

A SIMPLE AND REGIOSELECTIVE PREPARATION OF 2- OR 3-SUBSTITUTED
QUINOLINE DERIVATIVES VIA DIALKYLQUINOLYLBORANES

Minoru Ishikura, Izumi Oda, and Masanao Terashima*

Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02, Japan

Abstract — Various quinoline derivatives possessing a substituent at the 2- or 3-position were prepared by the reaction of dialkylquinolylboranes and organic bromides in the presence of a palladium catalyst.

Since numerous quinolines occur in natural sources and have valuable chemotherapeutic, tumorinhibiting and fungicidal properties, much attention has been paid to the syntheses of substituted quinolines, but the general methods for regioselective introduction of an aryl, a heteroaryl, or an alkenyl group into quinoline nucleus are scarce.¹ We have previously reported a convenient procedure for the regioselective introduction of various substituents (i.e., aryl, heteroaryl, alkenyl) into the 3- or 4-position of pyridine by the palladium-catalyzed cross-coupling reaction between diethylpyridylboranes and organic halides.² We wish to report here a simple and regioselective preparation of 2- or 3-substituted quinoline derivatives (3) from dialkylquinolylboranes (1)³ and organic bromides (2) in the presence of a palladium catalyst.

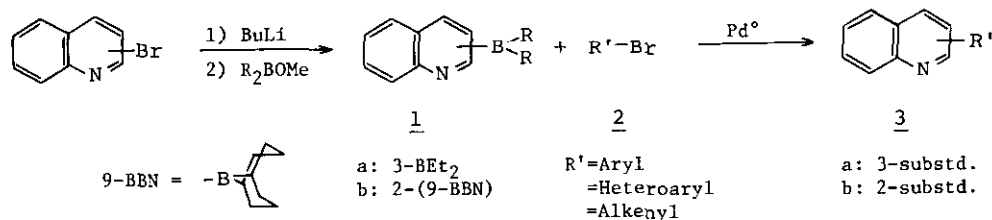


Chart 1

Reaction of 1a (1 mol eq.) with 2 (1.5 mol eq.) was carried out in the presence of powdered KOH (3 mol eq.), Bu₄NBr (0.5 mol eq.) and Pd(Ph₃P)₄ (0.1 mol eq.) in THF under nitrogen atmosphere at refluxing temperature to give 3a. Substituents (i. e., acetyl, amino, ester) on the phenyl ring of aryl bromides were unchanged during the reaction (Table 1), and a heteroaryl or an alkenyl group was also successfully introduced (Table 2).

Reaction of 1b with 2 under the same conditions gave 2-substituted quinoline derivatives (3b), as listed in Table 3 and 4. In these cases, the use of benzene instead of THF gave slightly improved results.

Furthermore, preparation of dubamine (4),⁴ graveoline (5)⁵ and (±)-cuspareine (8)⁶ could be realized as follows (Chart 2).

Reaction of 1b with 3,4-methylenedioxybromobenzene in the presence of KOH, Bu₄NBr and Pd(Ph₃P)₄ in refluxing benzene under nitrogen atmosphere afforded dubamine (4) in 42% yield. N-Methylation of 4 with methyl trifluoromethanesulfonate followed by oxidation with K₃Fe(CN)₆ under a basic condition produced graveoline (5) in 65% yield based on 4.

A similar treatment of 1b with 3,4-dimethoxy-β-bromostyrene gave 6 in 50% yield, which was subsequently subjected to the catalytic hydrogenation with PtO₂ in EtOH under atmospheric pressure (7; 75% yield) followed by N-methylation with methyl iodide to produce (±)-cuspareine (8) in 80% yield.

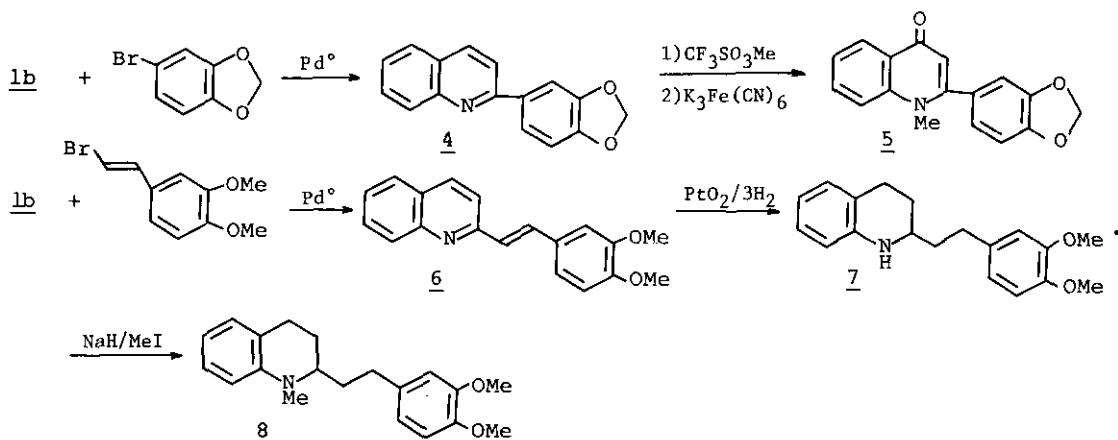
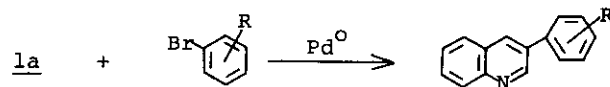


Chart 2

Table 1 Preparation of 3-arylquinolines*



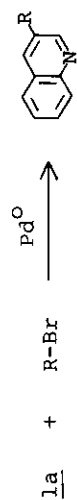
R	Yield ^{a)} (%)	mp(°C) or bp(°C/mmHg)	¹ H-NMR(CDCl ₃) δ :	Formula	Analysis(%) or High-MS(m/e) Calcd (Found)
H	76	mp 51-53 ^{b)} (lit. ⁷ 51-52)	7.20-7.80(m, 8H), 7.90-8.20 (m, 2H), 9.05(d, 1H, J=2 Hz)	—	—
2-Me	71	syrup mp 182-184 ^{c)}	2.26(s, 3H), 7.20-8.20(m, 9H), 8.83(d, 1H, J=2 Hz)	C ₂₂ H ₁₆ N ₄ O ₇	C, 58.98; H, 3.60; N, 12.50 (C, 59.03; H, 3.80; N, 12.30)
4-Me	74	mp 74-76 ^{b)} (lit. ⁸ 77-79)	2.33(s, 3H), 7.16(d, 2H, J=7 Hz), 7.35-7.80(m, 5H), 7.90-8.20(m, 2H), 9.05(d, 1H, J=2 Hz)	—	—
2-OMe	63	syrup mp 255-256 ^{c)}	3.70(s, 3H), 6.80-7.80 (m, 8H), 8.10(d, 1H, J=2 Hz), 9.03(d, 1H, J=2 Hz)	C ₂₂ H ₁₆ N ₄ O ₈	C, 56.90; H, 3.47; N, 12.07 (C, 56.73; H, 3.38; N, 11.85)
4-OMe	70	mp 83-85 ^{b)}	3.77(s, 3H), 6.95(d, 2H, J=8 Hz), 7.40-7.85(m, 5H), 8.05(d, 2H, J=8 Hz), 9.06 (d, 1H, J=2 Hz)	C ₁₆ H ₁₃ NO	C, 81.68; H, 5.57; N, 5.95 (C, 81.51; H, 5.59; N, 5.83)
2-NH ₂	41	syrup	3.50-4.50(br s, 2H), 6.70- 6.90(m, 1H), 7.00-7.85(m, 5H), 8.00-8.30(m, 2H), 8.70-9.00(m, 2H)	C ₁₅ H ₁₂ N ₂	220.1001 (220.1011)

Table 1 (continued)

R	Yield ^{a)} (%)	mp(°C) or bp(°C/mmHg)	¹ H-NMR(CDCl ₃) δ :	Formula	Analysis(%) or High-MS(m/e) Calcd (Found)
4-NH ₂	58	mp 176-177 ^{d)} (lit. ⁷ 175.5-177)	3.60-4.20(br s, 2H), 6.73 (d, 1H, J=7 Hz), 7.30-8.20 (m, 8H), 9.06(d, 1H, J=2 Hz)	—	—
2-NO ₂	44	syrup mp 230-231 ^{c)}	7.20-8.20(m, 9H), 8.76(d, 1H, J=2 Hz)	C ₂₁ H ₁₃ N ₅ O ₉	C, 52.62; H, 2.73; N, 14.61 (C, 52.66; H, 2.68; N, 14.63)
4-COCH ₃	45	mp 137-138 ^{e)}	2.63(s, 3H), 7.40-8.35(m, 9H), 9.13(d, 1H, J=2 Hz)	C ₁₇ H ₁₃ NO	C, 82.57; H, 5.30; N, 5.66 (C, 82.42; H, 5.14; N, 5.52)
2-COOMe	36	syrup mp 215-217 ^{c)}	3.60(s, 3H), 7.20-8.25(m, 9H), 8.76(d, 1H, J=2 Hz)	C ₂₃ H ₁₆ N ₄ O ₉	C, 56.10; H, 3.28; N, 11.38 (C, 56.13; H, 3.36; N, 11.23)
4-COOMe	54	mp 123-125 ^{b)}	3.86(s, 3H), 7.40-7.90(m, 5H), 8.00-8.40(m, 4H), 9.10 (d, 1H, J=2 Hz)	C ₁₇ H ₁₃ NO ₂	C, 77.55; H, 4.98; N, 5.32 (C, 77.71; H, 5.03; N, 5.37)

* THF was used as the reaction solvent. a) isolated yield based on 1a b) recrystallized from hexane c) picrate;
 recrystallized from EtOH d) recrystallized from benzene e) recrystallized from benzene-hexane

Table 2 Preparation of 3-substituted quinoline derivatives*



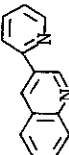
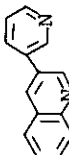
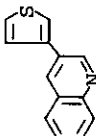
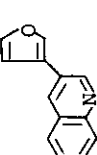
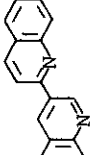
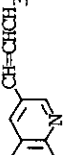
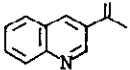
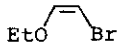
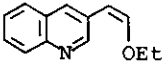
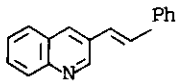
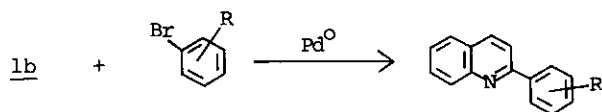
R-Br	Product	Yield ^{a)} (%)	mp (°C) or bp (°C/mmHg)	¹ H-NMR(CDCl ₃) δ:	Formula	Analysis (%) Calcd (Found)
						C H N
		54	mp 99-100 ^{b)} (lit. ⁹ 99)	7.05-7.90(m, 6H), 8.00-8.20(m, 1H), 8.55-8.80(m, 2H), 9.46(d, 1H, J=2 Hz)	—	—
		51	mp 128-129 ^{b)}	7.20-8.30(m, 7H), 9.03(d, 1H, J=2 Hz), 9.58(d, 1H, J=5 Hz), 9.88(s, 1H)	C ₁₄ H ₁₀ N ₂	81.53 4.89 13.58 (81.66 4.94 13.76)
		43	mp 88-89 ^{c)}	7.15-7.80(m, 6H), 7.85-8.20(m, 2h), 9.06(d, 1H, J=2 Hz)	C ₁₃ H ₉ NS	73.91 4.30 6.48 (73.78 4.29 6.46)
		30	mp 92-93 ^{c)}	6.68(s, 1H), 7.30-7.85(m, 5H), 7.90-8.20(m, 2H), 8.93(d, 1H, J=2 Hz)	C ₁₃ H ₉ NO	79.98 4.65 7.17 (79.94 4.72 7.18)
		47	mp 175-176 ^{c)} (lit. ¹⁰ 170-171)	7.20-8.20(m, 10H), 8.73(d, 1H, J=2 Hz), 9.63(d, 1H, J=2 Hz)	—	—
		75	oil mp 197-199 ^{d)}	1.80-2.00(m, 3H), 5.70-6.70(m, 2H), 7.20-8.20(m, 5H), 8.75-8.95(m, 1H)	C ₁₈ H ₁₄ N ₂ O ₇	54.27 3.54 14.07 (54.15 3.66 13.91)

Table 2 (continued)

R-Br	Product	Yield ^{a)} (%)	mp(°C) or bp(°C/mmHg)	¹ H-NMR(CDCl ₃) δ :	Formula	Analysis(%) Calcd(Found)		
						C	H	N
		67	bp 98/1	2.20(s, 3H), 5.20(s, 1H), 5.52(s, 1H), 7.30-7.80(m, 3H), 7.90-8.10(m, 2H), 9.03(s, 1H)	C ₁₂ H ₁₁ N	85.17 (85.07)	6.55 6.58	8.28 8.33
		40	oil mp 191-193 ^{d)}	1.36(t, 3H, J=7 Hz), 3.92 (q, 2H, J=7 Hz), 5.30(d, 1H, J=6 Hz), 6.30(d, 1H, J=6 Hz), 7.30-7.80(m, 3H), 7.85-8.10(m, 1H), 8.26(d, 1H, J=2 Hz), 8.95(d, 1H, J=2 Hz)	C ₁₉ H ₁₆ N ₄ O ₈	53.27 (53.23)	3.77 3.71	13.08 12.97
		40	mp 98-99 ^{c)}	7.00-7.75(m, 10H), 7.80- 8.20(m, 2H), 8.95(d, 1H, J=2 Hz)	C ₁₇ H ₁₃ N	88.28 (88.49)	5.67 5.69	6.06 6.03

* THF was used as the reaction solvent. a) isolated yield based on 1a b) recrystallized from pet. ether
c) recrystallized from hexane d) picrate; recrystallized from EtOH

Table 3 Preparation of 2-arylquinolines



R	yield ^{a)} (%)	mp(°C) or bp(°C/mmHg)	¹ H-NMR (CDCl ₃) δ :
H	51	mp 84-85 ^{b)} (lit. ¹¹ 84)	7.20-7.80 (m, 4H), 7.85-8.30 (m, 7H)
2-Me	40	mp 77-78 ^{b)} (lit. ¹² 76-76.2)	2.37 (s, 3H), 7.15-7.80 (m, 8H), 8.00-8.20 (m, 2H)
4-Me	50	mp 81-82 ^{b)} (lit. ¹³ 82-83)	2.43 (s, 3H), 7.10-8.20 (m, 10H)
2-OMe	40	viscous oil mp 180-181 ^{c)} (lit. ¹⁴ 177-178)	3.70 (s, 3H), 6.80-8.20 (m, 10H)
4-OMe	50	mp 120-122 ^{b)} (lit. ¹⁵ 124)	3.80 (s, 3H), 6.95 (d, 2H, J=8 Hz), 7.30-7.80 (m, 5H), 7.95-8.20 (m, 3H)
2-COOMe	35	syrup	3.60 (s, 3H), 7.35-7.90 (m, 8H), 8.00-8.20 (m, 2H) ^{e)}
4-COOMe	50	mp 151-153 ^{d)}	3.93 (s, 3H), 7.30-8.30 (m, 10H) ^{f)}

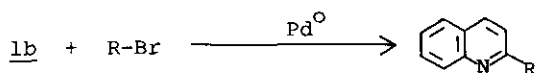
* Benzene was used as the reaction solvent.

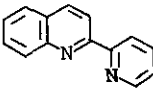
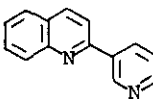
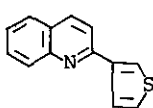
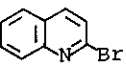
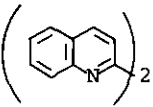
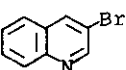
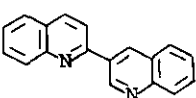
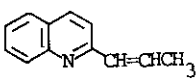
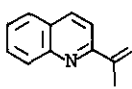
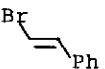
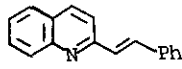
a) isolated yield based on **1b** b) recrystallized from ether c) picrate;
recrystallized from EtOH d) recrystallized from hexane e) High-MS (m/e):

Calcd for C₁₇H₁₃NO₂ 263.0947. Found: 263.09599. f) High-MS (m/e):

Calcd for C₁₇H₁₃NO₂ 263.0947. Found: 263.09348.

Table 4 Preparation of 2-substituted quinoline derivatives*



R-Br	Product	Yield ^{a)} (%)	mp(°C) or bp(°C/mmHg)	¹ H-NMR (CDCl ₃) δ :
		41	mp 98-99 ^{b)} (lit. ⁹ 98)	7.10-7.90(m, 5H), 8.00-8.30(m, 2H), 8.40-8.80(m, 3H)
		40	mp 70-71 ^{b)} (lit. ⁹ 66.5)	7.10-8.75(m, 9H), 9.26(d, 1H, J=2 Hz)
		40	mp 130-131 ^{c)e)}	7.30-8.20(m, 9H)
		30	mp 197-198 ^{d)} (lit. ¹⁶ 193-194)	7.30-7.85(m, 12H), 8.05-8.40(m, 8H), 8.75(d, 4H, J=8 Hz)
		30	mp 175-176 ^{d)}	7.20-8.20(m, 10H), 8.73(d, 1H, J=2 Hz), 9.63(d, 1H, J=2 Hz)
CH ₃ CH=CHBr		50	bp 130/1 (lit. ¹⁷ 80/0.01)	1.85 and 2.00(two singlets, 3H), 6.50-6.95(m, 2H), 7.20-7.85(m, 4H), 7.80-8.10(m, 2H)
		40	bp 130/1 (lit. ¹⁸ 120/3)	2.35(s, 3H), 5.42(d, 1H, J=1 Hz), 5.86(d, 1H, J=1 Hz), 7.30-7.80(m, 4H), 7.85-8.20(m, 2H)
		40	mp 96-97 ^{c)} (lit. ¹⁹ 99-100)	7.10-7.80(m, 11H), 7.90-8.20(m, 2H)

* Benzene was used as the reaction solvent. a) isolated yield based on 1b

b) recrystallized from pet. ether c) recrystallized from hexane d) re-

crystallized from ether e) Anal. Calcd for C₁₃H₉NS : C, 73.91 ; H, 4.30 ;

N, 6.48. Found : C, 73.90 ; H, 4.29 ; N, 6.63.

EXPERIMENTAL

All melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. THF and benzene were distilled from sodium benzophenone ketyl before use. IR spectra were recorded with a Hitachi 270-30 spectrometer. NMR spectra were determined with a Hitachi R-40 and a JEOL FX-90Q spectrometers. Chemical shifts are reported relative to internal tetramethylsilane and given in δ -value. Coupling constants are reported in Hz and splitting patterns are designated as follows; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were recorded on a JEOL JMS-QH100 and a JEOL-D300 spectrometers. Flash chromatography was performed on silica gel 230-400 mesh ASTM obtained from Merck.

Typical procedure for the preparation of substituted quinolines (3): 3-Phenylquinoline — A mixture of 1a (394 mg, 2 mmol), bromobenzene (468 mg, 3 mmol), powdered KOH (336 mg, 6 mmol), Bu_4NBr (322 mg, 1 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (231 mg, 0.2 mmol) in THF (10 ml) was refluxed for 8 h under nitrogen atmosphere. The mixture was diluted with AcOEt (60 ml), washed with brine (40 ml), and dried over MgSO_4 . After removal of the solvent, the residue was purified by flash chromatography with AcOEt-hexane (1:4) to give 311 mg (76%) of 3-phenylquinoline. Other derivatives (3), obtained by the same procedure, are summarized in Tables 1, 2, 3 and 4.

Dubamine (4) — A mixture of 1b (498 mg, 2 mmol), 3,4-methylenedioxybromobenzene (600 mg, 3 mmol), powdered KOH (336 mg, 6 mmol), Bu_4NBr (322 mg, 1 mmol) and $\text{Pd}(\text{Ph}_3\text{P})_4$ (231 mg, 0.2 mmol) in benzene (10 ml) was refluxed under nitrogen atmosphere for 12 h. The mixture was diluted with AcOEt (50 ml), washed with brine (40 ml), and dried over MgSO_4 . After removal of the solvent, the residue was purified by flash chromatography with AcOEt-hexane (1:15) to give 209 mg (42%) of 4, mp 94-95°C (acetone-hexane) (lit.,⁴ mp 95-96°C). IR(KBr): 1610, 1596, 1556, 1496, 1486, 1444, 1426 cm^{-1} . $^1\text{H-NMR}(\text{CDCl}_3)$ δ : 5.95 (s, 2H), 6.89 (d, 1H, $J=7$ Hz), 7.30-7.80 (m, 6H), 8.00-8.30 (m, 2H). High resolution MS (m/e): Calcd for $\text{C}_{16}\text{H}_{11}\text{NO}_2$ 249.07891. Found 249.07840.

Graveoline (5) — A mixture of 4 (150 mg, 0.6 mmol) and methyl trifluoromethanesulfonate (185 mg, 1.2 mmol) was warmed at 50°C for 1 h. After cooling, the

precipitate was collected, washed with ether and dried. The crystalline substance was added to a suspension of $K_3Fe(CN)_6$ (395 mg, 1.2 mmol) in 20% NaOH solution (20 ml) and then stirred at room temperature for 1 h. The mixture was extracted with AcOEt, the extract was washed with brine (40 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography with AcOEt to give 109 mg (65%) of 5, mp 199-201°C (acetone-hexane) (lit.,⁵ mp 204-205°C). IR(KBr): 1622, 1600, 1578, 1542, 1492, 1472, 1448 cm^{-1} . 1H -NMR ($CDCl_3$) δ : 3.63 (s, 3H), 6.06 (s, 2H), 6.29 (s, 1H), 6.80-7.00 (m, 2H), 7.20-7.95 (m, 4H), 8.50 (dd, 1H, $J=2,8$ Hz). High resolution MS (m/e): Calcd for $C_{17}H_{13}NO_3$ 279.08947. Found 279.08827.

2-(3,4-Dimethoxystyryl)quinoline (6) — A mixture of 1b (498 mg, 2 mmol), 3,4-dimethoxy- β -bromostyrene (726 mg, 3 mmol), powdered KOH (336 mg, 6 mmol), Bu_4NBr (322 mg, 1 mmol) and $Pd(Ph_3P)_4$ (231 mg, 0.2 mmol) in benzene (10 ml) was refluxed under nitrogen atmosphere for 10 h. The mixture was diluted with AcOEt (60 ml), washed with brine (40 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography with AcOEt-hexane (1:3) to give 291 mg (50%) of 6, a colorless viscous oil. IR($CHCl_3$): 1626, 1616, 1590, 1558, 1512, 1466, 1444, 1422 cm^{-1} . 1H -NMR($CDCl_3$) δ : 3.85 (s, 3H), 3.90 (s, 3H), 6.60-7.80 (m, 10H), 8.00 (d, 1H, $J=6$ Hz). High resolution MS (m/e): Calcd for $C_{19}H_{17}NO_2$ 291.12595. Found 291.12685.

2-(3,4-Dimethoxy- β -phenethyl)-1,2,3,4-tetrahydroquinoline (7) — A mixture of 6 (200 mg) and PtO_2 (15 mg) in EtOH (10 ml) was stirred at room temperature under atmospheric pressure of hydrogen. After hydrogen up-take ceased, the solvent and catalyst were removed, and then the residue was purified by flash chromatography with AcOEt-hexane (1:3) to give 153 mg (75%) of 7, a viscous oil. IR($CHCl_3$): 3450, 1608, 1592, 1512, 1484, 1466, 1444 cm^{-1} . 1H -NMR($CDCl_3$) δ : 1.65-2.00 (m, 4H), 2.50-2.90 (m, 4H), 3.10-3.50 (m, 2H), 3.83 (s, 6H), 6.30-7.00 (m, 7H). High resolution MS (m/e): Calcd for $C_{19}H_{23}NO_2$ 297.17276. Found 297.17236.

($\pm$)-Cuspareine (8) — A THF solution (10 ml) of 7 (110 mg, 0.37 mmol) was added dropwise to a THF suspension (5 ml) of NaH (50% dispersion in mineral oil, 28 mg, 0.6 mmol) under nitrogen atmosphere at 0°C, and the whole was stirred for 30 min. Methyl iodide (71 mg, 0.5 mmol) was added, the mixture was stirred at 0°C for 30

min, and then at room temperature for 1 h. Saturated NH_4Cl solution (1 ml) was added under ice-cooling, and the mixture was extracted with AcOEt (50 ml). The extract was washed with brine (30 ml), and dried over MgSO_4 . After removal of the solvent, the residue was purified by flash chromatography with AcOEt-hexane (1:3) to give 92 mg (80%) of 8, a viscous oil, bp $200^\circ\text{C}/1\text{ mmHg}$ (bath temperature) (lit.,⁶ bp $180\text{--}190^\circ\text{C}/1\text{ mmHg}$). IR(CHCl_3): 1602, 1574, 1502, 1480, 1466, 1454 cm^{-1} . $^1\text{H-NMR}(\text{CDCl}_3)$ δ : 1.50–2.10 (m, 4H), 2.40–2.90 (m, 4H), 2.90 (s, 3H), 3.10–3.50 (m, 1H), 3.83 (s, 6H), 6.40–7.20 (m, 7H). High resolution MS (m/e): Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_2$ 311.18844. Found 311.18774.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 59570902) from the Ministry of Education, Science and Culture of Japan, which is gratefully acknowledged.

REFERENCES

1. P. A. Claret and A. G. Osborne, "The Chemistry of Heterocyclic Compounds", Vol. 32, Part 2, ed. by G. Jones, John Wiley & Sons, Inc., 1982, p 1.
2. M. Ishikura, M. Kamada, T. Ohta and M. Terashima, Heterocycles, 1984, 22, 2475, and references cited therein.
3. M. Ishikura, T. Mano, I. Oda and M. Terashima, Heterocycles, 1984, 22, 2471.
4. G. P. Sidiyakin, V. I. Pastukhova and S. Yu. Yunusov, Uzbeksk. Khim. Zh., 1962, 6, 56; Chem. Abstr., 1963, 58, 4608g.
5. H. R. Arthur and L. Y. S. Loh, J. Chem. Soc., 1961, 4360.
6. J. Schläger and W. Leeb, Monatsh. Chem., 1950, 81, 714.
7. C. E. Kaslow and B. Buchner, J. Org. Chem., 1958, 23, 271.
8. E. E. Mikhлина, K. F. Turchin, A. D. Yanina, Yu. N. Sheinker and L. N. Yakhontov, Khim. Geterotsikl. Soedin., 1973, 839; Chem. Abstr., 1973, 79, 91964n.
9. D. H. Hey and J. M. Williams, J. Chem. Soc., 1950, 1678.
10. K. Noda, M. Minemoto, K. Narimatsu and M. Hamana, Yakugaku Zasshi, 1975, 95, 1078.
11. R. J. Wood, Le Fever and F. C. Mathur, J. Chem. Soc., 1930, 2236.

12. W. Oldman and I. B. Johns, J. Am. Chem. Soc., 1939, 61, 3289.
13. H. Giezendanner, H. J. Rosenkranz, H. J. Hansen and H. Schmid, Helv. Chim. Acta, 1973, 56, 2588.
14. H. Gilman and S. M. Spatz, J. Am. Chem. Soc., 1944, 66, 621.
15. T. Kaku, Yakugaku Zasshi, 1927, 47, 577.
16. G. M. Badger and W. H. F. Sasse, J. Chem. Soc., 1956, 616.
17. H. Gilman, J. Eisch and T. S. Soddy, J. Am. Chem. Soc., 1959, 81, 4000.
18. G. Bryant and D. D. Micucci, J. Am. Chem. Soc., 1948, 70, 2381.
19. S. Miyano and N. Abe, Chem. Pharm. Bull., 1967, 15, 511.

Received, 3rd June, 1985