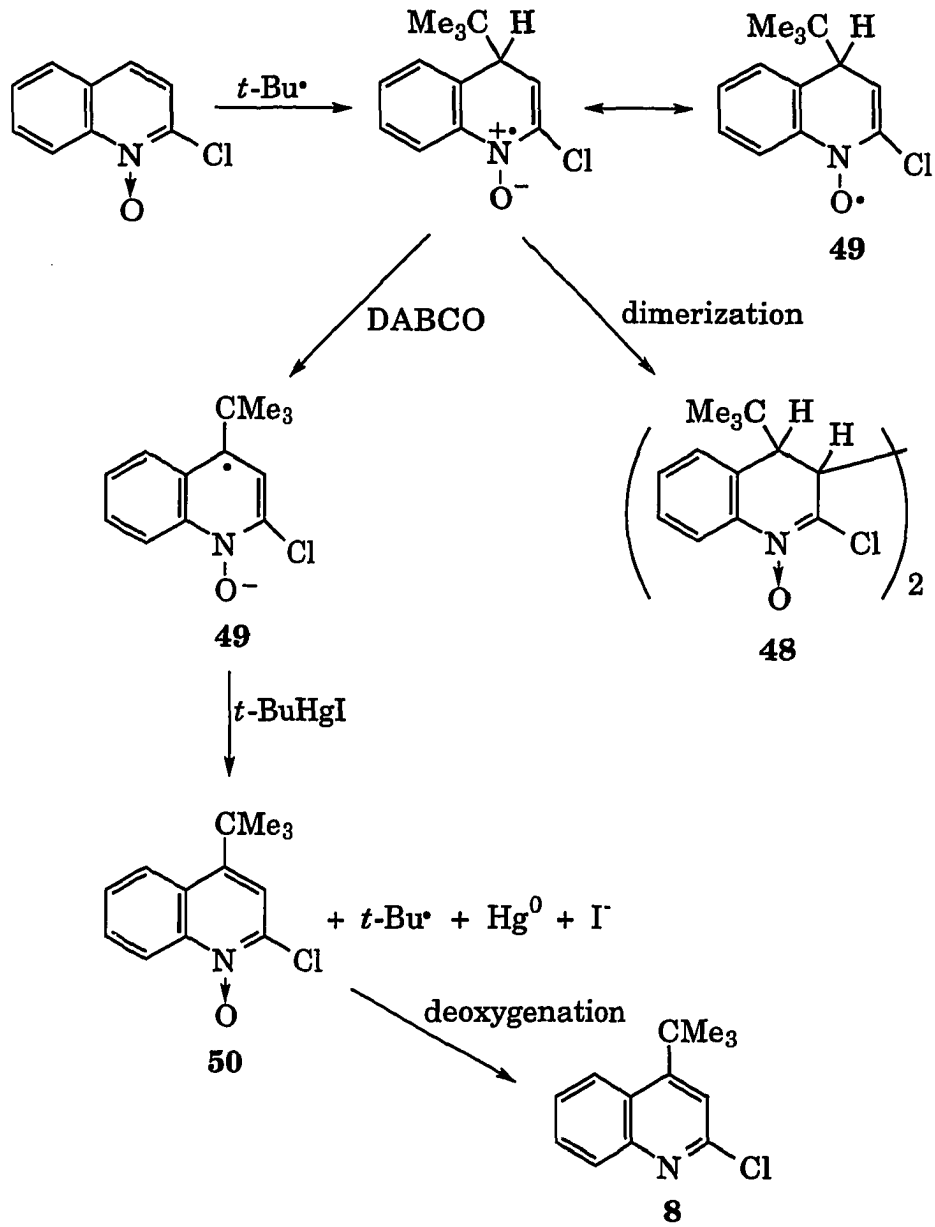
equivalents				yield (%)[b]	
t-BuHgCl	KI	DABCO	time (h)	**48**	**8**
4	0	0	2	8	–
4	4	0	2	46	–
4	8	0	2	56	–
4	8	4	2	22	3[c]
4	8	4	5	20	5

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] ~4% of 4-*tert*-Butyl-2-chloroquinoline *N*-oxide detected by GCMS.

Scheme XXIII. Photolysis of *t*-BuHgX with 2-Chloroquinoline *N*-Oxide.



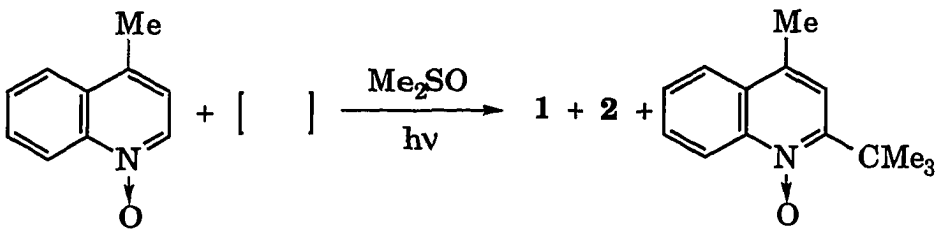
nitroxide radical and was not reduced by *t*-BuHgCl/KI reagent. In the presence of DABCO, the formation of dimer **48** was also observed. Moreover, the 4-*tert*-butyl-2-chloroquinoline *N*-oxide **50** could be detected at short reaction periods. At longer reaction times, the *N*-oxide appeared to undergo deoxygenation to yield 4-*tert*-butyl-2-chloroquinoline **8**, a product not observed in the absence of DABCO.

4-Substituted Quinoline *N*-Oxides

Photolysis of *t*-BuHgX with 4-methylquinoline *N*-oxide produced the major products 2-*tert*-butyl-4-methylquinoline **1** and 2,6-di-*tert*-butyl-4-methylquinoline **2**. Only a trace of 2-*tert*-butyl-4-methylquinoline-*N*-oxide **51** was detected by GCMS. With 4 equiv of *t*-BuHgCl and 8 equiv of KI, the yields increased from 30 and 7% at 2 h to 59 and 20% at 9 h (Table XVI). Again, deoxygenation of the *N*-oxide appears to be the major initial step in the reaction. In the presence of DABCO, the formation of **51** was increased to 30% after photolysis for 1 h in the presence of *t*-BuHgCl (4 equiv), KI (8 equiv), and DABCO (4 equiv) (Scheme XXIV).

Photolysis of *t*-BuHgX with 4-chloroquinoline *N*-oxide yielded both the deoxygenated product 2-*tert*-butyl-4-chloroquinoline **6** and the substitutive product 2-*tert*-butyl-4-chloroquinoline *N*-oxide **53** (Table XVII). It seems that the adduct radical **54** is initially formed. Since the dimerization of **54** is impossible, the nitroxide may be converted either to **53** by losing a proton,

Table XVI. Reactions of *t*-BuHgCl with 4-Methylquinoline *N*-Oxide in Me_2SO.[a]



51

equivalents					yield (%)[b,c]		
t-BuHgCl	KI	PTSA	DABCO	time (h)	**1**	**2**	**51**
4	4	0	0	2	27	tr	tr
4	4	0	0	9	50	10	–
4	8	0	0	2	30	7	tr
4	8	0	0	9	59	20	–
4	8	4	0	2	28	3	–
4	8	0	4	1	5	–	30

[a] 0.2 Mmol in 4 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] Traces of 4-methylquinoline detected.

Scheme XXIV. Reaction of *t*-BuHgX with 4-Methylquinoline *N*-Oxide.

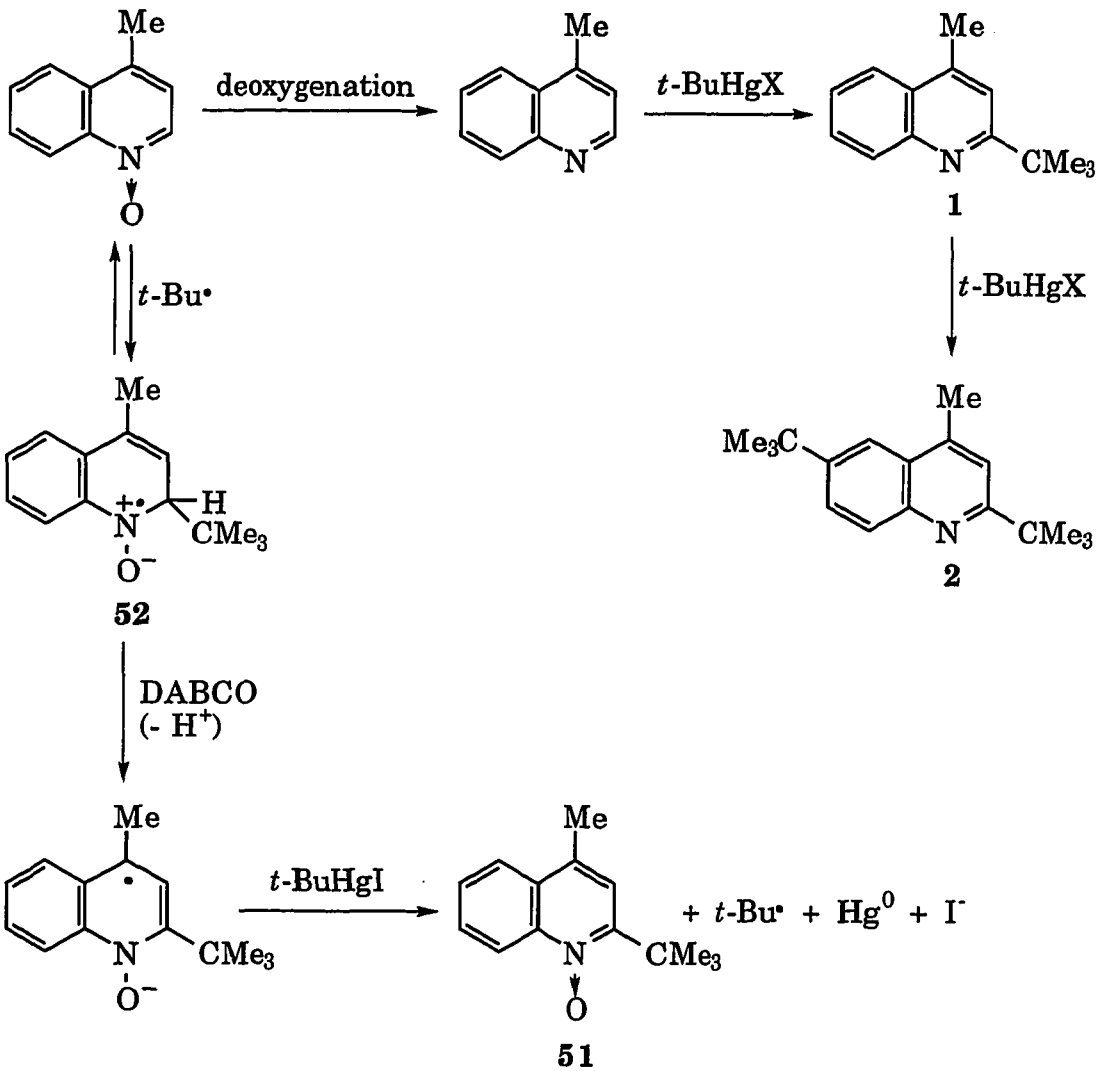
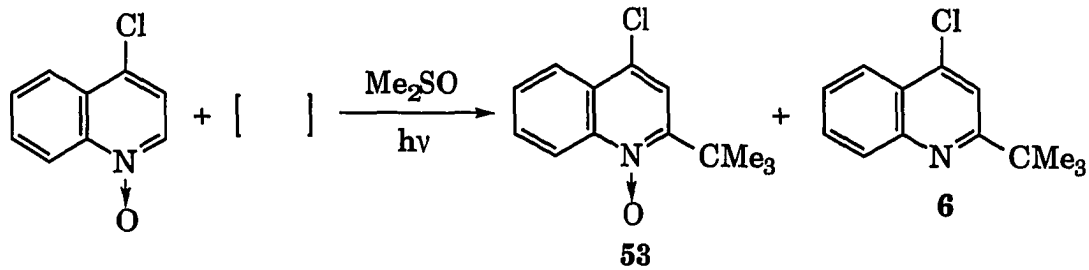


Table XVII. Photostimulated Reactions of *t*-BuHgX with 4-Chloroquinoline *N*-Oxide in Me_2SO.[a]



equivalents					yield (%)[b]	
t-BuHgCl	KI	PTSA	DABCO	time (h)	**6**	**53**
4	0	0	0	2	20	10
4	4	0	0	2	35	22
4	4	0	0	9	86	–
4	8	0	0	2	68	20
4	8	0	0	9	84	–
4	4	4	0	2	17	13
4	8	4	0	2	56	13
4	8	0	4	2	7	39
4	8	0	4	5[c]	39	29

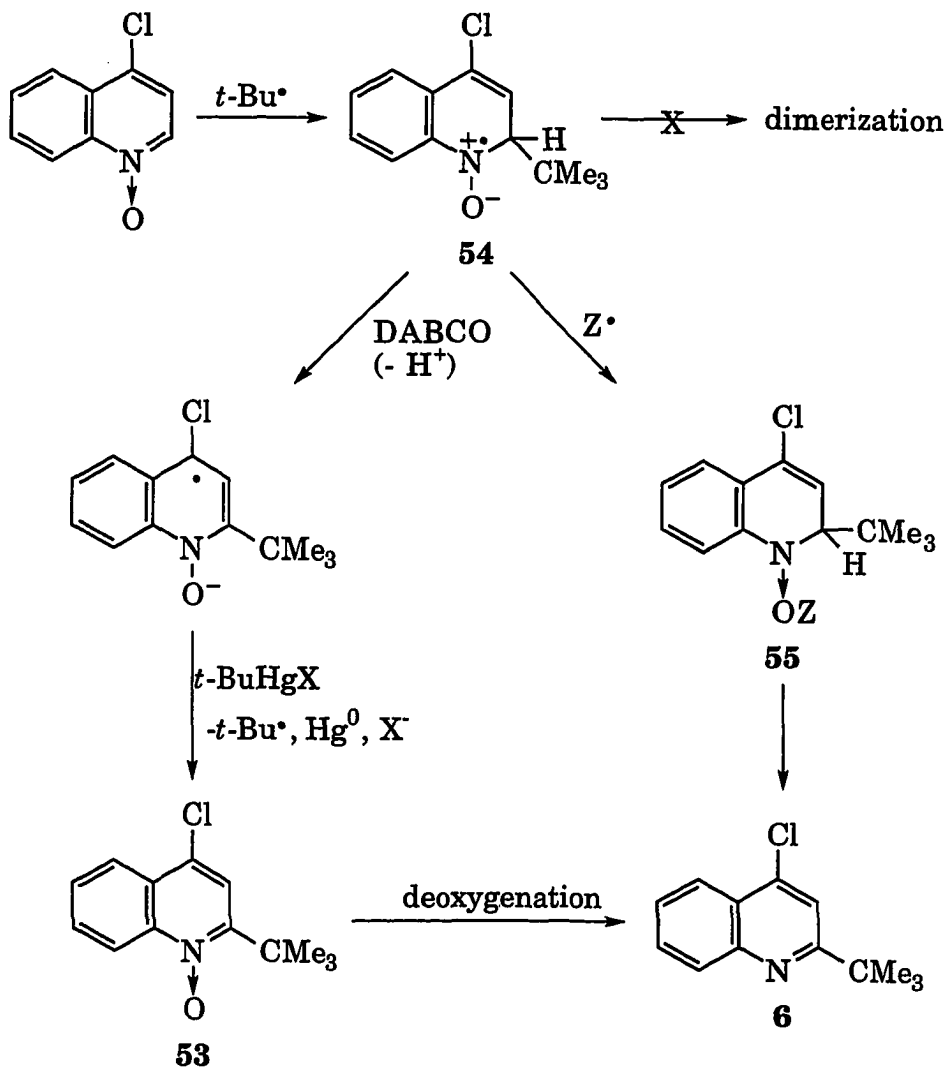
[a] 0.5 Mmol in 10 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with toluene as an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] 0.1 Mmol in 2 mL Me_2SO.

followed by the oxidation reaction with *t*-BuHgX or to some intermediates of the general structure **55** (Z = H, Me_3C, HgI) which can undergo elimination to form **6** (Scheme XXV)[54].

Scheme XXV. Reaction of *t*-BuHgX with 4-Chloroquinoline *N*-oxide.

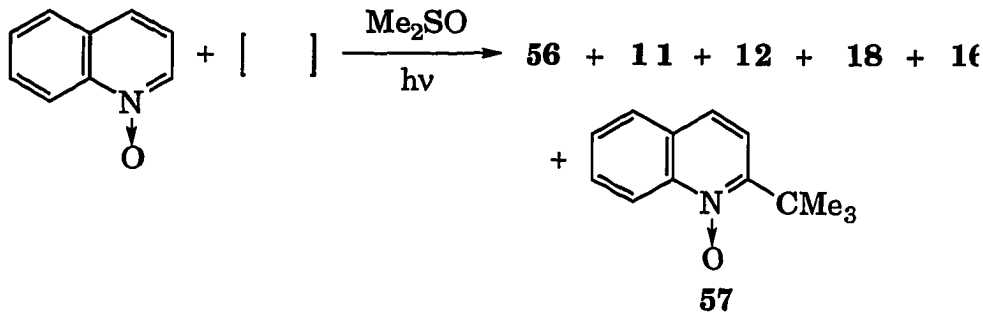


Addition of DABCO resulted in the major initial reaction product being **53** instead of **6**. Again, at longer reaction times, **53** underwent deoxygenation to form **6**.

Quinoline *N*-Oxide

Photolysis of pyridine *N*-oxide with *t*-BuHgCl/KI did not lead to significant reaction. No significant reaction was observed upon photolysis of *t*-BuHgCl with quinoline *N*-oxide. In the presence of KI, quinoline *N*-oxide reacted slowly to give mainly quinoline **56** and the products previous observed in the *tert*-butylation of quinoline, 2-*tert*-butylquinoline **11**, 2,4-di-*tert*-butylquinoline **12**, *trans* 2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline **18** and the hydrate **16** (see Chapter I) (Table XVIII). The yield of the hydrate was increased by the addition of H_2O to the Me_2SO solvent. Initially formed quinoline is apparently converted to 2-*tert*-butylquinoline **11** and 4-*tert*-butyl-1,4-dihydroquinoline **19**. Further reaction of the dihydroquinoline formed **18** while 2-*tert*-butylquinoline was slowly converted to **12, 13, and 16** (Scheme XXVI). Addition of PTSA had no significant effects upon the reaction of quinoline *N*-oxide. At a short reaction time (1 h), up to 7% of 2-*tert*-butylquinoline *N*-oxide **57** could be detected. However, at longer reaction times, the substituted quinoline *N*-oxide was not observed apparently because it was deoxygenated to give 2-*tert*-butylquinoline. In the presence of DABCO, the yield of **57** was increased to 20% in 1 h.

Table XVIII. Reaction of *t*-BuHgCl with Quinoline *N*-Oxide in Me_2SO.[a]



equivalents				yield (%)[b]					
t-BuHgCl	KI	DABCO	time (h)	56	11	12	18	16	57
4	0	0	9	tr	4	8	0	0	–
4	4	0	4	10	28	6	0	4	–
4	8	0	1	0	34	5	1	tr	7
4	8	0	4	10	48	7	3	3	–
4	8	0	18[c]	0	18	6	17	31	–
4	8	0	18[c,d]	0	20	5	15	32	–
4	8	4	1[e]	8	8	–	–	–	20

[a] 0.5 Mmol in 10 mL Me_2SO irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

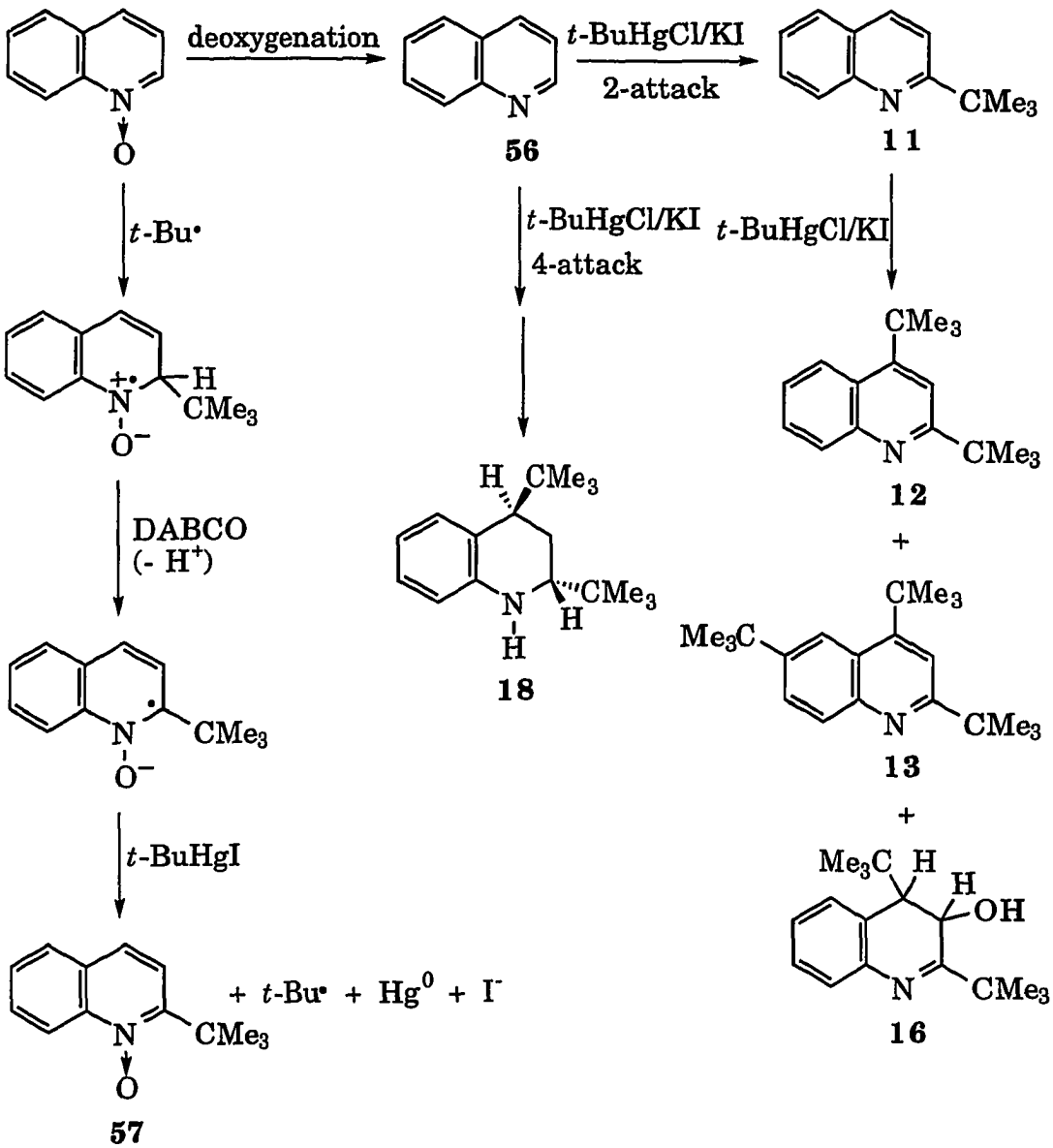
[b] By ^1H NMR with an internal standard after neutralization and workup with aqueous $Na_2S_2O_3$.

[c] 1 or 10% of H_2O added.

[d] With air passing through reaction mixture.

[e] 0.1 Mmol in 2 mL Me_2SO.

Scheme XXVI. Reaction of *t*-BuHgX with Quinoline *N*-Oxide.



Conclusion

Photostimulated reaction of *tert*-BuHgCl with 4-substituted *N*-methyl or *N*-methoxyquinolinium salts in the presence of KI generated the reductive *tert*-butylation products by one electron reduction. With 4-substituted quinoline *N*-oxides and quinoline *N*-oxide itself, the C-2 adduct radicals were deprotonated by DABCO to yield after one electron oxidation the 2-*tert*-butylquinoline *N*-oxides. The adduct radical cations formed by *t*-Bu· attack at the C-4 position of quinolinium ions seldom lose the C-4 proton, but react by reduction, hydration or in the case of 2-chloroquinoline *N*-oxide, by dimerization. The loss of the proton from the 2-adducts but not from the 4-adducts seems to be stereoelectronic in origin. With *N*-methylquinolinium cation, the addition of *t*-Bu· occurs selectively (> 90%) at C-4, while with *N*-methoxyquinolinium perchlorate, the reaction products result from the selective addition of *t*-Bu· at C-2 (> 90%). In some cases, demethylation of *N*-methylquinolinium salts or deoxygenation of quinoline *N*-oxides may occur before *tert*-butylation.

Experimental Section

General Consideration

^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT 300 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane (300 MHz for ^{1}H NMR) or for ^{13}C NMR measured relative to the central line of internal $CDCl_3$ at 77.000 ppm (75.4 MHz for ^{13}C NMR).

Analytical gas chromatography (GC) was performed on a Perkin-Elmer 3920 gas chromatography equipped with a Hitachi D-2500 Chromato-integrator. GCMS were recorded on a Finnegan 4000 spectrometer with an Incos data system or Magnum MS and high resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Infrared spectra (IR) were recorded on an IBM IR-98 FT spectrometer or Digital FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

The products were isolated by flash column chromatography on silica gel (Merck, grade 9385, 230-400 mesh, 60 Å) with mixed solvents (hexane/ethyl acetate) as eluents. *tert*-Butylated quinoline N-oxides were isolated by thin layer chromatography using 5–17 μm, 60 Å Merck silica gel plates (Aldrich Chemical Company). Hexane/ethyl acetate were used as eluents. GC yields were determined by using an internal standard (toluene). ^{1}H NMR spectroscopy yields were determined by integration with a known amount of an internal standard (toluene or diiodomethane).

Solvents and Reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride and stored over 4 Å molecular sieves under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium metal. Other solvents were purchased and used without further purification.

Chemical reagents in high purity grades were purchased mostly from Aldrich Chemical Co. In most cases, the reagents were used without further purification.

tert-Butylmercury chloride was prepared as previously described (see Chapter I).

Preparation of *N*-Methylated Quinolinium Salts

1,4-Dimethylquinolinium Iodide

4-Methylquinoline and excess methyl iodide were stirred at room temperature for 24 hours. Unreacted methyl iodide was evaporated and the solid residue was washed with hexane and recrystallized from acetone: mp 173–174 °C (lit.[55] 174 °C); ^{1}H NMR (Me_2SO-d_6) δ 8.57 (d, J = 5.7 Hz, 1 H), 7.67 (t, J = 8.7 Hz, 2 H), 7.40–7.46 (m, 1 H), 7.19–7.25 (m, 2 H), 3.76 (s, 3 H), 2.17 (s, 3 H).

Other *N*-methylated heterocyclic compounds were prepared by the literature procedure.[56] A solution of the appropriate heterocyclic compound (quinoline, 2-chloroquinoline and 4-chloroquinoline) and excess methyl iodide in acetone was refluxed for several hours and then the resulting precipitate was collected by filtration, washed with acetone and recrystallized from acetone.

1-Methylquinolinium Iodide

This compound had mp 143–144 °C (lit.[56] 142–144 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.58 (d, J = 5.7 Hz, 1 H), 9.33 (d, J = 8.4 Hz, 1 H), 8.53 (t, J = 8.7 Hz, 2 H), 8.31 (t, J = 7.8 Hz, 1 H), 8.21 (dd, J = 8.4, 5.7 Hz, 1 H), 8.08 (t, J = 7.5 Hz, 1 H), 4.68 (s, 3 H).

2-Chloro-1-methylquinolinium Iodide

This compound had mp 220–221 °C; ^{1}H NMR (Me_2SO-d_6) δ 7.87 (d, J = 9.6 Hz, 1 H), 7.69 (d, J = 7.8 Hz, 1 H), 7.60 (td, J = 8.7, 1.5 Hz, 1 H), 7.50 (d, J = 8.7 Hz, 1 H), 7.24 (t, J = 7.5 Hz, 1 H), 6.59 (d, J = 9.6 Hz, 1 H), 3.59 (s, 3 H).

4-Chloro-1-methylquinolinium Iodide

This compound had mp 207–210 °C (decomp) (lit.[57] 208–210 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.55 (d, J = 6.3 Hz, 1 H), 8.60 (d, J = 8.4 Hz, 2 H), 8.52 (d, J = 6.3 Hz, 1 H), 8.39 (t, J = 7.8 Hz, 1 H), 8.19 (t, J = 7.8 Hz, 1 H), 4.63 (s, 3 H).

Preparation of *N*-Methoxypyridinium and Quinolinium Salts

1-Methoxypyridinium Iodide

1-Methoxypyridinium iodide was prepared by refluxing the oxide with excess of methyl iodide.[58] The solid residue was washed with anhydrous

methylene chloride and the pure product was obtained as pale yellow deliquescent needles, rapidly darking in light: mp 88–90 °C (decomp) (lit.[58] 90 °C), ^{1}H NMR (Me_2SO-d_6) δ 9.56 (dd, J = 6.9, 0.9 Hz, 2 H), 8.70 (td, J = 7.5, 0.9 Hz, 1 H), 8.32 (t, J = 7.2 Hz, 2 H), 4.50 (s, 3 H).

1-Methoxyquinolinium perchlorate, 1-methoxy-2-methylquinolinium perchlorate, and 1-methoxy-4-methylquinolinium perchlorate were prepared by the literature procedure.[59]

1-Methoxyquinolinium Perchlorate[59]

Quinoline-1-oxide (1.95 g) and dimethyl sulfate (1.3 mL) were mixed, and when the initial reaction had subsided, heated at 95 °C for 2 hours, cooled, and the melt dissolved in dry ethyl alcohol (2.5 mL); 70% perchloric acid (1.4 mL) was added and the product was precipitated with ethyl acetate (10 mL) to give after crystallization from methanol, the perchlorate (2.2 g, 63%): mp 110–111 °C (lit.[59] 110–111 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.99 (dd, J = 6.3, 0.9 Hz, 1 H), 9.30 (d, J = 8.4, 1 H), 8.53–8.57 (m, 2 H), 8.34 (ddd, J = 8.4, 7.2, 0.9 Hz, 1 H), 8.26 (dd, J= 8.1, 6.3 Hz, 1 H), 8.10 (t, J = 8.1 Hz, 1 H), 4.54 (s, 3 H).

1-Methoxy-2-methylquinolinium Perchlorate[59]

This compound had mp 129–131 °C (lit.[60] 131–132 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.11 (d, J = 8.4 Hz, 1 H), 8.46 (t, J = 8.1 Hz, 2 H), 8.27 (ddd, J = 8.4, 6.9, 0.9

Hz, 1 H), 8.15 (d, J = 8.7 Hz, 1 H), 8.02 (t, J = 7.5 Hz, 1 H), 4.40 (s, 3 H), 3.07 (s, 3 H).

1-Methoxy-4-methylquinolinium Perchlorate[59]

This compound had mp 130–131 °C (lit.[60] 130–131 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.84 (d, J = 6.6 Hz, 1 H), 8.56 (d, J = 8.4 Hz, 1 H), 8.30 (ddd, J = 8.4, 7.2, 1.2 Hz, 1 H), 8.51 (d, J = 8.7 Hz, 1 H), 8.06–8.13 (m, 2 H), 4.48 (s, 3 H), 3.00 (s, 3 H).

Preparation of 2-Methylquinolinium Perchlorate

2-Methylquinolinium Perchlorate[61]

Perchloric acid (60%) was added slowly to an equivalent amount of base in chloroform. The solution was concentrated and the white precipitate formed was recrystallized from acetone-chloroform (1:1). This salt had mp 128–129 °C (lit.[61] 129–130 °C); ^{1}H NMR (Me_2SO-d_6) δ 9.02 (d, J = 8.7 Hz, 1 H), 8.28 (d, J = 8.4 Hz, 1 H), 8.14–8.06 (m, 2 H), 7.95 (d, J = 8.7 Hz, 1 H), 7.88 (ddd, J = 8.1, 6.6, 1.8 Hz, 1 H), 2.93 (s, 3 H).

Preparation of Quinoline *N*-Oxides

Quinoline-1-oxide

Quinoline-1-oxide was prepared from quinoline-1-oxide hydrate.[62] Quinoline-1-oxide hydrate was stored in a vacuum desiccator for 2 days over phosphorus pentoxide. The degree of hydration of quinoline-1-oxide was ascertained by ^{1}H NMR spectroscopy.

2-Methylquinoline-1-oxide and 4-methylquinoline-1-oxide were prepared by the literature procedure.[63]

2-Methylquinoline-1-oxide

A solution of 2-methylquinoline (quinaldine, 10 g), acetic acid (50 mL) and 30% H_2O_2 (10 mL) was heated for 3 hours. After cooling, PtO_2 (20 mg) was added and the solution allowed to stand at room temperature overnight. After concentration, the solution was neutralized with sodium carbonate, and extracted with chloroform. The chloroform fraction was recrystallized for acetone-ethyl ether to yield 2-methylquinoline-1-oxide: mp 76–77 °C (lit.[63] 75–77 °C); ^{1}H NMR (Me_2SO-d_6) δ 8.77 (d, J = 8.7 Hz, 1 H), 7.81 (d, J = 8.1 Hz, 1 H), 7.70–7.76 (m, 1 H), 7.62 (d, J = 8.4 Hz, 1 H), 7.54–7.59 (m, 1 H), 7.29 (d, J= 8.7 Hz, 1 H), 2.71 (s, 3 H).

4-Methylquinoline-1-oxide[63]

4-Methylquinoline-1-oxide was prepared from 4-methylquinoline (lepidine) by the method used for the 2-methyl isomer. This compound had mp 116–117 °C (lit.[63] 116–117 °C); ^{1}H NMR (Me_2SO-d_6) δ 8.55 (d, J = 8.4 Hz, 1 H), 8.46 (d, J = 6.3 Hz, 1 H), 8.06 (d, J = 8.1 Hz, 1 H), 7.70–7.82 (m, 2 H), 7.28 (d, J = 6.3 Hz, 1 H), 2.58 (s, 3 H).

2-Chloroquinoline-1-oxide

2-Chloroquinoline-1-oxide was prepared by the literature procedure.[51] To a stirred solution of maleic anhydride (14 g) in chloroform (30 mL), 30% hydrogen peroxide (2.8 g) was added under ice-cooling. After 2 hours of stirring, 2-chloroquinoline (1.6 g) was added and the mixture was kept in a refrigerator for five days. Deposited maleic acid was treated with a small amount of concd. potassium carbonate solution, dried over potassium carbonate, and the solvent evaporated cautiously at water pump pressure (below 60 °C). The residue was taken up with chloroform and chromatographed on alumina with chloroform as eluent. The chloroform eluate gave an oil, which solidified on addition of a few drops of water. Recrystallization from acetone-petroleum ether afforded 2-chloroquinoline-1-oxide, mp 85–92 °C (0.8–1.1 g). Drying of the sample over phosphorus pentoxide raised the mp to 104–105 °C (lit.[51] 105 °C); ^{1}H NMR ($CDCl_3$) δ 8.75 (d, J = 8.7 Hz, 1 H), 7.86–7.76 (m, 2 H), 7.65 (d, J = 9.0 Hz, 2 H), 7.47 (d, J = 8.7 Hz, 1 H).

4-Chloroquinoline-1-oxide was prepared from 4-nitroquinoline-1-oxide.[64] 4-Nitroquinoline-1-oxide was prepared by the literature procedure.[64]

4-Nitroquinoline-1-oxide[64]

Quinoline-1-oxide hydrate (12 g) was dissolved in 26 mL of sulfuric acid (density 1.84 g/mL). To this solution at 65–70 °C, 9 g of nitric acid (density 1.36 g/mL) was added portionwise over a period of 35 to 40 minutes. The mixture was maintained an additional two hours at 70 °C with frequent swirling, cooled, and poured onto ice. The nitro compound precipitated as an orange powder which was collected and washed with water, dilute sodium carbonate solution, water, and a small amount of alcohol, in that order. The powder then was dried and recrystallized from acetone. 4-Nitroquinoline-1-oxide was obtained as yellow needles, mp 153–154 °C (lit.[64] 153–154 °C), in the amount of 9 g (64%); ^{1}H NMR ($CDCl_3$) δ 8.84–8.79 (m, 1 H), 8.76–8.71 (m, 1 H), 8.52 (d, J = 6.9 Hz, 1 H), 8.21 (d, J = 6.9 Hz, 1 H), 7.91–7.84 (m, 2 H).

4-Chloroquinoline-1-oxide[64]

To 25 mL of acetyl chloride at 0 °C, 5 g of 4-nitroquinoline-1-oxide was added in portions with ice cooling. The reaction mixture was carefully held below 40 °C for 40 minutes, and then treated with ice-water. Neutralization with sodium carbonate freed 2,4-dichloroquinoline which was swept out by steam-distillation. The residue was made basic by the addition of sodium

carbonate and was extracted with chloroform. The yellow needle-like residue from evaporation of the chloroform solution was recrystallized from acetone, giving 4.6 g (97%) of 4-chloroquinoline-1-oxide: mp 134–135 °C (lit.[64] 133–133.5 °C); ^{1}H NMR ($CDCl_3$) δ 8.78 (d, J = 8.7 Hz, 1 H), 8.45 (d, J = 6.6 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 7.74–7.86 (m, 2H), 7.38 (d, J = 6.3 Hz, 1 H).

General Procedure for the Photostimulated Reactions

The substrate (0.2–1.0 mmol), *t*-BuHgCl (0.2–4 .0 mmol), and KI (0–8 mmol) with or without added PTSA (or DABCO) were placed in a Pyrex test tube, and 2–10 mL of deoxygenated Me_2SO 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 $Na_2S_2O_3$ (3x 50 mL) and saturated brine (50 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. Products were isolated by flash column chromatography or thin layer chromatography with hexane/ethyl acetate as eluent. All the solids were recrystallized from hexane/ethyl acetate.

Photostimulated *tert*-Butylation Followed by $NaBH_4$ Reduction

A dry Pyrex tube containing substrate and coreactants dissolved in 2–10 mL of deoxygenated Me_2SO was equipped with a rubber septum. The solution was irradiated under N_2 atmosphere by a 275 W General Electric florescence sunlamp ca. 25 cm from the reaction tube. After the reaction, the solution was

cooled and 1 mL of MeOH was added. Excess $NaBH_4$ was added in small portions over a period of 10 min until gas emission stopped. Water (25 mL) was added to the reaction mixture followed by extraction with three 15 mL portions of CH_2Cl_2. The combined CH_2Cl_2 extract was washed with water three times (50 mL each) and dried over $MgSO_4$. The solvent was evaporated and the NMR yield was determined with a known amount of internal standard. The mixture was analyzed by GC and each compound was isolated by flash column chromatography using hexane/ethyl acetate as eluents.

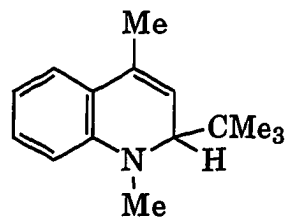
Purity of Products

Isolated products showed no significant impurities by GC and/or by ^1H NMR and are determined to be at least 97% pure.

Characterization of Products

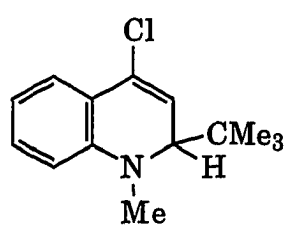
The characterization of 2-*tert*-butylpyridine, 4-*tert*-butylpyridine, 2,4-di-*tert*-butylpyridine, 2-*tert*-butylquinoline, 2-*tert*-butyl-4-methylquinoline, 4-*tert*-butyl-2-methylquinoline, *cis*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline, *trans*-2,4-di-*tert*-butyl-1,2,3,4-tetrahydroquinoline, 4-*tert*-butyl-1,2,3,4-tetrahydro-2-methylquinoline, 2,4-di-*tert*-butyl-3,4-dihydro-3-hydroxyquinoline, 4-*tert*-butyl-1,2-dimethyl-1,4-dihydroquinoline, 2-*tert*-butyl-4-chloroquinoline have been described in Chapter I or previously reported.[31]

2-(1,1-Dimethylethyl)-1,2-dihydro-1,4-dimethylquinoline (25)



This compound was isolated as an oil; ^{1}H NMR ($CDCl_3$) δ 7.13–7.05 (m, 2 H), 6.59 (td, J = 7.5, 0.9 Hz, 1 H), 6.48 (d, J = 7.8 Hz, 1 H), 5.48 (dd, J = 6.0, 0.9 Hz, 1 H), 3.59 (d, J = 6.3 Hz, 1 H), 3.09 (s, 3 H), 2.05 (s, 3 H), 0.82 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.28 (s), 130.61 (s), 128.35 (d), 123.52 (s), 123.17 (d), 119.70 (d), 115.24 (d), 111.04 (d), 70.25 (d), 43.42 (q), 41.77 (s), 26.21 (q), 18.98 (q); HRMS cacld for $C_{15}H_{21}N$ (M^+) 215.1674, found 215.1670.

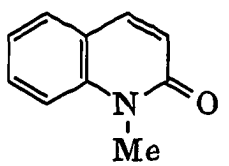
4-Chloro-2-(1,1-dimethylethyl)-1,2-dihydro-1-methylquinoline (27)



This compound was isolated as an oil; ^{1}H NMR ($CDCl_3$) δ 7.38 (dd, J = 7.8, 1.5 Hz, 1 H), 7.14 (td, J = 8.4, 1.5 Hz, 1 H), 6.63 (td, J = 8.1, 0.6 Hz, 1 H), 6.49 (d, J = 8.4 Hz, 1 H), 5.78 (d, J = 6.3 Hz, 1 H), 3.72 (d, J = 6.6 Hz, 1 H), 3.10 (s, 3 H), 0.85 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.56 (s), 129.87 (d), 128.97 (s), 124.48 (d), 120.03 (s), 119.44 (d), 115.77 (d), 111.46 (d), 71.51 (d), 43.33 (q), 41.98 (s), 25.98 (q);

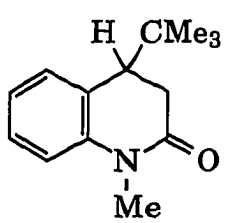
GCMS m/z (relative intensity) 237 (0.3), 235 (M^+, 0.9), 180 (30), 178 (100); 143 (7), 128 (6); HRMS calcd for $C_{14}H_{18}NCl$ 235.1128, found 235.1133.

1-Methyl-2(1 H)-quinolinone (28)



This compound was isolated as a solid: mp 71-72 °C (lit.[65] 72-73 °C); ^1H NMR ($CDCl_3$) δ 7.66 (d, J = 9.6 Hz, 1 H), 7.60–7.54 (m, 2 H), 7.36 (d, J = 9.0 Hz, 1 H), 7.23 (td, J = 7.8, 0.6 Hz, 1 H), 6.71 (d, J = 9.6 Hz), 3.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 162.23 (s), 139.90 (s), 138.87 (d), 130.53 (d), 128.66 (d), 122.03 (d), 121.63 (d), 120.55 (s), 114.05 (d), 29.35 (q); GCMS m/z (relative intensity) 159 (M^+, 100), 130 (55), 77 (25), 63 (19), 51 (22).

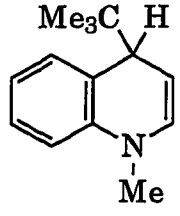
4-(1,1-Dimethylethyl)-3,4-dihydro-1-methyl-2(1H)-quinolinone (29)



This compound was isolated as an oil; ^1H NMR ($CDCl_3$) δ 7.27 (t, J = 7.8 Hz, 1 H), 7.14 (d, J = 7.5 Hz, 1 H), 7.01 (t, J = 7.5 Hz, 2 H), 3.31 (s, 1 H), 2.92 (d, J = 15.6 Hz, 1 H), 2.69–2.58 (m, 2 H), 0.90 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 170.31 (s), 140.72 (s), 130.74 (d), 127.51 (d), 126.72 (s), 122.00 (d), 114.85 (d), 46.22 (d), 34.63

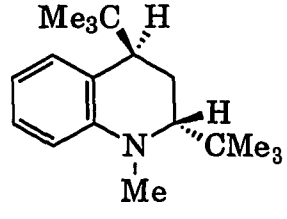
(s), 33.56 (t), 29.14 (q), 27.49 (q); GCMS m/z (relative intensity) 217 (M^+, 16), 160 (100), 132 (15), 77 (10), 57 (13); HRMS calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1473; FTIR (film) 2963, 1673 cm^{-1}.

4-(1,1-Dimethylethyl)-1,4-dihydro-1-methylquinoline (31)



This compound was isolated as an oil; ^1H NMR ($CDCl_3$) δ 7.18–7.12 (m, 1 H), 7.00 (dd, J = 7.5, 1.5 Hz, 1 H), 6.86 (td, J = 7.5, 1.2 Hz, 1 H), 6.70 (dd, J = 7.2, 0.9 Hz, 1 H), 6.13 (d, J = 7.8 Hz, 1 H), 4.65 (dd, J = 7.8, 5.7 Hz, 1 H), 3.10 (d, J = 5.7 Hz, 1 H), 3.04 (s, 3 H), 0.80 (s, 9 H); GCMS (relative intensity) 201 (M^+, 5), 186 (2), 144 (100), 145 (18), 129 (6), 128 (6), 115 (4), 77 (4); HRMS calcd for $C_{14}H_{19}N$ 201.1518, found 201.1519.

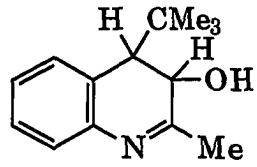
***trans*-2,4-Bis(1,1-dimethylethyl)-1,2,3,4-tetrahydro-1-methylquinoline (32)**



This compound was isolated as a solid: mp 32–33 °C; ^1H NMR ($CDCl_3$) δ

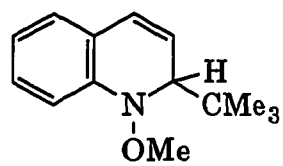
7.08 (ddd, J = 7.8, 7.2, 1.5 Hz, 1 H), 6.85 (dd, J = 7.2, 1.5 Hz, 1 H), 6.64–6.56 (m, 2 H), 3.02 (s, 3 H), 2.91 (dd, J = 11.1, 7.8 Hz, 1 H), 2.37 (dd, J = 6.0, 2.4 Hz, 1 H), 2.27 (ddd, J = 14.4, 7.8, 2.4 Hz, 1 H), 1.80 (ddd, J = 14.4, 11.1, 6.0 Hz, 1 H), 0.89 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 149.63 (s), 129.35 (d), 128.99 (s), 127.11 (d), 116.18 (d), 115.79 (d), 66.68 (d), 46.91 (d), 44.49 (q), 38.56 (s), 34.00 (s), 30.18 (t), 28.99 (q), 27.68 (q); GCMS m/z (relative intensity) 259 (M^+, 24), 202 (100), 174 (20), 144 (58); HRMS calcd for $C_{18}H_{29}N$ 259.2300, found 259.2292; Anal. Calcd for $C_{18}H_{29}N$: C, 83.33; H, 11.27; N, 5.40. Found: C, 83.39; H, 11.55; N, 5.70.

4-(1,1-Dimethylethyl)-3,4-dihydro-3-hydroxy-2-methylquinoline (41)



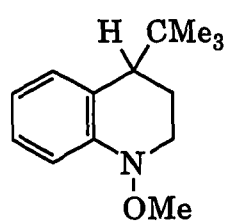
This compound was isolated as a solid: mp 127 °C; ^{1}H NMR ($CDCl_3$) δ 7.32–7.10 (m, 4 H), 4.08 (s, 1 H), 2.90 (br s, 1 H), 2.62 (s, 1 H), 2.28 (s, 3 H), 0.84 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 169.47 (s), 142.80 (s), 132.09 (d), 127.85 (d), 126.34 (d), 126.10 (d), 124.78 (s), 65.58 (d), 53.42 (d), 33.58 (s), 28.05 (q), 25.51 (q); FTIR ($CDCl_3$) 3227, 1639 cm^{-1}; HRMS calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1470; Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.88; N, 6.44. Found: C, 76.99; H, 8.94; N, 6.26.

2-(1,1-Dimethylethyl)1,2-dihydro-1-methoxyquinoline (44)



A pure sample of **44** could not be isolated by column chromatography because of decomposition to form 2-*tert*-butylquinoline. The structure of **44** is based on its conversion to 2-*tert*-butylquinoline with either acid or base. After aq $Na_2S_2O_3$ workup and extraction by CH_2Cl_2, the crude **44** had: ^1H NMR ($CDCl_3$) δ 7.21 (td, J = 7.5, 1.2 Hz, 1 H), 7.13–7.08 (m, 2 H), 6.95 (td, J = 7.2, 1.2 Hz, 1 H), 6.63 (d, J = 8.1 Hz, 1 H), 4.83 (dd, J = 8.1, 5.7 Hz, 1 H), 3.84 (s, 3 H), 3.08 (d, J = 5.7 Hz, 1 H), 3.84 (s, 3 H), 3.08 (d, J = 5.7 Hz, 1 H), 0.85 (s, 9 H); GCMS m/z (relative intensity) 217 (M^+, 11), 202 (10), 170 (11), 161 (14), 160 (79), 130 (100), 117 (11), 84 (24), 57 (19).

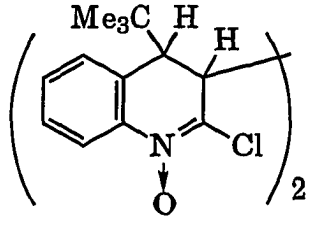
4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydro-1-methoxyquinoline



Workup with $NaBH_4$/MeOH of the *tert*-butylation products from *N*-methoxyquinolinium perchlorate gave low yields of this compound which was isolated as an oil: ^1H NMR ($CDCl_3$) δ 7.19–7.11 (m, 2 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.82 (ddd, J = 7.5, 6.6, 2.1 Hz, 1 H), 3.75 (s, 3 H), 3.54 (dt, J = 9.9, 6.3 Hz, 1 H),

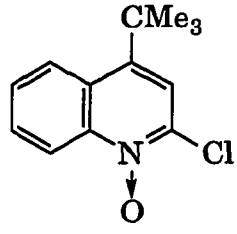
3.01–2.93 (m, 1 H), 2.58 (dd, J = 8.7, 4.5 Hz, 1 H), 2.23–2.11 (m, 1 H), 1.99 (ddt, J = 14.4, 8.7, 6.0 Hz, 1 H), 0.91 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 150.00 (s), 130.84 (d), 126.65 (d), 126.21 (s), 119.50 (d), 112.50 (d), 60.79 (q), 51.48 (t), 45.40 (d), 35.73 (s), 28.42 (q), 23.94 (t); GCMS m/z (relative intensity) 219 (M^+, 14), 189 (12), 162 (36), 132 (100); HRMS calcd for $C_{14}H_{21}NO$ 219.1623, found 219.1627.

3,3'-Bi[2-chloro-4-(1,1-dimethylethyl)-3,4-dihydroquinoline-1-oxide] (48)



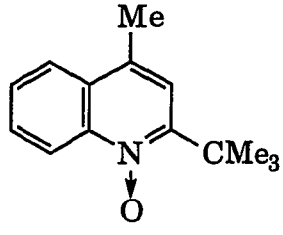
This compound was isolated as a solid: mp 155–156 °C; ^{1}H NMR ($CDCl_3$) δ 8.25 (dd, J = 8.1, 0.9 Hz, 1 H), 7.44 (td, J = 7.8, 1.2 Hz, 1 H), 7.17 (td, J = 7.5, 1.2 Hz, 1 H), 6.43 (dd, J = 7.8, 0.9 Hz, 1 H), 3.56 (s, 1 H), 2.17 (s, 1 H), 0.78 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 139.83 (s), 134.31 (s), 130.48 (d), 129.51 (d), 128.54 (d), 127.31 (s), 120.05 (d), 48.26 (d), 45.78 (d), 35.10 (s), 27.26 (q); CIMS (NH_3) m/z (relative intensity) 490 (M + NH_4^+, 0.1), 473 (MH^+, 6), 236 (M^+/2, 4), 180 (100); HRMS calcd for $C_{26}H_{30}Cl_2N_2O_2$ 472.1684, found 472.1675; FTIR ($CDCl_3$) 1587 cm^{-1}; Anal. Calcd for $C_{26}H_{30}Cl_2N_2O_2$: C, 65.96; H, 6.39; N, 5.92. Found: C, 65.43; H, 6.59; N, 5.73.

2-Chloro-4-(1,1-dimethylethyl)quinoline-1-oxide (50)



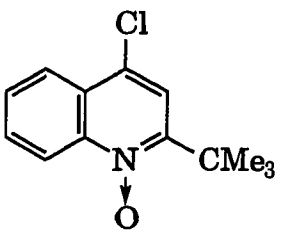
This compound was detected by GCMS m/z (relative intensity) 237 (13), 236 (7), 235 (M^+, 39), 219 (3), 197 (6), 179 (16), 145 (5), 127 (7), 76 (16), 62 (73), 56 (100).

2-(1,1-Dimethylethyl)-4-methylquinoline-1-oxide (51)



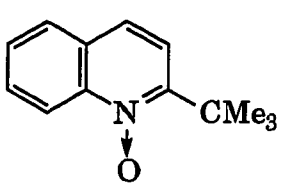
This compound was isolated as a solid: mp 83–84 °C; ^{1}H NMR ($CDCl_3$) δ 8.86 (d, J = 8.7 Hz, 1 H), 7.92 (dd, J = 8.1, 0.9 Hz, 1 H), 7.74 (ddd, J = 8.4, 6.9, 1.2 Hz, 1 H), 7.62 (ddd, J = 8.1, 6.9, 0.9 Hz, 1 H), 7.28 (s, 1 H), 2.65 (s, 3 H), 1.64 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 153.43 (s), 142.65 (s), 133.10 (s), 129.97 (d), 128.60 (s), 127.62 (d), 124.40 (d), 120.64 (d), 120.49 (d), 36.60 (s), 27.11 (q), 18.64 (q); GCMS m/z (relative intensity) 215 (M^+, 21), 198 (38), 173 (100), 157 (31), 156 (36), 142 (22), 115 (28), 77 (11); HRMS calcd for $C_{14}H_{17}NO$ 215.1310, found 215.1308; Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.92; H, 8.14; N, 6.42.

4-Chloro-2-(1,1-dimethylethyl)quinoline-1-oxide (53)



This compound was isolated as a solid: mp 103–104 °C; ^{1}H NMR ($CDCl_3$) δ 8.81 (d, *J* = 8.7 Hz, 1 H), 8.14 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.79 (ddd, J = 8.4, 6.9, 1.2 Hz, 1 H), 7.68 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1 H), 7.53 (s, 1 H), 1.62 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 154.02 (s), 143.64 (s), 130.86 (d), 128.90 (s), 128.55 (d), 126.58 (s), 124.66 (d), 120.30 (d), 120.14 (d), 36.68 (s), 26.70 (q); GCMS m/z (relative intensity) 237 (22), 236 (12), 235 (M^+, 66), 219 (13), 192 (9), 178 (4), 127 (3), 89 (10), 77 (10), 63 (80), 57 (17), 51 (100) HRMS calcd for $C_{13}H_{14}ClNO$ 235.0764, found 235.0767; Anal. Calcd for $C_{13}H_{14}ClNO$: C, 66.27; H, 5.99; N, 5.94. Found: C, 66.01; H, 5.99; N, 5.82.

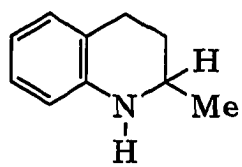
2-(1,1-Dimethylethyl)quinoline-1-oxide (57)



This compound was isolated as a solid: mp 91–92 °C; ^{1}H NMR ($CDCl_3$) δ 8.80 (d, *J* = 8.7 Hz, 1 H), 7.81 (d, *J* = 8.1, Hz, 1 H), 7.73 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1 H), 7.65 (d, *J* = 8.7 Hz, 1 H), 7.58 (ddd, *J* = 8.1, 6.9, 0.9 Hz, 1 H),7.46 (d, *J* = 8.7 Hz, 1 H), 1.63 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 150.45 (s), 136.09 (s), 130.24 (s), 129.49 (s),

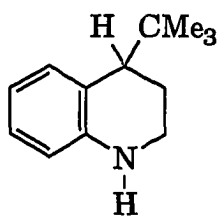
127.86 (d), 127.72 (d), 124.90 (d), 120.07 (d), 119.94 (d), 36.72 (s), 26.98 (q); GCMS m/z (relative intensity) 201 (M^+, 82), 185 (10), 169 (17), 168 (23), 58 (54), 56 (36), 51 (100); HRMS calcd for $C_{13}H_{15}NO$ 201.1154, found 201.1152; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.50; H, 7.57; N, 6.91.

2-Methyl-1,2,3,4-tetrahydroquinoline



This compound was detected by GCMS m/z (relative intensity) 148 (4), 147 (M^+, 37), 132 (100), 117 (17), 77 (12).

4-(1,1-Dimethylethyl)-1,2,3,4-tetrahydroquinoline



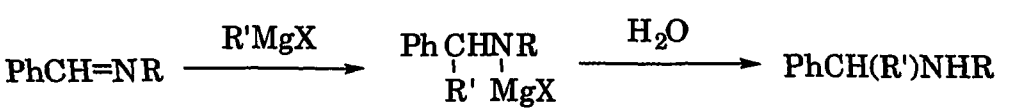
This compound was detected by GCMS m/z (relative intensity) 190 (2), 189 (M^+, 13), 132 (100), 130 (14).

CHAPTER III. *tert*-BUTYLATION OF *N*-BENZYLIDENEANILINES AND AZOBENZENES

Introduction

The condensation of primary amines with carbonyl compounds was first reported by Schiff,[66] and the condensation products are often referred to as Schiff bases.

The addition reactions of azomethine compounds are mainly composed of reactions in which a variety of reagents add to the polarized C=N double bond. Therefore, nucleophilic reagents attack the carbon atom of the C=N moiety. For example, Grignard reagents react with azomethine compounds to form addition products which on hydrolysis result in secondary amines.[67-69] In this addition reaction the alkyl group of the Grignard reagent is attached to the carbon atom of the azomethine compound.



N-Benzylidene-*tert*-butylamine reacts with methyllithium to yield *N*-α-methylbenzyl-*tert*-butylamine.[70]

Russell has reported that the addition of *t*-Bu· to Schiff bases, such as c-$C_6H_{11}N$=CHPh and PhN=CHPh, in the presence of PTSA occurs exclusively at the carbon atom of the C=N double bond.[34] The amine radical cations [$R^1NHCH(R^2)CMe_3^{+\cdot}$] formed from the iminium ions are readily reduced by *t*-BuHgCl/KI to form the amine in a chain reaction.

Azobenzene is a weak base and the azo group is potentially nucleophilic.[71,72] Electron-rich radicals, such as *tert*-butyl radical, can attack the N atom to form the alkylation products.[33]

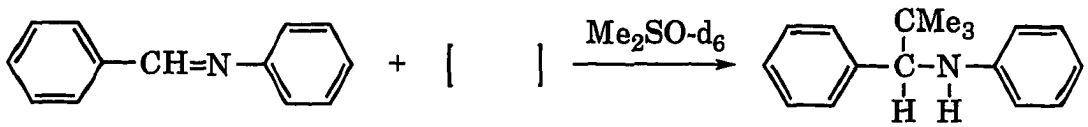
In this chapter, the *tert*-butylation of Ar-CH=N-Ar and Ar-N=N-Ar by *t*-BuHgX and the effect of KI on the reactions will be discussed.

Results and Discussion

tert-Butylation of *N*-Benzylideneanilines

Photostimulated *tert*-butylation of *N*-benzylideneaniline by *t*-BuHgI/I^- produced exclusively the reductive product, *N*-(2,2-dimethyl-1-phenylpropyl)aniline. The reaction was promoted by PTSA and NH_4I. Addition of PTSA increased the product yield from 53 to 100% in a 5 h reaction (Table XIX). There was no reaction in the dark between *t*-BuHgI/I^- and *N*-benzylideneaniline. Addition of NH_4I had no effect, while addition of PTSA promoted the reaction dramatically in the dark. Reaction of *N*-

Table XIX. Reaction of *t*-BuHgI with *N*-Benzylideneaniline.[a]



58

equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**58**
2	2	0	0	hν[c]	5	53
2	0	2	0	hν[c]	5	81
2	2	0	2	hν[c]	5	100
2	2	0	0	dark[d]	10	–
2	0	2	0	dark[d]	10	–
2	2	0	2	dark[d]	24	95
2	2	0	0	dark[e]	10	–
2	2	0	2	dark[f]	3.5	–

[a] 0.05 Mmol *N*-benzylideneaniline in 0.5 mL Me_2SO-d_6.

[b] By ^1H NMR with toluene as internal standard.

[c] 275 W fluorescent sunlamp at 35–40 °C.

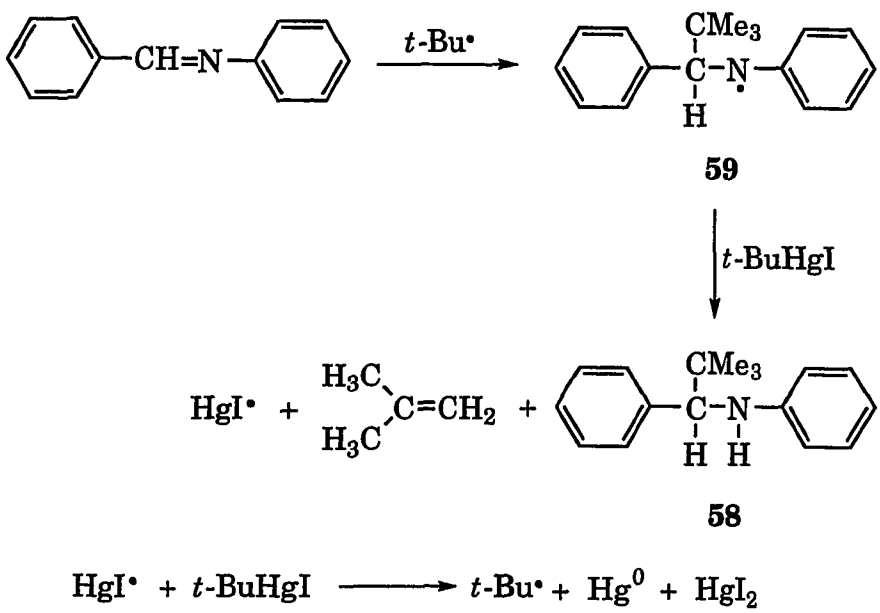
[d] Room temperature.

[e] 35–40 °C.

[f] 10 Mol % di-*tert*-butylnitroxide added.

benzylideneaniline with 4 equiv of *t*-BuHgI and 4 equiv of KI for 24 h in the presence of 4 equiv of PTSA yielded 95% of **58** in the dark. Attack of *t*-Bu· at the carbon of the C=N moiety of the *N*-benzylideneaniline forms the *N*-centered radical **59**, which extracts a hydrogen atom from *t*-BuHgI or *t*-$BuHgI_2^-$ to form the reductive product **58** (Scheme XXVII).

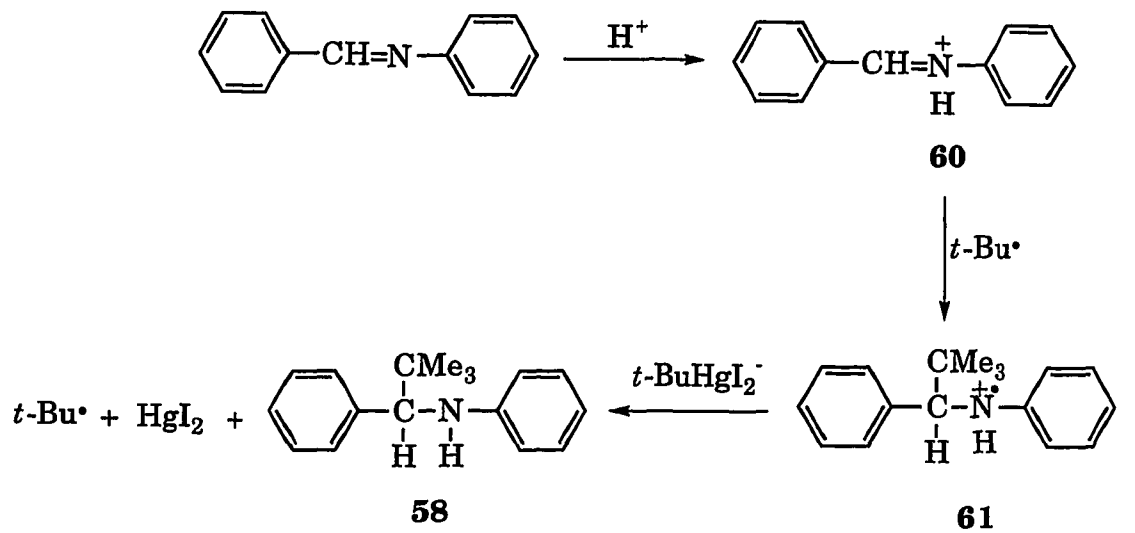
Scheme XXVII. *tert*-Butylation of *N*-Benzylideneaniline.



$$HgI^{\bullet} + t\text{-BuHgI} \longrightarrow t\text{-Bu}^{\bullet} + Hg^0 + HgI_2$$

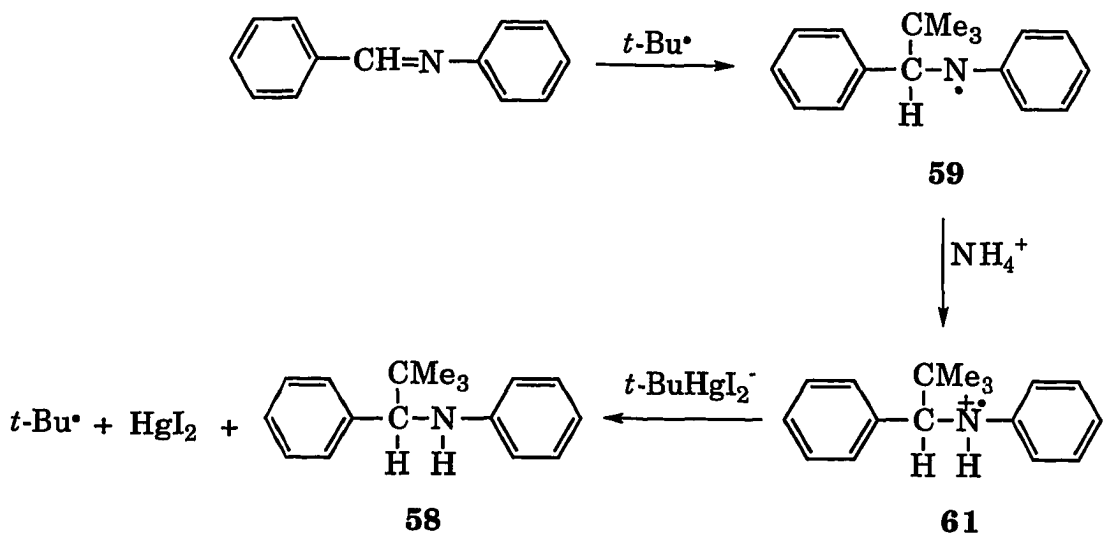
Protonation of *N*-benzylideneaniline on N speeds up the reaction dramatically. Iminium salts are more electron-deficient compared to imines, thus *t*-Bu· reacts faster with an iminium ion to form the radical cation **61**, which is reduced by *t*-$BuHgI_2^-$ to give the reductive product **58**. The *t*-Bu· formed continues the chain process (Scheme XXVIII).

Scheme XXVIII. *tert*-Butylation of *N*-Benzylideneaniline in the Presence of PTSA.



The p*K*a of NH_4^+ is 9.2 in water and 10.5 in Me_2SO.[73] The p*K*a of *N*-*p*-chlorobenzylideneaniline is 2.8 in water[74] and not available in Me_2SO. The p*K*a of $PhNH_3^+$ is 4.6 in water and 3.6 in Me_2SO.[73] It seems that **60** is a stronger acid than NH_4^+; therefore, its conjugated base *N*-benzylideneaniline can only be very slightly protonated by NH_4^+. From the experimental results (Table XIX), no *tert*-butylation was observed in the presence of 2 equiv of NH_4I in the dark, while 95% of *tert*-butylation product **58** was formed in the presence of 2 equiv of PTSA. This suggests that *N*-benzylideneaniline is not basic enough to be protonated by NH_4^+. However, protonation of radical adduct **59** by NH_4^+ is possible, since **59** is more basic than *N*-benzylideneaniline itself (the p*K*a of $PhNH_2^{+\cdot}$ is 7.0[75]) (Scheme XXIX).

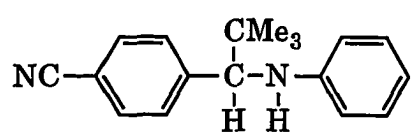
Scheme XXIX. *tert*-Butylation of *N*-Benzylideneaniline in the Presence of NH_4I.



tert-Butylation of *N*-benzylideneaniline in the presence of PTSA in the dark was totally inhibited by adding 10 mol % di-*tert*-butylnitroxide for 3.5 h. This result suggests that the *tert*-butylation process is a free radical chain reaction.

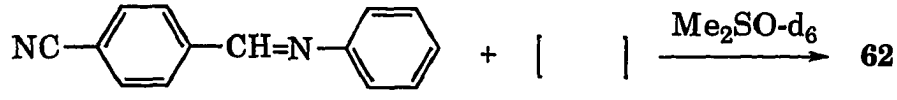
tert-Butylation of *N*-*p*-cyanobenzylideneaniline by *t*-BuHgI is shown in Table XX. The results are similar to those in Table XIX. The product yields showed no difference after workup with aqueous $Na_2S_2O_3$ solution.

The yields of isobutene and Hg^0 were measured. Photolysis of *N*-*p*-cyanobenzylideneaniline with 2 equiv of *t*-BuHgI and 2 equiv of KI yielded at 6 h



62

Table XX. Reaction of *t*-BuHgI with *N*-*p*-Cyano-benzylideneaniline.[a]



equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**62**
2	2	0	0	hν[c]	5.5	67
2	2	0	0	hν[c]	7.5	87
2	2	0	0	hν[c]	7.5[e]	86
2	0	2	0	hν[c]	5.5	88
2	0	2	0	hν[c]	7.5	88
2	0	2	0	hν[c]	7.5[e]	84
2	2	0	2	hν[c]	4.5	99
2	2	0	2	hν[c]	4.5[e]	97
2	2	0	0	dark[d]	10	–
2	0	2	0	dark[d]	10	–
2	2	0	2	dark[d]	10	60
2	2	0	2	dark[d]	24	95

[a] 0.05 Mmol *N*-*p*-cyanobenzylideneaniline in 0.5 mL Me_2SO-d_6.

[b] By ^1H NMR with toluene as internal standard.

[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.

[e] Workup with aq $Na_2S_2O_3$.

the product **62**, isobutene and Hg^0 in a ratio of ~1:0.5:1 (Table XXI).

It is reasonable that the detected isobutene is less than the expected 1 equiv relative to product **62** because isobutene is a gas and some of the isobutene produced during the reaction may be released from the solution.

Table XXI. Detection of Products from the Photolysis of *t*-BuHgI and *N*-*p*-Cyanobenzylideneaniline.[a]

equivalents						yield (%)[b]	
t-BuHgI	KI	NH_4I	PTSA	time (h)	**62**	isobutene	Hg^0
2	2	0	0	6	78	33	80
1	1	0	0	9	45	15	*c*
1	0	1	0	5	68	11	*c*
1	1	0	1	3	91	~6	tr

[a] Photolysis of 0.05 mmol of *N*-*p*-cyanobenzylideneaniline in 0.5 mL Me_2SO-d_6 by a 275 W fluorescent sunlamp at 35–40 °C.

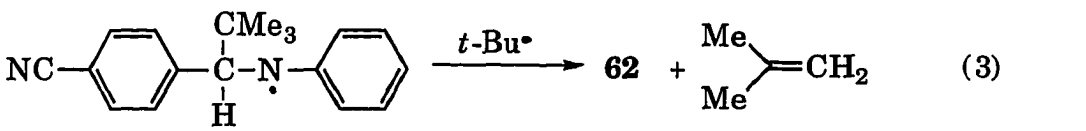
[b] By ^1H NMR with toluene as internal standard.

[c] Very fine Hg^0 formed.

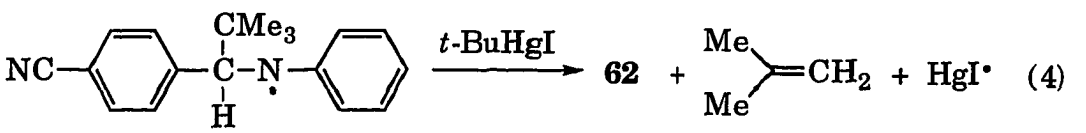
Bubbles were observed when the NMR tube was shaken during the photolysis. Photolysis of *N*-*p*-cyanobenzylideneaniline with 1 equiv of *t*-BuHgI and 1 equiv of KI for 9 h produced **62** in 45% yield, and isobutene in 15% yield. The yield of Hg^0 could not be measured, because very fine Hg^0 powder was formed. The less than 50% yield of **62** formed supports the mechanism in Scheme XXVII. Not surprisingly, photolysis of *N*-*p*-cyanobenzylideneaniline with 1 equiv of *t*-

BuHgI and 1 equiv of KI in the presence of 1 equiv of PTSA produced 91% of **62**. PTSA protonates the imine to form the iminium ion which captures the *t*-Bu· to form a radical cation that is reduced by electron transfer from I^- or *t*-$BuHgI_2^-$.

One may argue that a 1:2 stoichiometry of *N*-*p*-cyanobenzylideneaniline and *t*-BuHgI might suggest the following two possible reactions.

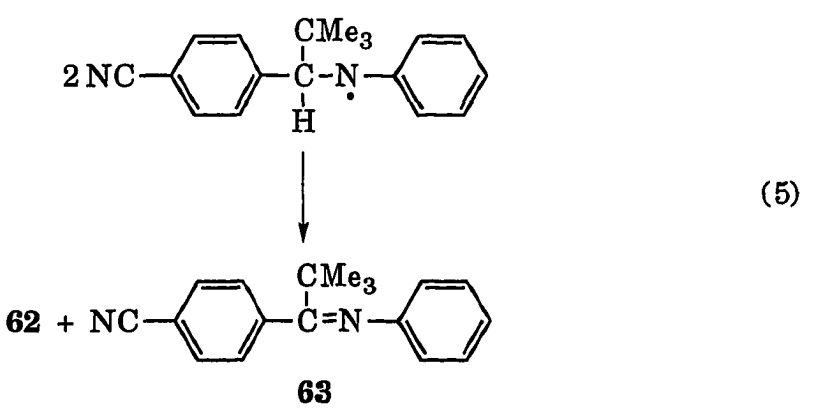


(3)



(4)

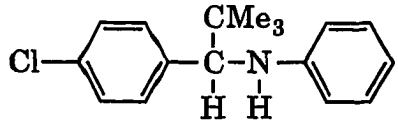
If reaction (3) is the process that forms product **62**, reaction (5) should also occur. The experiments have showed no evidence of the formation of compound **63**.Therefore, reaction (4) may well be the major route to form the product **62**.



(5)

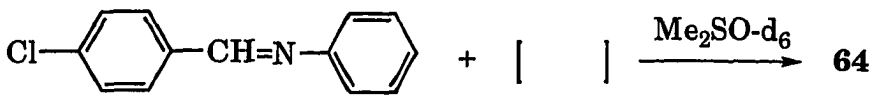
63

Some other *N*-*p*-substituted benzylideneanilines have been studied and all the reactions give similar results (Table XXII–XXVI).



64

Table XXII. Reaction of *t*-BuHgI with *N*-*p*-Chlorobenzylideneaniline.[a]



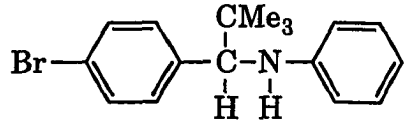
equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**64**
2	2	0	0	hν[c]	5	50
2	0	2	0	hν[c]	5	86
2	2	0	2	hν[c]	5	98
2	2	0	0	dark[d]	10	–
2	0	2	0	dark[d]	10	–
2	2	0	2	dark[d]	10	55
2	2	0	2	dark[d]	24	95

[a] 0.05 Mmol *N*-*p*-chlorobenzylideneaniline in 0.5 mL Me_2SO-d_6.

[b] By ^1H NMR with toluene as internal standard.

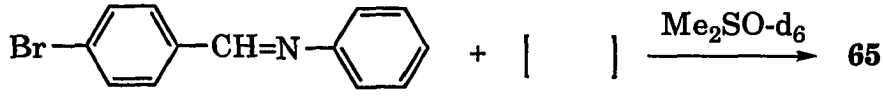
[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.



65

Table XXIII. Reaction of *t*-BuHgI with *N*-*p*-Bromobenzylideneaniline.[a]



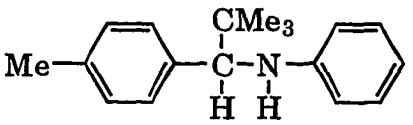
equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**65**
2	2	0	0	hν[c]	5	56
2	0	2	0	hν[c]	5	87
2	2	0	2	hν[c]	5	99
2	2	0	2	dark[d]	24	92

[a] 0.05 Mmol *N*-*p*-bromobenzylideneaniline in 0.5 mL Me_2SO-d_6.

[b] By ^1H NMR with toluene as internal standard.

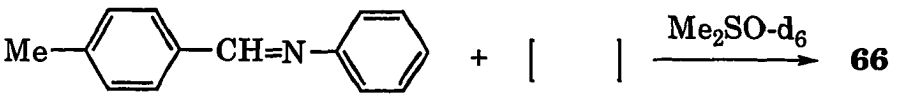
[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.



66

Table XXIV. Reaction of *t*-BuHgI with *N*-*p*-Methylbenzylideneaniline.[a]



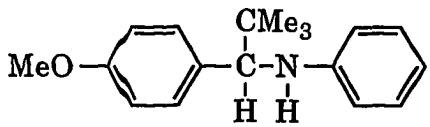
equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**66**
2	2	0	0	hν[c]	5.5	53
2	0	2	0	hν[c]	5.5	81
2	2	0	2	hν[c]	5.5	100
2	2	0	2	dark[d]	24	92

[a] 0.05 Mmol *N*-*p*-methylbenzylideneaniline in 0.5 mL Me_2SO-d_6.

[b] By ^1H NMR with toluene as internal standard.

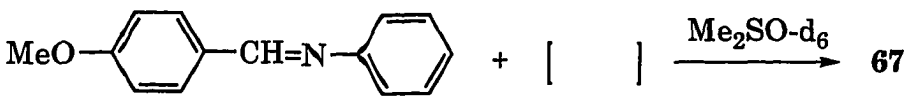
[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.



67

Table XXV. Reaction of *t*-BuHgI with *N*-*p*-Methoxybenzylideneaniline.[a]

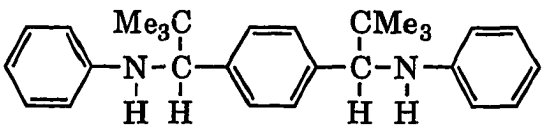


equivalents						yield (%)[b]	
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**67**	isobutene
2	2	0	0	hν[c]	5	56	34
2	0	2	0	hν[c]	5	82	35
2	2	0	2	hν[c]	24	100	12

[a] 0.05 Mmol *N*-*p*-methoxybenzylideneaniline in 0.5 mL Me_2SO-d_6.

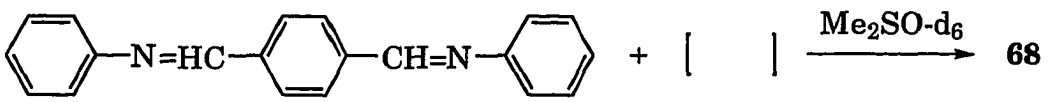
[b] By ^1H NMR with toluene as internal standard.

[c] 275 W fluorescent sunlamp at 35–40 °C.



68

Table XXVI. Reaction of *t*-BuHgI with 1,4-Diphenylaminomethylenebenzene.[a]



equivalents						yield (%)[b]
t-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**68**
2	2	0	0	hν[c]	5	50
2	0	2	0	hν[c]	5	81
2	2	0	2	hν[c]	5	98
2	2	0	2	dark[d]	30	92

[a] 0.05 Mmol 1,4-diphenylaminomethylenebenzene in 0.5 mL Me_2SO-d_6.

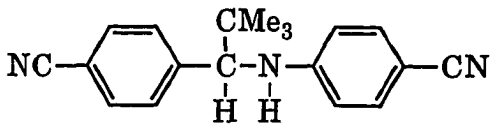
[b] By ^1H NMR with toluene as internal standard.

[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.

tert-Butylation of *N*-(*p*-cyanobenzylidene)-*p*-cyanoaniline by *t*-BuHgX (X = Cl, I) has been studied. *N*-(*p*-Cyanobenzylidene)-*p*-cyanoaniline cannot be alkylated by *t*-BuHgCl (4 equiv) alone in 5 h under sunlamp irradiation. In the presence of KI, 27% of **69** and 20% of isobutene were formed in 1 h. The system

t-BuHgCl/KI and *t*-BuHgI/KI have the same effect on the alkylation of *N*-*p*-(cyanobenzylidene)-*p*-cyanoaniline and are faster than *t*-BuHgI alone (Table XXVII). The fact that KI is required for the reaction to take place indicates that RHgI is more reactive than RHgCl.



69

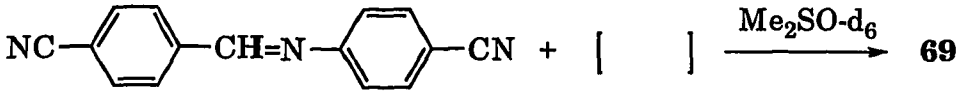
Surprisingly, photolysis of *t*-BuHgI with *N*-cinnamylideneaniline gave none of the expected product and none of the *N*-cinnamylideneaniline was recovered.

Reactivities of some *p*-substituted compounds relative to *N*-benzylideneaniline have been studied in the presence of PTSA. Table XXVIII shows the results. Substituents such as CN, Cl, and Br have no effect on the reaction. There might be two effects which would influence the reactivities. (1). An electron-withdrawing group R decreases the basicity of C=N moiety. (2). An electron-withdrawing group R makes $[ArCH=NHPh]^+$ a better electron-acceptor and increases the rate of *t*-Bu· attack. Apparently, these two effects cancel and the reactivity is independent of R.

tert-Butylation of Azobenzenes

It has been reported that photostimulated *tert*-butylation of *t*-BuHgCl with azobenzene in the presence of KI gives the reductive *N*-alkylation product

Table XXVII. Reaction of *t*-BuHgI with *N*-*p*-(Cyanobenzylidene)-*p*-cyanoaniline.[a]



equivalents							yield (%)[b]	
t-BuHgCl	*t*-BuHgI	KI	NH_4I	PTSA	condition	time (h)	**69**	isobutene
4	0	0	0	0	hν[c]	5	–	tr
0	4	0	0	0	hν[c]	1	27	20
4	0	8	0	0	hν[c]	1	34	29
0	4	4	0	0	hν[c]	1	36	27
0	4	4	0	0	hν[c]	5[e]	92	67
0	2	2	0	0	hν[c]	5	58	43
0	2	0	2	0	hν[c]	5	85	48
0	2	2	0	2	hν[c]	1.5	98	15
0	2	2	0	2	hν[c]	5	100	12
0	2	2	0	0	dark[d]	24	–	–
0	2	2	0	2	dark[d]	24	92	5

[a] 0.05 Mmol *N*-*p*-cyanobenzylidene-*p*-cyanoaniline in 0.5 mL Me_2SO-d_6.

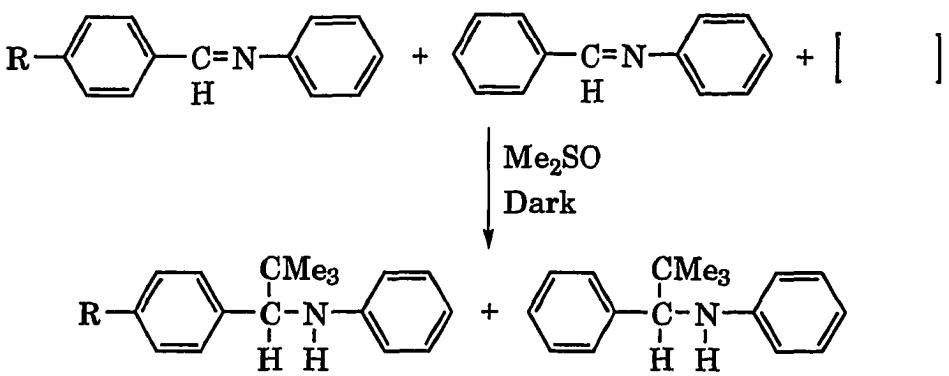
[b] By ^1H NMR with toluene as internal standard.

[c] 275 W fluorescent sunlamp at 35–40 °C.

[d] Room temperature.

[e] 11 Mg Hg^0 detected.

Table XXVIII. Reactivities Relative to *N*-Benzylideneaniline in the Presence of PTSA.[a]



70 **58**

	equivalents				yield (%)[b]	
R	*t*-BuHgI	KI	PTSA	time (h)	**70**	**58**
CN	4	4	2	1.67	~20	20
Cl	4	4	2	1.67	~20	20
Br	4	4	2	1.67	~20	20

[a] 0.05 mmol *N*-*p*-substituted-benzylideneaniline and 0.05 mmol *N*-benzylideneaniline in 0.5 mL Me_2SO-d_6 in the dark at room temperature.
[b] By ^1H NMR with toluene as internal standard.

71, according to Scheme XXX.[33] However, no observation of the intermediate PhN(CMe_3)N(HgX)Ph **72** has been reported.

The reaction of *t*-BuHgX with azobenzene was carried out in Me_2SO-d_6 and the result is reported in Table XXIX. No intermediate **72** was observed by ^1H NMR in Me_2SO-d_6. A different mechanism is suggested (Scheme XXXI).

Scheme XXX. *tert*-Butylation of Azobenzene via Intermediate **72**.

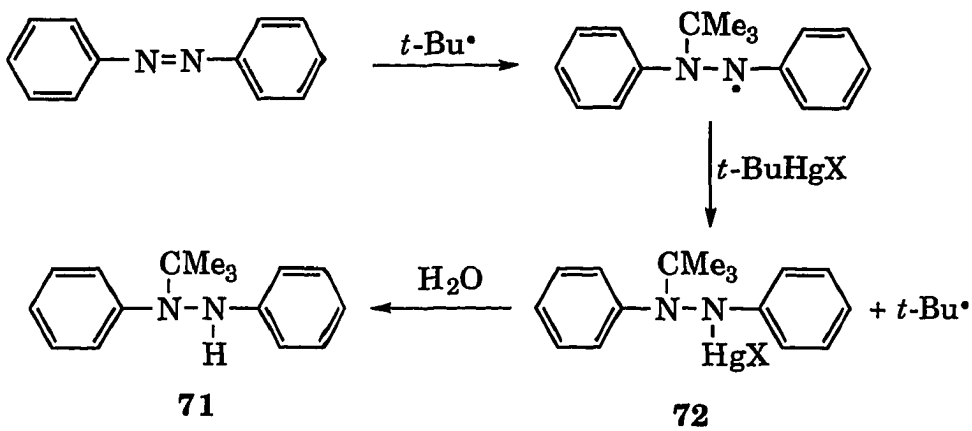
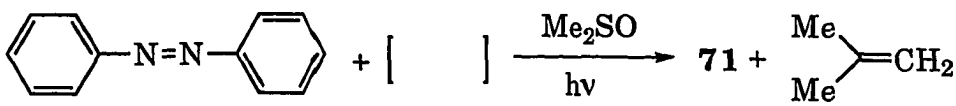


Table XXIX. Reaction of *t*-BuHgX with Azobenzene.[a]



equivalents			yield (%)[b]	
t-BuHgX	KI	time (h)	**71**	isobutene
Cl, 2	4	3.5[c]	–	–
Cl, 2	4	19	34	25
I, 2	2	22	38	22

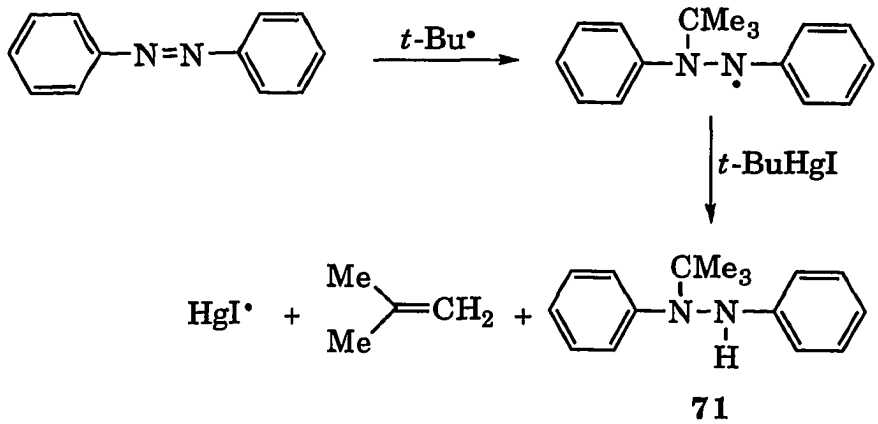
[a] 0.1 Mmol azobenzene in 0.5 mL Me_2SO-d_6 irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with diiodomethane as internal standard.

[c] Wrapped with aluminum foil.

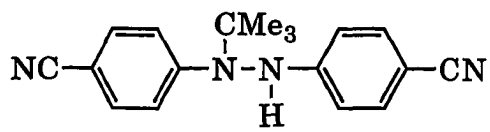
Photostimulated *tert*-butylation of *p,p'*-dicyanoazobenzene gave the reductive alkylation product *p,p'*-dicyano-*N-tert*-butylhydrazobenzene **73**. There was no reaction between *t*-BuHgCl and *p,p'*-dicyanoazobenzene when KI was added.Addition of $K_2S_2O_8$ speeds up the reaction. With 2 equiv of $K_2S_2O_8$,

Scheme XXXI. *tert*-Butylation of Azobenzene.



71

$$HgI^{\bullet} + t\text{-BuHgI} \longrightarrow t\text{-Bu}^{\bullet} + Hg^{0} + HgI_2$$

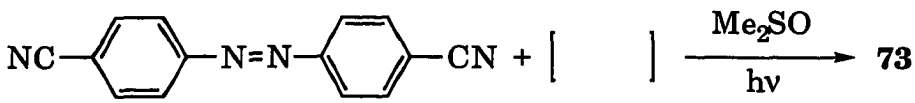


73

p,p'-dicyanoazobenzene reacted with 4 equiv of *t*-BuHgI and 4 equiv of KI in 5 h to form *N-tert*-butyl-*p,p'*-dicyanohydrazobenzene in 97% yield (Table XXX). Apparently, $K_2S_2O_8$ accelerates the formation of *tert*-butyl radical (Scheme XXXII).

The reaction with *p,p'*-dicyanoazobenzene is faster than with azobenzene itself, because the electron-withdrawing CN group facilitates attack by the nucleophilic *t*-Bu·. Photolysis of *t*-BuHgX with *p,p'*-dimethoxyazobenzene gave a mixture in low yield with or without KI. Even addition of $K_2S_2O_8$ did not improve the reaction. The electron-donating MeO group apparently inhibits the *tert*-butylation.

Table XXX. Reaction of *t*-BuHgX with *p,p'*-Dicyanoazobenzene.[a]



	equivalents			yield (%)[b]
t-BuHgX	KI	$K_2S_2O_8$	time (h)	**73**
Cl, 4	0	0	19	–
Cl, 4	8	2	5	92
I, 4	4	0	19	87
I, 4	4	2	5	97

[a] 0.2 Mmol *p,p'*-dicyanoazobenzene in 4 mL Me_2SO-d_6 irradiated with a 275 W fluorescent sunlamp at 35–40 °C.

[b] By ^1H NMR with diiodomethane as internal standard.

Scheme XXXII. Formation of *tert*-Butyl Radical in the Presence of $K_2S_2O_8$.

$$I^- + S_2O_8^{2-} \longrightarrow SO_4^{2-} + SO_4^{-\bullet} + I^\bullet$$

$$I^\bullet + t\text{-BuHgX} \longrightarrow IHgX + t\text{-Bu}^\bullet$$

$$SO_4^{-\bullet} + t\text{-BuHgX} \longrightarrow XHgOSO_3^- + t\text{-Bu}^\bullet$$

Conclusion

Reactions of *t*-BuHgI with *N*-benzylideneanilines give exclusively the reductive alkylation products. *t*-Bu· reacts at the C atom of the C=N moiety. *t*-BuHgCl does not react with benzylideneanilines under sunlamp irradiation conditions while *t*-BuHgI reacts readily. A 1:2 ratio of *N*-benzylideneaniline and *t*-BuHgI (or *t*-BuHgX/I^-) is required in order to achieve a 100% yield of the reductive alkylation product. Addition of PTSA promotes the reaction dramatically. Now yields approaching 100% can be obtained with only 1 equiv of *t*-BuHgI. The *tert*-butylation can even occur in the dark in high yield in the presence of PTSA. Quantitative yields have been obtained in the system *t*-BuHgI/KI/PTSA upon sunlamp irradiation. A radical process is followed. I^- has very important effects on the *tert*-butylation which are explained by: (1) Faster generation of the *tert*-butyl radical. (2) Electron transfer from *t*-$BuHgI_2^-$ to the protonated adduct radical cation. (3) In the absence of PTSA, *t*-BuHgI/I^- is a better H-atom donor.

Photolysis of *t*-BuHgI with azobenzenes also gives the reductive

alkylation products. Addition of $K_2S_2O_8$ speeds up the *tert*-butylation by fast formation of the *tert*-butyl radical.

Experimental Section

General Consideration

^1H and ^{13}C NMR spectra were recorded on a Nicolet NT 300 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane (300 MHz for ^1H NMR) or for ^{13}C NMR measured relative to the central line of internal $CDCl_3$ at 77.000 ppm (75.4 MHz for ^{13}C NMR). Analytical gas chromatography (GC) was performed on a Perkin-Elmer 3920 gas chromatography equipped with a Hitachi D-2500 Chromato-integrator. GCMS were recorded on a Finnegan 4000 spectrometer with Incos data system or Magnum MS and high resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

The products were isolated by flash column chromatography on silica gel (Merck, grade 9385, 230–400 mesh, 60 Å, Aldrich Chemical Co.) with mixed solvents (hexane/ethyl acetate) as eluents. ^1H NMR yields were determined by integration with a known amount of an internal standard (toluene or diiodomethane).

Solvents and Reagents

Solvents were purchased from Fisher and Baker Chemical Co. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride and stored over 4 Å molecular sieves under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium metal. Other solvents were purchased and used without further purification.

Chemical reagents in high purity grades were purchased mostly from Aldrich Chemical Co. In most cases, the reagents were used without further purification.

tert-Butylmercury chloride was prepared as previously described (see Chapter I).

Preparation of *tert*-Butylmercury Iodide

tert-Butylmercury iodide was prepared by a modified anion exchange method.[76] *tert*-Butylmercury chloride (0.03 mol) was mixed with a two-fold excess of potassium iodide in 40 mL of dimethyl sulfoxide. The solution was stirred for 2 hours at room temperature. The reaction was quenched by adding 100 mL of water and the mixture extracted twice with ether (70 mL) and the combined organic extract filtered through a celite-filled sintered glass funnel and washed three times with water (100 mL). The solution was dried over anhydrous magnesium sulfate and the solvent was evaporated until white crystals precipitated. The solution was filtered immediately. The white crystals turned pale yellow when exposed to the air. ^1H NMR ($CDCl_3$) δ 1.53 (s,

9 H). The material decomposed before a clear melting point could be determined.

Materials

N-Benzylideneaniline was purchased from Aldrich Chemical Co. Other *N*-benzylideneanilines were prepared by condensation of the corresponding benzaldehydes and anilines.[77,78] A 1:1 molar ratio of *p*-substituted aldehyde and aniline was stirred in absolute ethanol at room temperature for several hours. When *p*-cyanoaniline was used, a 1:1 molar ratio mixture of *p*-cyanoaniline and *p*-cyanobenzaldehyde was refluxed in absolute ethanol for several hours. The product was collected by filtration and recrystallized in ethanol.

_N_-*p*-Cyanobenzylideneaniline

This compound had mp: 97–98 °C (lit.[79] 97–98 °C). ^{1}H NMR (Me_2SO-d_6) δ 8.71 (s, 1 H), 8.08 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 8.1 Hz, 2 H), 7.42 (t, J = 7.8 Hz, 2 H), 7.31–7.27 (m, 3 H).

_N_-*p*-Chlorobenzylideneaniline

This compound had mp: 65–66 °C (lit.[79] 64–65 °C). ^{1}H NMR (Me_2SO-d_6) δ 8.61 (s), 7.93 (d, J = 8.7 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.40 (t, J = 7.8 Hz, 2 H), 7.24 (m, 3 H).

_N_-_p_-Methylbenzylideneaniline

This compound had mp: 44–45 °C (lit.[79] 43.5–44.5 °C). ^{1}H NMR (Me_2SO-d_6) δ 8.41 (s, 1 H), 7.79 (d, J = 8.1 Hz, 2 H), 7.41–7.36 (m, 2 H), 7.29–7.19 (m, 5 H), 2.41 (s, 3 H).

_N_-_p_-Methoxybenzylideneaniline

This compound had mp: 53–54 °C (lit.[79] 56–57 °C). ^{1}H NMR (Me_2SO-d_6) δ 8.50 (s, 1 H), 7.86 (d, J = 8.7 Hz, 2 H), 7.40–7.35 (m, 2 H), 7.21–7.19 (m, 3 H), 7.05 (d, J = 8.4 Hz, 2 H), 3.81 (s, 3 H).

_N_-(_p_-Cyanobenzylidene)-_p_-cyanoaniline

This compound had mp 230–231 °C. ^{1}H NMR (Me_2SO-d_6) δ 8.71 (s, 1 H), 8.09 (d, J = 8.1 Hz, 2 H), 7.99 (d, J = 8.1 Hz, 2 H), 7.89 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 8.4 Hz, 2 H); HRMS calcd for $C_{15}H_9N_3$ 231.0797, found 231.0803.

1,4-Bis(phenylaminomethylene)benzene

This compound had mp 161–162 °C. ^{1}H NMR ($CDCl_3$) δ 8.52 (s, 2 H), 8.01 (s, 4 H), 7.44– 7.39 (m, 4 H), 7.28–7.24 (m, 6 H); HRMS calcd for $C_{20}H_{16}N_2$ 284.1314, found 284.1315.

N-Cinnamylideneaniline

This compound had mp: 105–106 °C. ^{1}H NMR (Me_2SO-d_6) δ 8.37 (d, J = 9.0 Hz, 1 H), 7.67–7.64 (m, 2 H), 7.43–7.32 (m, 6 H), 7.22–7.10 (m, 4 H).

Azobenzene was purchased from Aldrich Chemical Co. *p,p'*-Dicyanoazobenzene and *p,p'*-dimethoxyazobenzene were prepared following literature methods.[80,81]

p,p'-Dicyanoazobenzene

A mixture of *p*-nitrobenzonitrile (8.9 g) and sodium hydroxide (9 g) in water (8 mL) and ethanol (36 mL) was treated with zinc dust (21 g) in small portions at a rate sufficient to maintain vigorous boiling. After all the zinc dust had been added, the reaction mixture was then filtered, and the zinc residues washed with boiling ethanol (30 mL). Air was then drawn through the solution for 6 hours (to oxidize any hydrazo compound), and the crude azo compound collected. Recrystallized from ethanol afforded *p,p'*-dicyanoazobenzene: mp 271–272 °C (lit.[80] 269–270 °C); ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 8.7 Hz, 2 H), 7.85 (d, J = 8.7 Hz, 2 H).

p,p'-Dimethoxyazobenzene

This compound had mp: 165–166 °C (lit.[80] 166–168 °C); ^{1}H NMR (Me_2SO-d_6) δ 7.82 (d, J = 9.0 Hz, 4 H), 7.10 (d, J = 8.7 Hz, 4 H), 3.83 (s, 6 H).

General Procedure for the Photostimulated Reactions of *N*-Benzylideneanilines

The substrate (0.05 mmol), *t*-BuHgCl (0.20 mmol) or *t*-BuHgI (0.05–0.20 mmol) and KI (0–0.40 mmol) or NH_4I (0–0.10 mmol) with or without added PTSA were placed in a NMR tube, and 0.5 mL of deoxygenated Me_2SO-d_6 was added under nitrogen. The solution was irradiated with a 275 W General Electric fluorescent sunlamp ca. 25 cm from the reaction tube. Toluene was added as an internal standard before the ^1H NMR spectroscopy was taken.

General Procedure for the *tert*-Butylation Reactions of *N*-Benzylideneanilines in the Dark.

The substrate (0.05 mmol), *t*-BuHgCl (0.20 mmol) or *t*-BuHgI (0.05–0.20 mmol) and KI (0–0.40 mmol) or NH_4I (0–0.10 mmol) with or without added PTSA were placed in a NMR tube, and 0.5 mL of deoxygenated Me_2SO-d_6 was added under nitrogen. The NMR tube was wrapped with Aluminum foil and either placed at room temperature or was irradiated with a 275 W General Electric fluorescent sunlamp ca. 25 cm from the tube.

General Procedure for the Isolation of the Reaction Products from the Reaction of *t*-BuHgI with *N*-Benzylideneanilines

The substrates (0.2 mmol), *t*-BuHgI (0.4 mmol), KI (0.4 mmol) and PTSA (0.4 mmol) were placed in a Pyrex test tube. 2 M
L of deoxygenated Me_2SO 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, and extracted with CH_2Cl_2. The extract was washed with saturated aqueous $Na_2S_2O_3$ (3 x 15 mL) and saturated brine (15 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. Products were isolated by flash column chromatography with hexane/ethyl acetate as the eluent. All the solids were recrystallized from hexane/ethyl acetate.

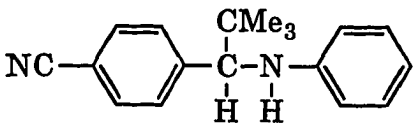
General Procedure for the *tert*-Butylation of Azobenzenes

The substrate (0.2 mmol), *t*-BuHgX (0–0.8 mmol), and KI (0–1.6 mmol) with or without added $K_2S_2O_8$ (0–0.4 mmol) were placed in a Pyrex test tube, and 4 mL of deoxygenated Me_2SO 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 three times with saturated aqueous $Na_2S_2O_3$ and saturated brine, dried over anhydrous $MgSO_4$, and concentrated under vacuum. Products were isolated by column chromatography with hexane/ethyl acetate as the eluent.

Characterization of Products

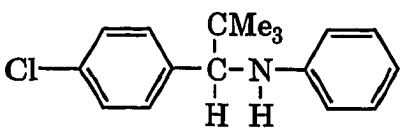
N-(2,2-Dimethyl-1-phenylpropyl)aniline and 1-phenyl-1-(phenylazo)-2,2-dimethylpropane have been isolated and characterizated.[33]

4-[2,2-Dimethyl-1-(phenylamino)propyl]benzonitrile (62).



This compound was isolated as a solid: mp 159–160 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.07–7.02 (m, 2 H), 6.62 (t, J = 7.2 Hz, 1 H), 6.43–6.40 (two doublets, J_1 = 8.7 Hz, J_2 = 8.4 Hz, 2 H), 4.26 (br d, J = 5.1 Hz, 1 H), 4.08 (d, J = 5.4 Hz, 1 H), 0.99 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 147.20 (s), 146.89 (s), 131.56 (d), 129.14 (d), 129.10 (d), 118.91 (s), 117.54 (d), 113.08 (d), 110.73 (s), 67.07 (d), 34.93 (s), 26.93 (q); GCMS m/z (relative intensity) 264 (M^+, 5), 207 (100), 104 (5), 77 (10); HRMS Calcd for $C_{18}H_{20}N_2$: 264.1632, found 264.1627; Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.62; N, 10.60. Found: C, 82.12, H, 7.79; N. 10.40.

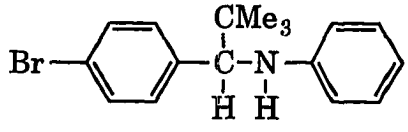
***N*-[1-(4-Chlorophenyl)-2,2-dimethylpropyl]aniline (64)**



This compound was isolated as a solid: mp 95–96 °C; ^{1}H NMR ($CDCl_3$) δ 7.23 (s, 4 H; m in Me_2SO-d_6), 7.04 (t, J = 8.1 Hz, 2 H), 6.60 (t, J = 8.1 Hz, 1 H), 6.45 (d,J = 8.1 Hz, 2 H), 4.20 (s, 1 H), 4.00 (s, 1 H), 0.96 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 147.32 (s), 139.69 (s), 132.39 (s), 129.71 (d), 129.01 (d), 127.87 (d), 117.15 (d), 113.13 (d), 66.62 (d), 34.82 (s), 26.97 (q); GCMS m/z (relative intensity) 273 (M^+, 2), 216

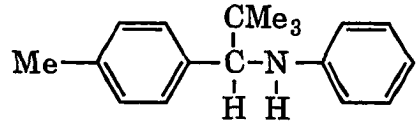
(100), 104 (10), 77 (18); HRMS Calcd for $C_{17}H_{20}NCl$ 273.1284, found, 273.1291; Anal. Calcd for $C_{17}H_{20}NCl$: C, 74.57; H, 7.36; N, 5.12. Found C, 73.45, H, 7.14, N, 4.90.

_N_-[1-(4-Bromophenyl)-2,2-dimethylpropyl]aniline (65)



This compound was isolated as a solid: mp 91–92 °C; ^1H NMR ($CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 7.04 (dd, J = 8.4, 7.5 Hz, 2 H), 6.60 (t, J = 7.2 Hz, 1 H), 6.45–6.42 (m, 2 H), 4.20 (s, 1 H), 3.98 (s, 1 H), 0.96 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 147.27 (s), 140.25 (s), 130.81 (d), 130.12 (d), 129.02 (d), 120.57 (s), 117.18 (d), 113.13 (d), 66.68 (d), 34.76 (s), 26.93 (q); GCMS m/z (relative intensity) 317 (M^+, 7), 260 (100), 180 (15), 104 (46); HRMS calcd for $C_{17}H_{20}BrN$ 317.0779, found 317.0780; Anal. Calcd for $C_{17}H_{20}BrN$: C, 64.16; H, 6.33; N, 4.40. Found: C, 63.78; H, 6.05; N, 4.27.

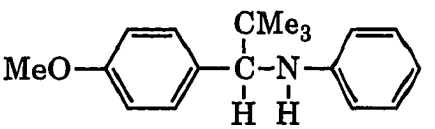
_N_-[2,2-Dimethyl-1-(4-methylphenyl)propyl]aniline (66)



This compound was isolated as a solid: mp 67–68 °C; ^1H NMR ($CDCl_3$) δ 7.17 (d, J = 8.1 Hz, 2 H), 7.04 (m, 4 H), 6.56 (td, J = 7.5, 0.9 Hz, 1 H), 6.47 (dd, J =

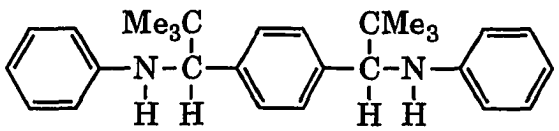
8.4, 0.9 Hz, 2 H), 4.22 (d, J = 6.0 Hz, 1 H), 4.00 (d, J = 6.3 Hz, 1 H), 2.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.73 (s), 137.94 (s), 136.11 (s), 128.93 (d), 128.33 (d), 128.30 (d), 116.74 (d), 113.09 (d), 66.81 (d), 34.84 (s), 27.04 (q), 21.05 (q); GCMS m/z (relative intensity) 253 (M^+, 4), 196 (100), 180 (1), 91 (2); HRMS calcd for $C_{18}H_{23}N$ 253.1830, found 253.1834; Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 84.06; H, 9.07; N, 5.32.

_N_-[1-(4-Methoxyphenyl)-2,2-dimethylpropyl]aniline (67)



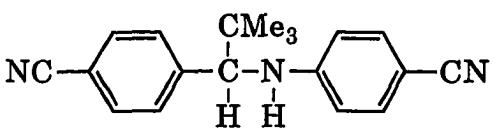
This compound was isolated as a solid: mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (d, J = 8.7 Hz, 2 H), 7.04 (dd, J = 8.7, 7.5 Hz, 2 H), 6.81 (d, J = 8.7 Hz, 2 H), 6.58 (td, J = 7.5, 0.9 Hz, 1 H), 6.47 (dd, J = 8.7, 0.9 Hz, 2 H), 4.21 (d, J = 5.1 Hz, 1 H), 3.98 (d, J = 5.1 Hz, 1 H), 3.79 (s, 3 H), 0.92 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 158.30 (s), 147.70 (s), 132.99 (s), 129.27 (d), 128.90 (d), 116.73 (d), 113.11 (d), 113.01 (d), 66.49 (d), 55.03 (q), 34.91 (s), 26.98 (q); GCMS m/z (relative intensity) 269 (M^+, 3), 212 (100), 197 (2), 168 (4), 104 (17); HRMS calcd for $C_{18}H_{23}NO$ 269.1780, found 269.1787; Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.09; H, 8.98; N, 5.11.

1,4-Bis-[2,2-dimethyl-1-(phenylamino)propyl]benzene (68)



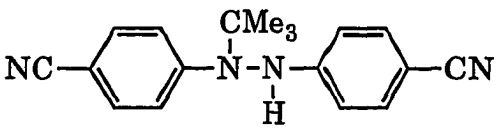
This compound was isolated as a solid: mp 131–132 °C; ^{1}H NMR ($CDCl_3$) δ 7.19 (s, 4 H), 7.04–7.00 (m, 4 H), 6.60–6.53 (m, 2 H), 6.46–6.42 (m, 4 H), 4.21 (br s, 2 H), 3.96 (d, J = 3.0 Hz, 2 H), 0.94 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 128.87 (d), 127.68 (d), 116.70 (d), 113.06 (d), 66.98 (d), 34.92 (s), 27.06 (q); GCMS m/z (relative intensity) 400 (M^+, 4), 343 (100), 286 (78), 236 (5), 209 (10), 143 (6), 104 (13), 77 (9); HRMS calcd for $C_{28}H_{36}N_2$ 400.2878, found 400.2869; Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.93; H, 9.06; N, 6.99. Found: C, 83.42; H, 9.15; N, 6.73.

***N*-[1-(4-Cyanophenyl)-2,2-dimethylpropyl]-4-cyanoaniline (69)**



This compound was isolated as a solid: mp 178–179 °C; ^{1}H NMR ($CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.7 Hz, 2 H), 6.41 (d, J = 9.0 Hz, 2 H), 4.78 (d, J = 6.0 Hz, 1 H), 4.13 (d, J = 6.3 Hz, 1 H), 1.01 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 150.12 (s), 145.65 (s), 123.34 (d), 131.65 (d), 128.94 (d), 120.22 (s), 118.61 (s), 112.69 (d), 110.94 (s), 98.68 (s), 66.30 (d), 34.81 (s), 26.68 (q); HRMS calcd for $C_{19}H_{19}N_3$ 289.1579, found 289.1575; Anal. Calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62, N, 14.52. Found: C, 78.58, H, 6.68; N, 14.25.

_N_-(4-Cyanophenyl)-_N_-(1,1-dimethylethyl)-_N'_-(4-cyanophenyl)hydrazine (73)



This compound was isolated as an oil; ^{1}H NMR ($CDCl_3$) δ 7.52 (d, J = 8.7 Hz, 2 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.27 (d, J = 8.7 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 6.68 (s, 1 H), 1.32 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 152.01 (s), 151.74 (s), 133.61 (d), 132.44 (d), 123.22 (d), 120.17 (s), 119.04 (s), 111.49 (d), 106.00 (s), 100.17 (s), 60.58 (s), 27.33 (q); HRMS calcd for $C_{18}H_{18}N_4$ 290.1532, found 290.1533.

GENERAL SUMMARY

Photostimulated *tert*-butylation of quinolines, *N*-methyl and *N*-methoxy quinolinium salts, and quinoline *N*-oxides by *tert*-butylmercury halides has been studied. The system *t*-BuHgCl/KI not only generates *t*-Bu· upon photolysis in Me_2SO, but also serves as an oxidizing or reducing agent toward easily oxidizable or reducible radicals or radical ions. With the 4-substituted quinolinium cations, the radical cations formed by attack of *t*-Bu· at C-2 readily lose a proton to form the substituted quinolinyl radicals that are easily oxidized by the alkylmercury halides. For the 4-substituted *N*-methyl or *N*-methoxy quinolinium cations, proton loss is not observed and the radical cations react by one electron reduction. With quinoline *N*-oxides and its 4-substituted derivatives, the C-2 adduct radicals are deprotonated by DABCO to yield after one electron oxidation the 2-*tert*-butylquinoline *N*-oxide. The adduct radical cations formed by attack of *t*-Bu· at C-4 of the 2-substituted quinolines, *N*-methyl or *N*-methoxy quinolinium salts seldom lose the C-4 proton, but undergo electron transfer to form the dihydro derivatives or undergo hydration. Photolysis of *tert*-butylmercury halides with 2-chloroquinoline forms the dimerization product. The loss of the proton from the 2-adducts, but not from the 4-adducts, seems to be stereoelectronic in origin. With *N*-methylquinolinium cation, the addition of *t*-Bu· occurs selectively (> 90%) at C-4 in contrast to the low selectivity observed in addition to quinolinium ion itself. However, with *N*-methoxyquinolinium perchlorate, the reaction products result from the selective addition of *t*-Bu· at C-2 (> 90%).

N-Benzylideneanilines undergo only reductive alkylation with *t*-BuHgI. *t*-Bu· attacks exclusively at the C of the C=N moiety to form the *N*-centered radical, which extracts a hydrogen atom from *t*-BuHgI to form the reductive alkylation product. PTSA promotes the reaction dramatically and a quantitative yield of the reductive product has been obtained in the presence of KI/PTSA. For azobenzenes, the *tert*-butylation occurs at N atom and gives only the reductive alkylation product. Addition of $KI/K_2S_2O_8$ promotes the *tert*-butylation by fast generation of *t*-Bu·. I^- plays an important role in the *tert*-butylation. It promotes the formation of *t*-Bu·. I^- or its ate complex *t*-$BuHgI_2^-$ also transfers one electron to the protonated adduct radical cation. In the absence of PTSA, *t*-BuHgI/I^- appears to react with amino radicals only as a hydrogen atom donor.

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