Radiation-Induced Alkylation of Quinoline Derivatives with Alcohol

Akira SUGIMORI,* Tetsuo YAMADA, Hiroaki ISHIDA, Masayuki NOSE, Keiko TERASHIMA, and Noriko OOHATA
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102
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Gamma-irradiation of quinoline and its derivatives in alcohols brings about alkylation at the 2- or 4-position of pyridine ring. Hydroxyalkyl radicals play important roles in the radiation-induced alkylation with alcohol. The radiation-induced substitution of CF_3CH_2- and $CF_3CH(OH)$- for H in pyridine and pyrimidine rings occurs in low yields.

The introduction of substituents in aromatic rings can be effectively done by the use of electrophilic reagents. However, electophilic substitution is not effective for the electron-deficient heteroaromatic rings such as pyridine nucleus.

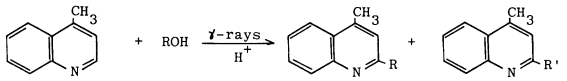
The method utilizing anionic species such as Grignard reagents and organolithium compounds have been developed for the introduction of alkyl groups in the pyridine ring.[1] Free radical species have also been used for the substitution in the pyridine ring. Alkylation and hydroxyalkylation initiated by peroxodisulfate have been studied extensively by Minisci et al.[2,3] Ultraviolet irradiation causes the alkylation of pyridine ring with alcohols[4] or alkanoic acids.[5]

The irradiation of ionizing radiation can generate free radical species but it has not been used effectively for the introduction of substituents in the electron-deficient heteroaromatic ring. We have reported the radiation-induced alkylation and hydroxyalkylation of pyridinecarboxylic esters,[6] pyridinecarboxamides,[7] and pyridinecarbonitriles[8] in alcohols.

In this paper, we describe the radiation-induced alkylation and hydroxyalkylation by alcohols using quinoline derivatives as fundamental pyridine derivatives. The method of γ-irradiation is compared with other methods generating free radical species.

Results and Discussion

Radiation-Induced Alkylation with Alcohol. The γ-irradiation of the alcoholic solutions of 4-methylquinoline (**1a**) in the presence of sulfuric acid brings about the alkylation at the 4-position in good radiation chemical yields (G-values) (Table 1). The alkyl groups introduced have mainly the same skeletal structures as those of the alcohols. However, with higher alcohols, especially with secondary alcohol (2-propanol), the alkyl groups of the smaller carbon numbers than those of the original alcohols are introduced.



R′: Alkyl group with smaller carbon number than R.

The radiation-induced alkylation in the pyridine ring occurs efficiently in the γ-irradiation of the quinolinium salt in alcohol in the presence and absence of sulfuric acid (Table 1).

The main reactive species formed in the radiolysis of alcohols are solvated electron, hydrogen atom, and 1-hydroxyalkyl radical. The G-values of e_{solv}^-, $\cdot H$, $\cdot OH$, $\cdot CH_2OH$, and $\cdot CH_3$ in the radiolysis of methanol have been reported to be 2.0, 1.1, 0.2, 2.7, and 0.2, respectively.[9]

Methyl radical can bring about methylation of the pyridine ring.[10,11] However, the methyl radical formed in the radiolysis of methanol can explain only a part of the radiation-induced methylation of **1a** with methanol, because the G(methylation) is larger than $G(\cdot CH_3)$. Thus, hydroxymethyl radical should play more important roles than methyl radical.

Hydroxymethyl radical can be produced by the hydrogen abstraction from methanol by free radicals pro-

Table 1. Radiation-Induced Alkylation of 4-Methylquinoline (**1a**) and 1,4-Dimethylquinolinium Methyl Sulfate (**1b**) in Alcohol

Substrate	Alcohol	Atmosphere	$[H_2SO_4]$ / mol dm^{-3}	Dose / 10^7 rad	Alkyl group introduced at the 2-position: Me G-value	Me Yield / %	Et G-value	Et Yield / %	*n*-Pr G-value	*n*-Pr Yield / %	*i*-Pr G-value	*i*-Pr Yield / %
1a	MeOH	Ar	0.10	1.0	2.05	(66)						
1b	MeOH	Ar	0.00	5.0	1.27	(80)						
1b	MeOH	Ar	0.50	5.0	2.38	(94)						
1b	MeOH	N_2O	0.00	5.0	1.15	(41)						
1a	EtOH	Ar	0.10	1.0	0.04	(2)	1.02	(41)				
1a	*n*-PrOH	Ar	0.10	1.0	0.05	(2)	0.43	(16)	0.68	(25)		
1a	*i*-PrOH	Ar	0.10	1.0	0.06	(3)	0.06	(3)			0.02	(1)

[**1a**]=0.06 mol dm^{-3}; [**1b**]=0.15 mol dm^{-3}. Yield=Amount of product/Amount of substrate reacted.

Table 2. Methylation of Quinoline and Isoquinoline by Hydroxymethyl Radicals

Substrate	Method for generating $\cdot CH_2OH$	Methylation product					
		1-Me		2-Me		4-Me	
		Yield %	(G-value)	Yield %	(G-value)	Yield %	(G-value)
Quinoline	Gamma-irradiation[a)]			8.6	(0.51)	15.6	(0.92)
	Thermal decomposition of *t*-BuCOOO-*t*-Bu at 65 °C[b)]			17.5		14.7	
	UV-irradiation in the presence of acetone[c)]			3.2		2.9	
Isoquinoline	Gamma-irradiation[a)]	9.4	(0.47)				
	Thermal decomposition of *t*-BuCOOO-*t*-Bu at 65 °C[b)]	10.1					
	UV-irradiation in the presence of acetone[c)]	1.8					

Yield=Amount of product/Amount of substrate reacted. a) [Substrate]=0.06 mol dm^{-3}; [H_2SO_4]=0.10 mol dm^{-3}; Dose, 1.0×10^7 rad. b) [Substrate]=0.06 mol dm^{-3}; [H_2SO_4]=0.10 mol dm^{-3}; [*t*-BuCOOO-*t*-Bu]=0.06 mol dm^{-3}; Heated at 64 or 65 °C for 4 h under Ar. c) [Substrate]=0.01 mol dm^{-3}; [H_2SO_4]=0.02 mol dm^{-3}; [Acetone]=2.0 mol dm^{-3}; Irradiated in a Pyrex vessel with a high-pressure mercury lamp for 16 h under Ar.

duced in the thermal decomposition of peroxides such as *t*-butyl peroxypivalate. The UV-irradiation of acetone in methanol can also produce hydroxymethyl radical via hydrogen abstraction of excited acetone from methanol.

$$CH_3COCH_3 \xrightarrow{h\nu} {}^1(CH_3COCH_3)^* \longrightarrow {}^3(CH_3COCH_3)^*$$

$${}^3(CH_3COCH_3)^* + CH_3OH \longrightarrow CH_3\dot{C}(OH)CH_3 + \cdot CH_2OH$$

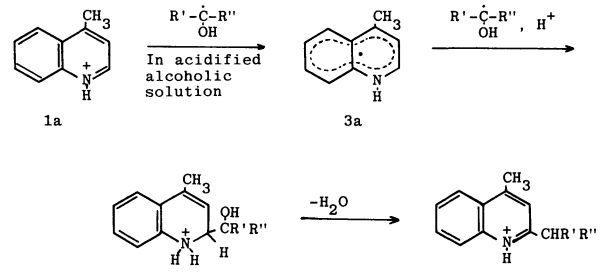
As is shown in Table 2, quinoline and isoquinoline are methylated similarily in radiation-induced reaction and in the reaction initiated by the thermolysis of *t*-butyl peroxypivalate. When the solution of quinoline or isoquinoline was irradiated in methanol in the presence of acetone with a high-pressure mercury lamp, the light from which is absorbed selectively by acetone, methylation of the pyridine rings occurs actually.

In the radiolysis of alcohol in the presence of sulfuric acid, solvated electron is converted to hydrogen atom.

$$e^-_{solv} + H^+ \longrightarrow \cdot H$$

Hydrogen atom can react either with methanol to give $\cdot CH_2OH$ radical or with quinolinium. The rate constants of $\cdot H$ with methanol (in acidified aqueous solutions) and with pyridinium ion are reported to be 2.4×10^6 [12] and 2.2×10^8 dm^3 mol^{-1} s^{-1} [13] respectively. Considering that the concentrations of methanol and quinolinium under our reaction conditions are 25 and 0.06 mol dm^{-3}, respectively, we can postulate that hydrogen abstraction from methanol is the more favorable process for hydrogen atom than the reaction with pyridinium.

As a mechanism for alkylation by hydroxyalkyl radical, the reaction path in Scheme 1 can be postulated.



Scheme 1.

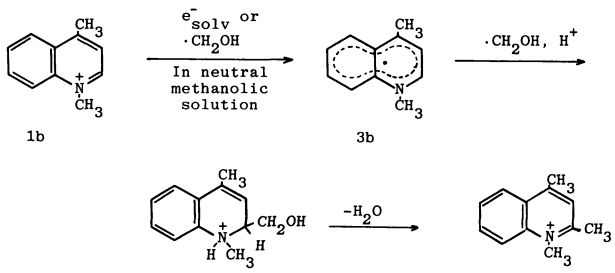
In the radiation-induced reaction of 1,4-dimethylquinolinium (**1b**) in neutral methanol, solvated electron would contribute to the methylation.

The radiation-induced methylation of **1b** is slightly affected by N_2O which converts solvated electron to hydroxymethyl radical via hydroxyl radical.

$$e^-_{solv} + N_2O \xrightarrow{H^+} \cdot OH + N_2$$

$$\cdot OH + CH_3OH \longrightarrow \cdot CH_2OH + H_2O$$

If the solvated electron does not contribute to the methylation, the *G*-value for methylation under Ar should be lower (about a half) than that under N_2O. The experimental results indicate that solvated electron and hydroxymethyl radical participate equivalently in the methylation. The lower chemical yield of methylation under N_2O than under Ar can not be explained at present.



Scheme 2.

Table 3. Radiation-Induced Reactions of Quinoline Derivatives and 4-Methylpyrimidine in CF_3CH_2OH. Dose rate, 1.0×10^6 rad h^{-1}; Dose, 5.0×10^7 rad

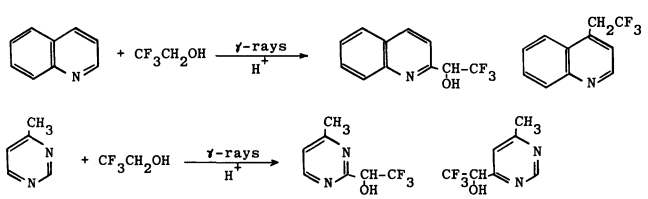
Substrate	[Substrate] mol dm^{-3}	[H_2SO_4] mol dm^{-3}	Substituent introduced	G-value	Yield %
4-Methylquinoline	0.15	0.25	2-CF_3CH_2-	0.08	6.7
			2-CF_3CH(OH)-	0.07	5.6
2-Methylquinoline	0.15	0.25	4-CF_3CH_2-	0.13	8.3
Quinoline	0.30	0.50	2-CF_3CH(OH)-	0.02	1.1
			4-CF_3CH_2-	0.09	5.5
4-Methylpyrimidine	0.50	1.00	2-CF_3CH(OH)-	0.09	0.3
			6-CF_3CH(OH)-	0.48	1.3

Yield=Amount of product/Amount of substrate reacted.

As a mechanism in which solvated electron and hydroxymethyl radical participate equivalently, the reaction paths in Scheme 2 can be postulated.

According to the mechanism in Schemes 1 and 2, the efficiency for alkylation should depend both on the efficiency for the formation of the radical **3** via the attack of electron or the electron transfer from hydroxyalkyl radical to the substrate and on the efficiency for the coupling of **3** with hydroxyalkyl radical. If the two efficiencies of the hydroxyalkyl radicals are in good balance, the alkylation should proceed efficiently. 1-Hydroxy-1-methylethyl radical which is formed in the radiolysis of 2-propanol is a good electron donor but is not a reactive free radical. The inefficiency of the second step would result in the low G-value for isopropylation by 2-propanol. Instead, in the radiation-induced reaction in 2-propanol ethylation occurs in greater G-value than isopropylation. Ethylation in 2-propanol is brought about probably by 1-hydroxyethyl radical which is formed by the cleavage of a C-C bond of 2-propanol.

Radiation-Induced Reaction in 2,2,2-Trifluoroethanol. As an extension of the radiation-induced alkylation with alcohols, we examined the radiation-induced reaction of 4-methylquinoline, 2-methylquinoline, quinoline, and 4-methylpyrimidine in 2,2,2-trifluoroethanol in the presence of sulfuric acid, aiming at the introduction of fluorinated alkyl groups in the pyridine and pyrimidine rings (Table 3). Although the trifluoroethylated quinolines are formed, their chemical yields (and their G-values) are low. Another difference between the reactions in CH_3CH_2OH and in CF_3CH_2OH is the substitution of the 2,2,2-trifluoro-1-hydroxyethyl group in the reaction in CF_3CH_2OH.



One of the reasons for the low G-values of trifluoroethylation is due to the low efficiency of the electron transfer from $CF_3\dot{C}HOH$ to the electron-deficient hetroaromatic molecules, because of the high electronegativity of fluorine in the radical. In the radiation-induced reaction of **1a** in a mixed solvent of CF_3CH_2OH, CH_3OH, and H_2O (6:3:1 by volume), 4-methyl-2-(2,2,2-trifluoroethyl)quinoline (**4**) and 4-methyl-2-(2,2,2-trifluoro-1-hydroxyethyl)quinoline (**5**) are formed in equal or greater G-values (G(**4**)=0.07 and G(**5**)=0.09) than in the reaction in a mixed solvent of CF_3CH_2OH and H_2O (9:1 by volume)(G(**4**)=0.07 and G(**5**)=0.07) in spite of the lower formation of $CF_3\dot{C}HOH$ because of the lower concentration of CF_3CH_2OH. The fact can be explained by the contribution of $\cdot CH_2OH$ radical from methanol to the formation of **4** and **5** by the electron transfer to the protonated **1** to give the radical **3**.

The fact that the radical reaction initiated by *t*-butyl hydroperoxide and iron(II) sulfate in CF_3CH_2OH brings about neither trifluoroethylation nor trifluorohydroxyethylation, suggests that the formation of $CF_3\dot{C}HOH$ radical is not a favorable process. (In this case quinoline is methylated by the methyl radical formed by the decomposition of *t*-BuO· radical). The unfavorable formation of $CF_3\dot{C}HOH$ radical is supported by the observation that the UV-irradiation of 4-methylquinoline in CF_3CH_2OH in the presence of sulfuric acid gives no trifluoroethylation nor trifluorohydroxyethylation products. The low efficiency of the formation of $CF_3\dot{C}HOH$ is another reason for the low yields of the introduction of CF_3CH_2- and CF_3CH(OH)- groups. Only the high energy radiation enables the reaction which is not realized by free radical or photochemical processes, although the efficiencies are not high.

The formation of a trifluorohydroxyethylated products can partly be explained by the low basicity of O atom to which H^+ attack to cause dehydration.

Experimental

Materials. Commercial quinoline (GR grade reagent of Wako Junyaku Co.), isoquinoline (EP grade reagent of

Wako Junyaku Co.), 4-methylquinoline(GR grade reagent of Tokyo Kasei Co.), 2-methylquinoline (EP grade reagent of Tokyo Kasei Co.), and 4-methylpyrimidine (made by Aldrich Co.; purity, 99.7%) were purified by vacuum distillation.

1,4-Dimethylquinolinium methyl sulfate was synthesized in the reaction of 4-methylquinoline with dimethyl sulfate.

Commercial methanol (GR grade reagent of Wako Junyaku Co.), ethanol (Nippon Alcohol Co.), 1-propanol (GR grade reagent of Wako Junyaku Co.), 2-propanol (EP grade reagent of Wako Junyaku Co.) were purified by distillation.

A solution of *t*-butyl hydroperoxide (70% of purity, supplied by Aldrich Co.) was used.

2,2,2-Trifluoroethanol and *t*-butyl peroxypivalate were kindly given by Japan Halon Co. and Nippon Oil and Fats Co., respectively.

Gamma-Irradiation. Solutions containing the substrate and sulfuric acid if necessary in alcohol were deaerated by bubbling Ar (in some cases by N_2O) for 45 min before irradiation.

The solution was irradiated by Co-60 γ-rays at the irradiation facility of Japan Atomic Energy Research Institute in Takasaki at the dose of 1.0×10^7 rad (at the dose rate of 5.0×10^5 rad h^{-1} for 20 h) or at the dose of 5.0×10^7 rad (at the dose rate of 1.0×10^6 rad h^{-1} for 50 h).

Reaction Initiated by Peroxides. A methanolic solution (100 cm^3) of quinoline or isoquinoline ([Substrate]=0.06 mol dm^{-3}), sulfuric acid (0.1 mol dm^{-3}), and *t*-butyl peroxypivalate (0.06 mol dm^{-3}) was deaerated by bubbling Ar and then heated at 64 or 65 °C for 4 h.

The free radical-initiated reaction in CF_3CH_2OH was carried out in the following procedure. To a solution of the substrate (0.01 mol), *t*-butyl hydroperoxide (0.02 mol), and sulfuric acid (0.5 cm^3) in trifluoroethanol (8.3 cm^3) kept below 10 °C, was added dropwise an aqueous solution of iron(II) sulfate (0.02 mol) and sulfuric acid under Ar. After the addition of the peroxide, the solution was kept at 10—20 °C for 80 min. The reaction mixture was treated in a similar manner to that for the radiation-induced reaction.

Photoreaction in the Presence of Acetone. Solutions of the substrate (0.01 mol dm^{-3}) in methanol or trifluoroethanol in the presence of acetone (2.0 mol dm^{-3}) and sulfuric acid (0.02 mol dm^{-3}) were irradiated with a high-pressure mercury lamp for 16 h. The work up of the reaction mixture was similar to that for the radiation-induced reaction.

Separation of Products. The products in the radiation-induced reactions in alcohol in the presence of sulfuric acid were separated by means of TLC (plate, GF_{254} Type 60 supplied by E. Merck Co.), after the removal of the most part of the solvent under reduced pressure, neutralization with sodium carbonate, and the extraction with dichloromethane.

The reaction mixture from the radiation-induced reactions in 2,2,2-trifluoroethanol in the presence of sulfuric acid was treated as follows. Most part of the solvent were removed under reduced pressure and the solution was neutralized with aqueous sodium carbonate solution. The products were extracted with dichloromethane and separated by TLC (plate, GF_{254} Type 60 of E. Merck Co.). The developing solvents for the separation of the products from quinoline, 2-methylquinoline, 4-methylquinoline, and 4-methylpyrimidine are dichloromethane, dichloromethane(90%)-ethyl acetate(10%), and dichlomethane(75%)-ethyl acetate(25%), respectively.

The products were further purified by preparative gas-chromatography (column, 2 m column of PEG 20M (5%)). The column temperatures for the separation of the products from quinoline, 2-methylquinoline, 4-methylquinoline, and 4-methylpyrimidine are 190, 180, 190, and 140 °C, respectively.

Identification of Products. The formation of 2,4-dimethyl-, 2-ethyl-4-methyl-, 4-methyl-2-propyl-, and 2-isopropyl-4-methylquinolines were identified by the agreement of the spectra and gas-chromatographic behavior with the authentic samples. Authentic 2,4-dimethylquinoline is commercially available. 2-Ethyl-4-methyl-, 4-methyl-2-propyl-, and 2-isopropyl-4-methylquinolines were prepared by the reaction of 4-methylquinoline with the alkanoic acids having the alkyl moiety to be introduced under the catalysis of ammonium peroxodisulfate and silver nitrate according to Minisci et al.[11]

2-Ethyl-4-methylquinoline: ^1H NMR ($CDCl_3$) δ=1.38 (3H, t, J=7.6 Hz, 2-$CH_2C\underline{H}_3$), 2.67 (3H, s, 4-CH_3), 2.95 (2H, q, J=7.6 Hz, 2-$C\underline{H}_2CH_3$), 7.15 (1H, s, ring H at the 3-position), and 7.45—8.07 (4H, m, H of benzene ring).

4-Methyl-2-propylquinoline: ^1H NMR δ=1.02 (3H, t, J=7.5 Hz, 2-$CH_2CH_2C\underline{H}_3$), 1.83 (2H, sextet, J=7.5 Hz, 2-$CH_2C\underline{H}_2CH_3$), 2.65 (3H, s, 4-CH_3), 2.89 (2H, t, J=7.5 Hz, 2-$C\underline{H}_2CH_2CH_3$), 7.12 (1H, s, ring H at the 3-position), and 7.44—8.07 (4H, m, H of benzene ring).

2-Isopropyl-4-methylquinoline: ^1H NMR δ=1.38 (6H, d, J=6.8 Hz, 2-$CH(C\underline{H}_3)_2$), 2.66 (3H, s, 4-CH_3), 3.21 (1H, septet, J=6.8 Hz, 2-$C\underline{H}(CH_3)_2$), 7.15 (1H, s, ring H at the 3-position), and 7.43—8.08 (4H, m, H of benzene ring).

The products from the radiation-induced reactions in 2,2,2-trifluoroethanol were identified on the basis of their spectral data.

4-Methyl-6-(1-hydroxy-2,2,2-trifluoroethyl)pyrimidine: White crystals; mp 75—76 °C (sublime); IR (KBr disk) 3120, 2870, 2730, 1600, 1540, 1470, 1380, 1360, 1340, 1320, 1280, 1260, 1170, 1140, 1130, 1110, 1045, 1000, 945, 900, 850, 810, 770, 740, 710, and 660 cm^{-1}; ^1H NMR δ=2.55 (3H, s, 4-CH_3), 5.10 (1H, q, J=6.8 Hz, 6-$C\underline{H}(OH)CF_3$), 7.60 (1H, s, ring H at the 5-position), and 8.98 (1H, s, ring H at the 2-position); MS (70 eV) m/z (rel intensity) 192 (M^+; 19), 124 (8), 123 (100), 95 (10), 94 (6), 93 (13), 68 (9), 67 (7), 66 (22), and 52 (6). Found: m/z 192.0507. Calcd for $C_7H_7F_3N_2O$: M, 192.0510.

2-(1-Hydroxy-2,2,2-trifluoroethyl)-4-methylpyrimidine: White crystals; mp 37—38 °C; IR (KBr disk) 3420, 3100, 1600, 1560, 1460, 1370, 1350, 1260, 1180, 1170, 1140, 1130, 1110, 1000, 930, 860, 840, 820, 790, 700, and 680 cm^{-1}; ^1H NMR (CD_3OD) δ=2.50 (3H, s, 4-CH_3), 5.10 (1H, q, J=6.7 Hz, 2-$C\underline{H}(OH)CF_3$), 7.33 (1H, d, J=7.2 Hz, ring H at the 5-position), and 8.61 (1H, d, J=7.2 Hz, ring H at the 6-position); MS (70 eV) m/z (rel intensity) 192 (M^+, 15), 125 (5), 124 (18), 123 (100), 95 (42), 94 (6), 93 (10), 68 (9), 66 (9), 53 (6), and 52 (6). Found: m/z 192.0508. Calcd for $C_7H_7F_3N_2O$: M, 192.0510.

4-(2,2,2-Trifluoroethyl)quinoline: IR (neat) 3450, 3080, 3050, 2970, 1600, 1580, 1520, 1430, 1400, 1360, 1320, 1280, 1260, 1240, 1170, 1140, 1100, 1040, 910, 830, 770, and 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.83 (2H, q, J=10 Hz, 4-CH_2CF_3), 7.26—8.19 (5H, m, ring H), and 8.85 (1H, d, J=4 Hz, ring H at the 2-position); MS (70 eV) m/z (rel intensity) 212 (13), 211 (M^+, 100), 143 (80), 142 (59), 116 (55), 115 (25). Found: m/z 211.0611. Calcd for $C_{11}H_8F_3N$: M, 211.0608.

2-(1-Hydroxy-2,2,2-trifluoroethyl)quinoline: White crys-

tals; mp 97—98 °C; IR (KBr disk) 3360, 3090, 2900, 2760, 1620, 1600, 1580, 1520, 1470, 1440, 1380, 1340, 1270, 1190, 1160, 1130, 1100, 1030, 980, 940, 860, 830, 805, 795, 770, 760, 710, and 630 cm^{-1}; ^1H NMR (CD_3OD) δ=5.22 (1H, q, J=7.8 Hz, 2-C<u>H</u>(OH)CF_3) and 7.50—8.40 (6H, m, ring H); MS (70 eV) m/z (rel intensity) 227 (M^+, 25), 207 (10), 159 (14), 158 (100), 156 (6), 130 (17), 129 (20), 128 (77), 103 (7), 102 (11), 101 (18), 77 (15), 76 (6), 75 (10), and 51 (8). Found: m/z 227.0558. Calcd for $C_{11}H_8F_3NO$: M, 227.0557.

2-Methyl-4-(2,2,2-trifluoroethyl)quinoline: White crystals; mp 47—48 °C; IR (KBr disk) 3450, 3370, 2990, 1600, 1560, 1520, 1380, 1370, 1330, 1280, 1260, 1230, 1200, 1150, 1140, 1100, 1050, 920, 910, 830, 770, 750, and 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.75 (3H, s, CH_3), 3.81 (2H, q, J=10.4 Hz, -CH_2CF_3), 7.27 (1H, s, ring H at the 3-position), and 7.50—8.10 (4H, m, H of benzene ring); MS (70 eV) m/z (rel intensity) 226 (14), 225 (M^+, 100), 205 (9), 156 (18), 129 (8), and 115 (5). Found: m/z 225.0763. Calcd for $C_{12}H_{10}F_3N$: M, 225.0765.

4-Methyl-2-(2,2,2-trifluoroethyl)quinoline: White crystals; mp 62—63 °C; IR (KBr disk) 3450, 3100, 3000, 2980, 2930, 1600, 1560, 1510, 1450, 1430, 1420, 1380, 1370, 1340, 1270, 1260, 1140, 1130, 1080, 1070, 970, 920, 860, 830, 770, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.66 (3H, s, CH_3), 3.70 (2H, q, J=10.8 Hz, -CH_2CF_3), 7.25 (1H, s, ring H at the 3-position), and 7.42—8.10 (4H, m, H of benzene ring); MS (70 eV) m/z (rel intensity) 226 (14), 225 (M^+, 100), 206 (13), 205 (57), 156 (16), 142 (6), 141 (5), 140 (6), 129 (6), 116 (9), and 115 (13). Found: m/z 225.0750. Calcd for $C_{12}H_{10}F_3N$: M, 225.0765.

4-Methyl-2-(2,2,2-trifluoro-1-hydroxyethyl)quinoline: White crystals; mp 117—118 °C; IR (KBr disk) 3100, 2870, 2700, 1600, 1570, 1510, 1450, 1420, 1370, 1270, 1260, 1190, 1180, 1140, 1130, 1120, 970, 900, 880, 860, 780, and 760 cm^{-1}; ^1H NMR (CD_3OD) δ=2.72 (3H, s, CH_3), 5.20 (1H, q, J=7.7 Hz, -C<u>H</u>(OH)CF_3), and 7.52—8.22 (5H, m, ring H); MS (70 eV) m/z (rel intensity) 241 (M^+, 24), 173 (13), 172 (100), 144 (10), 143 (14), 142 (28), 140 (5), 116 (9), and 115 (18). Found: m/z 241.0715. Calcd for $C_{12}H_{10}F_3NO$: M, 241.0714.

The products from the reaction of 1,4-dimethylquinolinium methyl sulfate (**1b**) in methanol could not be separated from the starting material by means of gel filtration (column, Sephadex G-10; eluent H_2O)

Quantitative Analyses. The irradiated alcoholic solutions were concentrated by distillation under reduced pressure and were neutralized with aqueous sodium hydrogencarbonate. The products were extracted several times with dichloromethane and were submitted to the GLC analyses (column, 2 or 3 m column of 5 or 10% PEG 20M; column temperature, 140 or 160 °C; internal standard, 3-pyridinecarbonitrile). The products from the peroxide-initiated and photochemical reactions were analyzed under similar conditions.

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