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Preparation of 2-Alkylquinolines by TiO₂-photocatalyzed Reaction of Arylamines in Alcohols

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Abstract

The TiO₂-photocatalyzed reaction of arylamines in alcohols afforded 4-alkoxy-2-alkyl-1,2,3,4-tetrahydroquinolines and 2-alkylquinolines in low to moderate yields. The TiO₂-photocatalyzed reaction of arylamines gave 4-alkoxy-2-alkyl-1,2,3,4-tetrahydroquinolines, which were converted into 2-alkylquinolines by UV irradiation.

Key-words : TiO₂, Photocatalyzed reaction, Arylamines, 2-Alkylquinolines

1. Introduction

TiO₂-photocatalyzed reaction is of interest because both oxidation and reduction processes can take place on the catalysts. The reactions of alcohols, amines, aldehydes, ketones, alkylbenzenes, olefins, ethers, sulfides, and nitro derivatives have been reported¹⁻³⁾. In our continuing study on the TiO₂-photocatalyzed reaction of nitrogen-containing organic compounds⁴⁻⁸⁾, that of arylamines was found to produce 2-alkylquinolines. 2-Methylquinolines are normally obtained by the reaction of arylamines with crotonaldehyde (Skraup synthesis)⁹⁾. We report here the TiO₂-photocatalyzed reaction of arylamines to produce 2-alkylquinolines by way of 4-alkoxy-1,2,3,4-tetrahydroquinolines.

2. Experimental

Instruments. Melting points were measured with a Yanagimoto MP-S 2 micro-melting-point apparatus. NMR spectra were recorded on a JEOL α -400 spectrometer. GCMS spectra were taken on a Shimadzu QP-1000 spectrometer.

Materials. Wako TiO₂ (Anatase) and P 25 (70% Anatase and 30% Rutile) were purchased from Wako Pure Chemical Industries Ltd. and Nippon Aerosil Co., Ltd, respectively. Anilines **1a-k** and 1-naphthylamine (**1l**) were purchased from Tokyo Kasei Co., Ltd. and Nacalai Tesque, Inc., respectively. Ethanol, propanol, and butanol were distilled and dried over Molecular Sieve 3 A before use.

TiO₂-photocatalyzed reaction ($\lambda > 320$ nm) of arylamines. To an alcohol solution (15 ml) of arylamines **1** (0.15 mmol) was added TiO₂ (30 mg). The suspension was sonicated for 5 min. Then, the suspension was irradiated with a 300 W high-pressure mercury lamp through a Uranium glass filter at room temperature. After the reaction was complete, the suspension was centrifuged. After evaporating the solvent, products were isolated by column chromatography (Silica gel, benzene : ethyl acetate = 5 : 1). The physical and spectral data of the products are shown below.

4-Ethoxy-2,6,7-trimethyl-1,2,3,4-tetrahydroquinoline (2a)

oil; ¹H NMR (CDCl₃) δ 1.25 (d, $J = 6.3$ Hz, 3 H), 1.27 (t, $J = 6.8$ Hz, 3 H), 1.49 (ddd, $J = 13.7$, 12.2, and 2.9 Hz, 1 H), 2.12 (ddd, $J = 13.7$, 2.9, and 2.9 Hz, 1 H), 2.19 (s, 6 H), 3.55-3.69 (m, 1 H), 3.63 (q, $J = 6.8$ Hz, 2 H), 3.77 (br s, 1 H), 4.29 (dd, $J = 2.9$ and 2.9 Hz, 1 H), 6.39 (s, 1 H), 6.93 (s, 1 H); ¹³C NMR (CDCl₃) δ 15.5, 18.6, 19.5, 22.1, 35.7, 42.1, 62.9, 72.6, 115.7, 117.5, 124.4, 131.7, 137.2, 142.8; EIMS (70 eV) m/z (rel intensity) 219 (M⁺; 5), 204 (9), 171 (100), 156 (66), 144 (25), 128 (24), 115 (23), 77 (41); UV (EtOH) $\lambda_{\max} = 311$ nm ($\epsilon = 2100$).

4-Ethoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2b)

oil; ¹H NMR (CDCl₃) δ 1.21 (t, $J = 6.8$ Hz, 3 H), 1.23 (d, $J = 6.3$ Hz, 3 H), 1.47 (ddd, $J = 13.7$, 12.2, and 2.9 Hz, 1 H), 2.08 (ddd, $J = 13.7$, 2.9, and 2.9 Hz, 1 H), 3.59 (q, $J = 6.8$ Hz, 2 H), 3.53-3.65 (m, 1 H), 3.88 (br s, 1 H), 4.29 (dd, $J = 2.9$ and 2.9 Hz, 1 H), 6.51 (dd, $J = 7.5$ and 1.5 Hz, 1 H), 6.63 (ddd, $J = 7.5$, 1.5, and 1.5 Hz, 1 H), 7.06 (ddd, $J = 7.5$, 1.5, and 1.5 Hz, 1 H), 7.11 (dd, $J = 7.5$ and 1.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 15.6,

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22.2, 35.4, 42.1, 63.1, 72.9, 114.4, 116.3, 119.7, 129.0, 131.0, 144.9; EIMS (70 eV) m/z (rel intensity) 191 (M^+ ; 14), 143 (52), 130 (100), 77 (20).

2, 7-Dimethyl-4-ethoxy-1, 2, 3, 4-tetrahydroquinoline (2c)

oil; ^1H NMR (CDCl_3) δ 1.20 (t, $J=6.8$ Hz, 3 H), 1.22 (d, $J=6.3$ Hz, 3 H), 1.45 (ddd, $J=13.7$, 12.2, and 2.9 Hz, 1 H), 2.06 (ddd, $J=13.7$, 2.9, and 2.9 Hz, 1 H), 2.22 (s, 3 H), 3.54–3.64 (m, 1 H), 3.57 (q, $J=6.8$ Hz, 2 H), 3.82 (br s, 1 H), 4.26 (dd, $J=2.9$ and 2.9 Hz, 1 H), 6.34 (s, 1 H), 6.45 (d, $J=7.8$ Hz, 1 H), 6.99 (d, $J=7.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 15.6, 21.3, 22.2, 35.7, 42.1, 62.9, 72.6, 114.8, 117.1, 117.4, 130.9, 138.9, 144.8; EIMS (70 eV) m/z (rel intensity) 205 (M^+ ; 3), 157 (97), 144 (100), 78 (17).

6, 7-Cyclohexa-4-ethoxy-2-methyl-1, 2, 3, 4-tetrahydroquinoline (2i)

oil; ^1H NMR (CDCl_3) δ 1.21 (d, $J=6.3$ Hz, 3 H), 1.23 (t, $J=6.8$ Hz, 3 H), 1.45 (ddd, $J=13.7$, 12.2 and 2.9 Hz, 1 H), 2.01 (quint, $J=7.3$ Hz, 2 H), 2.07 (ddd, $J=13.7$, 2.9, and 2.9 Hz, 1 H), 2.77 (t, $J=7.3$ Hz, 2 H), 2.78 (t, $J=7.3$ Hz, 2 H), 3.52–3.64 (m, 1 H), 3.58 (q, $J=6.8$ Hz, 2 H), 3.74 (br s, 1 H), 4.26 (dd, $J=2.9$ and 2.9 Hz, 1 H), 7.24 (s, 1 H), 7.36 (s, 1 H); ^{13}C NMR (CDCl_3) δ 15.6, 22.2, 25.7, 31.8, 32.8, 35.7, 42.2, 62.9, 73.1, 110.3, 118.1, 126.3, 132.4, 143.5, 145.3; EIMS (70 eV, isobutane) m/z (rel intensity) 232 (M^+ ; 1), 227 (6), 186 (100), 174 (5).

2, 6, 7-Trimethylquinoline (3a)

mp 58–59°C; ^1H NMR (CDCl_3) δ 2.34 (s, 3 H), 2.37 (s, 3 H), 2.63 (s, 3 H), 7.10 (d, $J=8.8$ Hz, 1 H), 7.41 (s, 1 H), 7.71 (s, 1 H), 7.84 (d, $J=8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 19.9, 20.4, 25.2, 121.1, 125.0, 126.7, 128.0, 135.1, 135.3, 139.5, 146.9, 157.9; EIMS (70 eV) m/z (rel intensity) 171 (M^+ ; 100), 156 (42), 128 (10), 115 (6).

2-Methylquinoline (3b)

oil; ^1H NMR (CDCl_3) δ 2.74 (s, 3 H), 7.26 (d, $J=8.3$ Hz, 1 H), 7.46 (ddd, $J=7.8$, 1.5, and 1.5 Hz, 1 H), 7.67 (ddd, 7.8, 1.5, and 1.5 Hz, 1 H), 7.91 (dd, $J=7.8$ and 1.5 Hz, 1 H), 8.01–8.03 (m, 2 H); ^{13}C NMR (CDCl_3) δ 25.3, 121.9, 125.6, 126.4, 127.4, 128.5, 129.3, 136.1, 147.8, 158.9; EIMS (70 eV) m/z (rel intensity) 143 (M^+ ; 100), 128 (83), 115 (82), 89 (20), 75 (30).

2, 7-Dimethylquinoline (3c)

oil; ^1H NMR (CDCl_3) δ 2.55 (s, 3 H), 2.72 (s, 3 H), 7.21 (d, $J=8.3$ Hz, 1 H), 7.31 (d, $J=8.3$ Hz, 1 H), 7.66 (d, $J=8.3$ Hz, 1 H), 7.80 (s, 1 H), 7.99 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 21.9, 25.3, 122.1, 124.5, 126.2, 126.9, 127.1, 135.8, 139.6, 148.0, 158.9; EIMS (70 eV) m/z (rel intensity) 157 (M^+ ; 100), 142 (16), 128 (8), 89 (8).

6-Methoxy-2-methylquinoline (3d)

oil; ^1H NMR (CDCl_3) δ 2.71 (s, 3 H), 3.92 (s, 3 H), 7.04 (d, $J=2.9$ Hz, 1 H), 7.24 (d, $J=8.3$ Hz, 1 H), 7.33 (dd, $J=8.8$ and 2.9 Hz, 1 H), 7.91–7.96 (m, 2 H); ^{13}C NMR (CDCl_3) δ 21.4, 25.2, 122.1, 126.3, 126.4, 128.2, 131.6, 135.3, 135.5, 146.4, 157.9; EIMS (70 eV) m/z (rel intensity) 173 (M^+ ; 100), 158 (15), 130 (8), 103 (17).

2, 6-Dimethylquinoline (3e)

oil; ^1H NMR (CDCl_3) δ 2.51 (s, 3 H), 2.72 (s, 3 H), 7.24 (d, $J=8.3$ Hz, 1 H), 7.51 (d, $J=8.8$ Hz, 1 H), 7.53 (s, 1 H), 7.91 (d, $J=8.3$ Hz, 1 H), 7.95 (d, $J=8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 21.4, 25.2, 122.1, 126.3, 126.4, 128.2, 131.6, 135.3, 135.5, 146.4, 157.9; EIMS (70 eV) m/z (rel intensity) 157 (M^+ ; 100), 142 (15), 128 (8), 115 (17), 89 (10).

6-Bromo-2-methylquinoline (3f)

oil; ^1H NMR (CDCl_3) δ 2.73 (s, 3 H), 7.31 (d, $J=8.3$ Hz, 1 H), 7.74 (dd, $J=8.8$ and 2.0 Hz, 1 H), 7.89 (d, $J=8.8$ Hz, 1 H), 7.91 (d, $J=2.0$ Hz, 1 H), 7.96 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 25.3, 119.4, 122.9, 127.6, 129.5, 130.3, 132.8, 135.2, 146.4, 159.5; EIMS (70 eV) m/z (rel intensity) 223 (M^+ ; 2; 99), 221 (M^+ ; 100), 142 (27), 115 (40), 71 (22).

6-Methoxy-2-methylquinoline (3g)

oil; ^1H NMR (CDCl_3) δ 2.64 (s, 3 H), 3.87 (s, 3 H), 7.06 (dd, $J=8.8$ and 2.4 Hz, 1 H), 7.08 (d, $J=8.3$ Hz, 1 H), 7.31 (d, $J=2.4$ Hz, 1 H), 7.57 (d, $J=8.8$ Hz, 1 H), 7.89 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 25.1, 53.5, 106.6, 118.8, 119.7, 121.6, 128.5, 136.0, 149.3, 159.1, 160.8; EIMS (70 eV) m/z (rel intensity) 173 (M^+ ; 100), 143 (32), 130 (74), 115 (11), 103 (20).

2, 5, 7-Trimethylquinoline (3h)

oil; ^1H NMR (CDCl_3) δ 2.49 (s, 3 H), 2.61 (s, 3 H), 2.72 (s, 3 H), 7.14 (s, 1 H), 7.21 (d, $J=8.8$ Hz, 1 H), 7.65 (s, 1 H), 8.13 (d, $J=8.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 18.4, 21.8, 25.2, 120.6, 123.8, 125.9, 128.5, 132.3, 133.9, 139.2, 148.4, 158.3; EIMS (70 eV) m/z (rel intensity) 171 (M^+ ; 100), 156 (84), 128 (21), 115 (13), 77 (15).

6, 7-Cyclohexa-2-methylquinoline (3i)

oil; ^1H NMR (CDCl_3) δ 2.15 (quint, $J=7.3$ Hz, 2 H), 2.71 (s, 3 H), 3.04 (t, $J=7.3$ Hz, 2 H), 3.09 (t, $J=7.3$ Hz, 2 H), 7.17 (d, $J=8.3$ Hz, 1 H), 7.54 (s, 1 H), 7.82 (s, 1 H), 7.94 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 25.1, 26.1, 32.4, 32.9, 120.9, 121.4, 122.9, 125.7, 135.7, 143.1, 147.5, 147.6, 157.6; EIMS (70 eV) m/z (rel intensity) 183 (M^+ ; 88), 182 (100), 168 (23), 115 (9), 90 (15).

2-Methylbenzo[h]quinoline (3l)

oil; ^1H NMR (CDCl_3) δ 2.83 (s, 3 H), 7.38 (d, $J=7.8$ Hz, 1 H), 7.63–7.75 (m, 4 H), 7.88 (d, $J=7.7$ Hz, 1

H), 8.04 (d, $J=8.3$ Hz, 1 H), 9.33 (dd, $J=7.6$ and 1.2 Hz, 1 H); ¹³C NMR (CDCl₃) δ 25.4, 122.1, 124.1, 124.4, 125.2, 126.6, 126.7, 127.7, 127.9, 131.3, 133.7, 135.9, 145.9, 157.7; EIMS (70 eV) m/z (rel intensity) 193 (M^+ ; 100), 165 (33), 151 (22), 84 (18).

2-Ethyl-3-methylbenzo[h]quinoline (3I')

oil; ¹H NMR (CDCl₃) δ 1.50 (t, $J=7.3$ Hz, 3 H), 2.47 (s, 3 H), 3.04 (q, $J=7.3$ Hz, 2 H), 7.56–7.71 (m, 4 H), 7.80 (s, 1 H), 7.85 (d, $J=7.8$ Hz, 1 H), 9.35 (dd, $J=8.3$ and 0.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 12.3, 18.9, 29.1, 124.2, 124.7, 124.8, 126.5, 126.6, 127.3, 127.5, 129.8, 131.6, 133.2, 135.7, 144.1, 161.1; EIMS (70 eV) m/z (rel intensity) 221 (M^+ ; 76), 220 (100), 193 (38), 165 (43), 152 (27), 139 (33), 115 (25).

3-Ethyl-2-propylbenzo[h]quinoline (3I'')

oil; ¹H NMR (CDCl₃) δ 1.11 (t, $J=7.3$ Hz, 3 H), 1.35 (t, $J=7.3$ Hz, 3 H), 2.02 (sextet, $J=7.3$ Hz, 2 H), 2.86 (q, $J=7.3$ Hz, 2 H), 3.03 (t, $J=7.3$ Hz, 2 H), 7.61–7.72 (m, 4 H), 7.86 (s, 1 H), 7.86 (d, $J=6.8$ Hz, 1 H), 9.33 (dd, $J=7.8$ and 0.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 14.3, 14.5, 22.1, 25.2, 37.3, 124.3, 124.8, 125.1, 126.5, 126.6, 127.3, 127.6, 131.6, 133.3, 134.0, 135.8, 143.9, 159.8; EIMS (70 eV) m/z (rel intensity) 249 (M^+ ; 30), 234 (47), 221 (100), 206 (15), 193 (21), 109 (16).

3. Results and Discussion

The TiO₂-photocatalyzed reaction ($\lambda > 320$ nm) of arylamines **1** in alcohols to produce 4-alkoxy-2-alkyl-1,2,3,4-tetrahydroquinolines **2** and 2-alkylquinolines **3** is summarized in **Scheme 1** and **Table 1**. 4-Ethoxy-2-methyl-1,2,3,4-tetrahydroquinoline (**2a**) and 2,6,7-trimethylquinoline (**3a**) were not provided in the absence of TiO₂ (run 1). The TiO₂-photocatalyzed reaction of **1a** in ethanol produced **2a** and **3a** (run 2). As the reaction time increased the yield of **2a** decreased and that of **3a** increased, suggesting that the compound **3a** is produced by way of **2a** (runs 2–5). No remarkable difference in the yield of **3a** between non-washed and washed TiO₂ was observed, indicating that acids contained as impurities did not affect the reaction (runs 4 and 6). When P 25 was used as the catalyst, the yield of **3a** also increased with increasing reaction time (runs

Scheme 1

Table 1 TiO₂-photocatalyzed reaction of arylamines **1**^a

Run	Compd	R ¹	R ²	R ³	R ⁴	R	TiO ₂	Time/h	Yield ^b /%	
									2	3
1	a	H	CH ₃	CH ₃	H	H	none	72	0 ^c	0 ^c
2	a	H	CH ₃	CH ₃	H	H	Wako (Anatase)	12	41	8
3	a	H	CH ₃	CH ₃	H	H	Wako (Anatase)	24	31	33
4	a	H	CH ₃	CH ₃	H	H	Wako (Anatase)	48	5	51
5	a	H	CH ₃	CH ₃	H	H	Wako (Anatase)	72	0	59
6	a	H	CH ₃	CH ₃	H	H	Wako (Anatase) ^d	48	8	41
7	a	H	CH ₃	CH ₃	H	H	P 25	24	79	7
8	a	H	CH ₃	CH ₃	H	H	P 25	48	75	8
9	a	H	CH ₃	CH ₃	H	H	P 25	72	51	18
10	b	H	H	H	H	H	Wako (Anatase)	72	7	30
11	c	H	CH ₃	H	H	H	Wako (Anatase)	72	2	38
12	d	H	OCH ₃	H	H	H	Wako (Anatase)	72	0	21
13	e	H	H	CH ₃	H	H	Wako (Anatase)	72	0	38
14	f	H	H	Br	H	H	Wako (Anatase)	72	0	16
15	g	H	H	OCH ₃	H	H	Wako (Anatase)	72	0	22
16	h	H	CH ₃	H	CH ₃	H	Wako (Anatase)	72	0	36
17	i	H	-CH ₂ CH ₂ CH ₂ -	H	H	H	Wako (Anatase)	72	trace	49
18	j	CH ₃	H	H	H	H	Wako (Anatase)	72	0	trace ^e
19	k	H	H	CF ₃	H	H	Wako (Anatase)	72	0	0
20	l	-CHCHCHCH-	H	H	H	H	Wako (Anatase)	24	0 ^f	4 ^f
21	l	-CHCHCHCH-	H	H	H	H	P 25	24	0	15 ^g
22	l'	-CHCHCHCH-	H	H	H	CH ₃	P 25	24	0	23
23	l''	-CHCHCHCH-	H	H	H	C ₂ H ₅	P 25	24	0	29

^aThe alcohol suspension (15 ml) of TiO₂ (30 mg) and arylamines **1** (0.15 mmol) was irradiated with a 300 W high-pressure mercury lamp through a Uranium glass filter ($\lambda > 320$ nm) at room temperature unless otherwise cited. The conversion of the starting material was 100 % unless otherwise indexed. ^bIsolated yields. ^cNo reaction. ^dTiO₂ washed with alkali, water, and acetone. ^eDetected by GCMS. ^f69 % conversion. ^gA trace amount of *N*-methyl-naphthyl(1,2,3)-2-azetidinone was detected by GCMS.

Scheme 2

7–9). However, the yield of **3a** by P 25 was lower than that by Wako TiO₂ (Anatase) (runs 5 and 9).

Unsubstituted, 3-methyl-, 3-methoxy-, 4-methyl-, 4-bromo-, 4-methoxy-, and 3,5-dimethylanilines (**1b–h**) and 5-aminoindan (**1i**) afforded the corresponding 2-methylquinolines **3b–i** in low to moderate yields (runs 10–17). 2-Methyl- and 4-(trifluoromethyl)anilines (**1j** and **1k**) did not produce **3** (runs 18 and 19). Unfortunately, the reaction of **1a** in propanol was complicated to give several products in low yields.

The TiO₂-photocatalyzed reaction of 1-naphthylamine (**1l**) by Wako TiO₂ (Anatase) in ethanol was slow and preferentially gave 2-methylbenzo[*h*]quinoline (**3l**) in a 4% yield (run 20). That of **1l** by P 25 was fast and produced **3l** in a 15% yield (run 21). The corresponding ethoxytetrahydro derivative **2l** was not detected in either of the reactions. Thus, P 25 was a good catalyst to form **3l**. The reactions of **1l** in propanol and butanol provided 2-ethyl-3-methyl- and 3-ethyl-2-propylbenzo[*h*]quinolines (**3l'** and **3l''**), respectively (runs 22 and 23).

A plausible mechanism for the formation of **2** and **3** is shown in **Scheme 2**. The photo-irradiation of a TiO₂ particle can form an electron (*e*[−]) and a hole (*h*⁺) (eq. 1)^{1–3}. Aldehydes **I** are formed by the oxidation of alcohols by *h*⁺ (eq. 2)¹⁰. An oxygen molecule can accel-

Scheme 3

Table 2 Reaction of **2a**^a

Run	TiO ₂	Temp/°C	Yield ^b of 3a /%
1 ^c	none	rt	0 ^d
2 ^c	none	50	0 ^d
3 ^c	Wako (Anatase)	rt	0 ^d
4	Wako (Anatase)	rt	61
5	P 25	rt	5 ^e
6	none	rt	65
7 ^f	none	rt	68

^aThe ethanol suspension (15 ml) of 4-ethoxy-2,6,7-trimethyl-1,2,3,4-tetrahydroquinoline (**2a**) was irradiated through a Uranium glass filter under an air atmosphere for 24 h unless otherwise cited. ^bIsolated yield. ^cWithout photo-irradiation. ^dNo reaction. ^e18% conversion. ^fUnder an argon atmosphere.

erate the formation of *e*[−] and *h*⁺ on the TiO₂ particle to produce a superoxide ion (eq. 3)¹¹. The superoxide ion can also react with alcohols to give the aldehydes **I** (eq. 4). The aldehydes **I** react with alcohols to give hemiacetals **II**, which can be dehydrated to give olefins **III**. Arylamines **1** react with the aldehydes **I** to produce *N*-alkylidene derivatives **IV**, which react with **III** to form 4-alkoxy-2-alkyl-1,2,3,4-tetrahydroquinolines **2**.

Next, the reaction of **2a** to produce **3a** was examined. The result is shown in **Scheme 3** and **Table 2**. The compound **3a** was not provided without photo-irradiation (runs 1 – 3). The photocatalyzed reaction of **2a** by Wako TiO₂ (Anatase) afforded **3a** in a 61% yield (run 4). When P 25 was used as a catalyst, the reaction was depressed (run 5). The compound **3a** was produced in a 65% yield even in the absence of TiO₂ (run 6). The compound **3a** was also obtained in a 68% yield under an argon atmosphere in the absence of TiO₂ (run 7). These results indicate that **3a** is formed not by the TiO₂-photocatalyzed reaction of **2a** but by the photo-reaction of **2a** in the absence of an oxygen molecule. Compound **2a** showed the absorption maximum at λ 311 nm (ε : 2100 dm³ mol^{−1} cm^{−1}) in ethanol. The particle size of Wako TiO₂ (Anatase) (135 nm) is bigger than that of P 25 (21 nm). Wako TiO₂ (Anatase) settles after stirring of the suspension has stopped. Meanwhile, P 25 is dispersed like a soft cotton in the suspension. Therefore, the compound **2a** may hardly absorb the irradiated light in the presence of P 25 to depress the formation of **3a**. The yield of **3l** by P 25 was higher than that by Wako TiO₂ (Anatase). In this case, the corresponding

1,2,3,4-tetrahydroquinoline intermediate may be easily aromatized due to the extended π -electron conjugated system of the products.

4. Conclusions

Anilines reacted with ethanol in the presence of titanium oxide (IV) under UV-irradiation ($\lambda > 320$ nm) to produce 4-ethoxy-2-methyl-1,2,3,4-tetrahydroquinolines, which were converted into 2-methylquinolines by the UV irradiation. Meanwhile, the TiO₂-photocatalyzed reaction of 1-naphthylamine in alcohols gave 2,3-dialkylbenzo[*h*]quinolines. A plausible mechanism starting from the oxidation of alcohols to give aldehydes which go on to react with arylamines was proposed.

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アルコール中でのアリールアミン類の二酸化チタン-光触媒反応による 2-アルキルキノリン類の生成

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要 旨

アルコール中でのアリールアミン類の二酸化チタン-光触媒反応によって4-アルコキシ-2-アルキル-1,2,3,4-テトラヒドロキノリン類と2-アルキルキノリン類が低から中程度の収率で得られた。アリールアミン類の二酸化チタン-光触媒反応によって4-アルコキシ-2-アルキル-1,2,3,4-テトラヒドロキノリン類を与え、この化合物は紫外光照射で2-アルキルキノリン類に変換された。