Synthesis of Isoindoles. Acid or Base Induced Cyclization of 2-Cyanobenzaldehyde with Alcohols

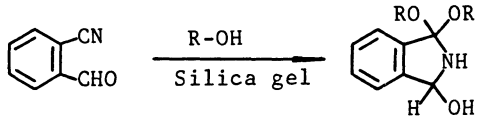
Ryu SATO,* Michiko OHMORI, Fumiko KAITANI, Akiko KUROSAWA, Toshihide SENZAKI, Takehiko GOTO, and Minoru SAITO
Department of Resource Chemistry, Faculty of Engineering, Iwate University, Morioka 020
(Received January 25, 1988)

Various 3,3-dialkoxy-2,3-dihydro-1-hydroxy-1*H*-isoindoles (**2**) were obtained by treating 2-cyanobenzaldehyde (**1**) with alcohols in the presence of an acid catalyst such as silica gel. In the reaction using a base catalyst such as triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 3-alkoxy-2,3-dihydro-1*H*-isoindol-1-ones (**4**) were formed via 3-alkoxy-1,3-dihydro-1-isobenzofuranimine (**3**). The use of 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) gave **2** besides **3** and **4**. A convenient and selective synthesis of isoindoles and its derivatives are described.

In the recent extensive studies on the chemistry of isoindoles, many chemists have directed their attention to the synthesis of 2,3-dihydro-1*H*-isoindol-1-ones and its derivatives, some of which are recognized to exhibit pharmacological and pesticidal activities.[1] In the previous paper we described the one-step formation of 3-amino-2,3-dihydro-1*H*-isoindol-1-ones from 2-cyanobenzaldehyde (**1**) with various amines and the 2-alkylation of the isoindole by the phase-transfer catalyst system.[2] To our knowledge, there have been only a few papers for the syntheses of 3-alkoxy-2,3-dihydro-1*H*-isoindol-1-ones by alkoxylation of 2,3-dihydro-3-hydroxy-1*H*-isoindol-1-one, which was prepared by electrolytic reduction from phthalimide, and its related reactions.[3] Hence our attention centered on the direct synthesis of the isoindoles and its derivatives having an alkoxy group on the isoindole ring by cyclization of **1** with alcohols. It is well-known that the nucleophilicities of alcohols are very poor, compared with those of amines. Therefore, based on the our previous results,[2] activation of substrates or reagents is necessary to bring about the reaction at ambient temperature. Recent interesting investigations on silica gel induced reactions[4] encouraged us to explore a facile formation of some isoindoles and its derivatives by acid, e.g. silica gel, or base, e.g. DABCO, induced cyclization of **1** with various alcohols. Here we describe the novel selective synthesis of isoindoles and its related compounds.

Results and Discussion

Reaction of 1 with Alcohols in the Presence of Acid Catalysts. Without catalyst, **1** did not react at all with any alcohols even under reflux conditions (Table 1, Run 1, Scheme 1), whereas in the presence of acid



1 2

Scheme 1.

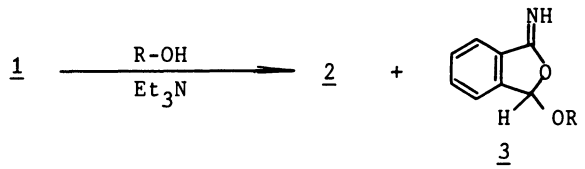
Table 1. Reactions of 2-Cyanobenzaldehyde (**1**) with Alcohol in the Presence of Various Catalysts

Run[a]	Alcohol R	Condition		Catalyst	mmol	Yield of **2**/%[b]
		Temp/°C	Time/h			
1	CH_3–	Reflux	24	—		0
2	CH_3–	Reflux	24	Phenol	0.5	95 **2a**
3	CH_3–	Reflux	24	Silica gel(C)[c]	0.1	97 **2a**
4	CH_3–	Reflux	16	Silica gel(G)[d]	0.1	99 **2a**
5	CH_3–	Reflux	24	$AlCl_3$	0.5	—
6	CH_3–	20	5(min)	12N-HCl	0.5(ml)	—
7	CH_3–	Reflux	5	Al_2O_3	0.5	82 **2a**
8	CH_3–	Reflux	7	Bu_4NI	0.1	79 **2a**
9	CH_3CH_2–	Reflux	12	Silica gel(G)	1.0	100 **2b**
10	$CH_3CH_2CH_2$–	Reflux	22	Silica gel(G)	1.0	86 **2c**
11	$(CH_3)_2CH$–	Reflux	48	Silica gel(G)	1.0	—
12	$CH_3CH_2CH_2CH_2$–	Reflux	52	Silica gel(G)	1.0	85 **2d**
13	$(CH_3)_3C$–	Reflux	75	Silica gel(G)	1.0	—
14	$(CH_3)_2CHCH_2$–	Reflux	75	Silica gel(G)	1.0	91 **2e**

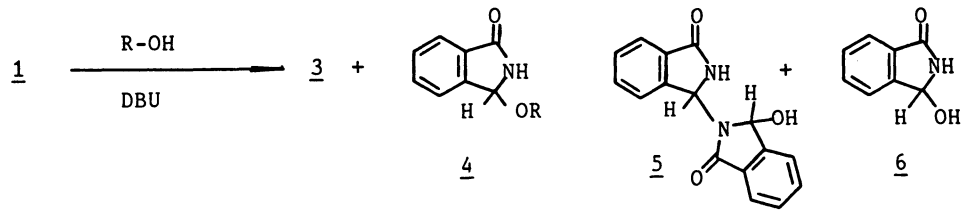
a) Substrate: 0.5 mmol, alcohol: 4 ml. b) Isolated yields based on the substrate. c) Wako gel G-300 (200—300 mesh). d) Wako gel G (30—50 mesh).

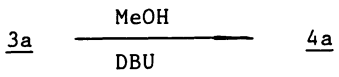
catalysts (phenol and silica gel) **1** readily reacted with methyl alcohol to give 2,3-dihydro-1-hydroxy-3,3-dimethoxy-1*H*-isoindole (**2**) in high yields (Runs 2—4). In this reaction the use of silica gel of large grain size (Wako gel G), even if the silica gel was employed without drying, gave a better yield of **2** than that when a small grain size silica gel (Wako gel C-300) which was dried at 150 °C for 5 h under vacuum was used (Runs 3 and 4). Other solid acid catalyst, for example, alumina (neutral) also catalyzed this reaction (Run 7). Interestingly, tetrabutylammonium iodide behaved similarly to other acid catalysts to give **2** in good yield (Run 8). The use of aluminium chloride and hydrogen chloride gave, however, an acetal compound, 2-cyanobenzaldehyde dimethyl acetal (Runs 5 and 6). Thus, the catalytic effect of silica gel for cyclization of **1** with methyl alcohol was confirmed and a generality of this procedure was also shown in Table 1 (Runs 9—14). Characteristically, butyl and isobutyl alcohols also gave **2** in good yields, but isopropyl and *t*-butyl alcohols did not react with **1** under the same conditions. These results suggest that a steric bulkiness of alcohols used is an important factor in this reaction. Although, unfortunately, α,ω-alkanediols such as ethylene glycol did not react with **1** even at high temperature such as 100 °C, the present silica gel induced cyclization of **1** with various alcohols should provide a novel and convenient synthetic method for new isoindoles such as **2a—e**.

Reactions of 1 with Alcohols in the Presence of Base Catalysts. Compound **1** was treated with various alcohols in the presence of base catalysts such as triethylamine, DBU, DABCO, and TMEDA. In the presence of triethylamine, interesting product, isobenzofurans **3a,b** and **d** were obtained in yields as shown in Table 2. To our surprise, however, **2b** and **2d**, which were the same type of products in the silica gel induced reactions, were also obtained (Runs 2 and 3). Next we employed DBU as a strong base in the reaction of **1** with methanol. Thus, in the reaction at



Scheme 2.





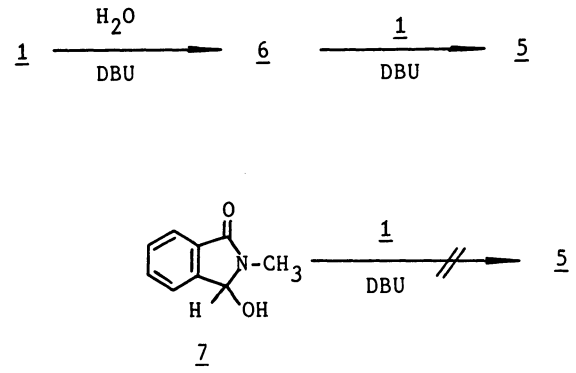
Scheme 3.

Table 2. Reactions of **1** with Alcohols in the Presence of Base Catalysts

Run[a]	Alcohol R	Condition		Catalyst	mmol	Yield of Product/%[b]		
		Temp/°C	Time/h			**2**	**3**	**4**
1	CH_3–	20	12	Et_3N	0.5	—	98 **3a**	—
2	CH_3CH_2–	30	48	Et_3N	0.5	13 **2b**	63 **3b**	—
3	$CH_3CH_2CH_2CH_2$–	30	49	Et_3N	0.5	24 **2d**	71 **3d**	
4	CH_3–	15	12	DBU	0.1	—	27 **3a**	58 **4a**
5	CH_3–	30	5	DBU	0.1	—	—	87 **4a**
6	CH_3CH_2–	50	7	DBU	0.2	—	—	20 **4b**
7	CH_3CH_2–	50	78	DBU	0.2	—	—	30 **4b**
8	$CH_3CH_2CH_2CH_2$–	40	45	DBU	0.2	—	—	29 **4d**
9	CH_3–	15	16	DABCO	0.1	52 **2a**	35 **3a**	—
10	CH_3–	Reflux	0.5	DABCO	0.1	97 **2a**	—	—
11	CH_3CH_2–	60	20	DABCO	0.2	83 **2b**	17 **3b**	—
12	$CH_3CH_2CH_2CH_2$–	60	20	DABCO	0.2	69 **2d**	31 **3d**	—
13	CH_3–	40	5	TMEDA	0.1	—	100 **3a**	—
14	CH_3CH_2–	40	30	TMEDA	0.1	67 **2b**	33 **3b**	—
15	$CH_3CH_2CH_2CH_2$–	40	30	TMEDA	0.1	52 **2d**	42 **3d**	—

a) Substrate: 0.5 mmol, alcohol: 4 ml. b) Isolated yields based on the substrate.

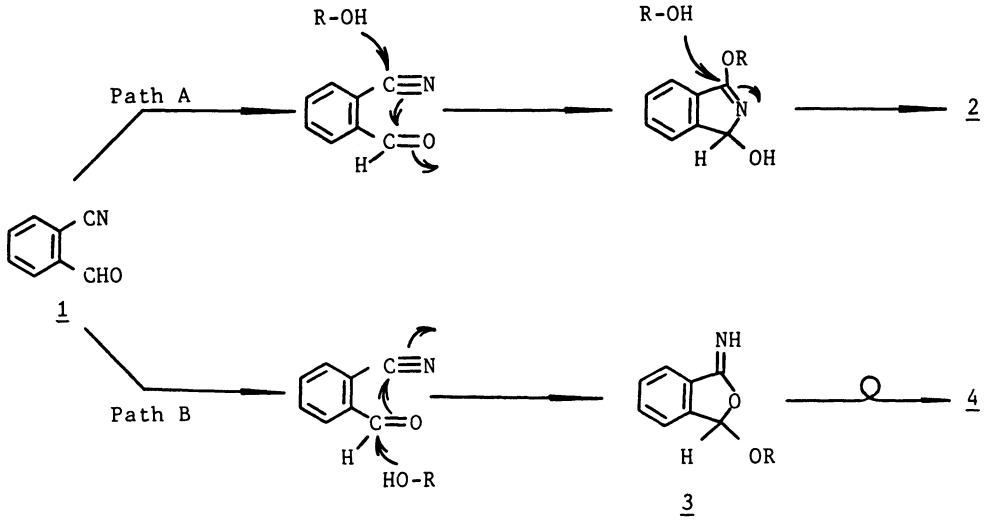
15 °C, **3a** was obtained in yield of 27% together with 2,3-dihydro-3-methoxy-1*H*-isoindol-1-one (**4a**, 58%) (Run 4), while only **4a** was given at 30 °C in yield of 87% (Run 5). In order to confirm an intermediacy, **3a** was actually treated with methanol in the presence of DBU under the same conditions, to afford the expected **4a** quantitatively. In the reaction of **1** with ethanol in the presence of DBU, a little different results were obtained. Thus, desired isoindole, 3-ethoxy-2,3-dihydro-1*H*-isoindol-1-one (**4b**), was given in a 30% yield. Furthermore, we found that 3'-hydroxy-1,2'-bi-2*H*-isoindole-1',3(1*H*)-dione (**5**) was formed in 66% yield at 50 °C for 78 h together with 2,3-dihydro-3-hydroxy-1*H*-isoindol-1-one (**6**) (trace) when a small amount of water was present in the system (Scheme 3). To clarify the pathway of the formation of **5** and **6**, we carried out some related reactions. Compound **6** was obtained quantitatively when **1** was treated with water in the presence of DBU at room temperature. It is very interesting that **6** reacted easily with **1** at 50 °C for 3 h under the same conditions, to give **5** quantitatively (see Experimental). This result suggests that the NH group of **6** was activated with DBU and then reacted with **1** as a nucleophile to give **5**. Further evidence for the formation of **5** was obtained by the reaction of **1** with 2,3-dihydro-3-hydroxy-2-methyl-1*H*-isoindol-1-one (**7**) under the similar conditions. Thus, **7** did not react at all with **1**, and **7** was recovered completely. Based on these results, the formations of **5** and **6** are illustrated as shown in Scheme 4.



Scheme 4.

It should be noted that unexpected products **2**, which were given by the silica gel induced reaction, were obtained as major product when **1** was treated with methanol in the presence of DABCO (Table 2, Run 9). Moreover, 2,3-dihydro-3,3-dimethoxy-1-hydroxy-1*H*-isoindole (**2a**) was formed exclusively under reflux (Table 2, Run 10). In contrast to these results, upon treating **1** with methanol in the presence of TMEDA, **3a** was exclusively obtained (Run 13), though the reactions with other alcohols, e.g. ethanol (Run 14) and 1-butanol (Run 15), gave a mixture of **2** and **3**. Based on these results, it seems that methanol behaves as a special nucleophile in connection with the points of reactivity and stereochemistry. In the reaction of **1** with alcohols, there are apparently two pathways, i. e., (1) double nucleophilic additions of alcohol toward cyano group involving cyclization (Scheme 5, path A) and (2) nucleophilic attack of alcohol toward formyl group and sequent intramolecular rearrangement after cyclization (Scheme 5, path B). Therefore, it is possible that in the presence of an acid catalyst the reaction path A is predominant, while both reactions, path A and B, could take place simultaneously in the presence of a base catalyst. These results also suggest that triethylamine, DABCO, and TMEDA can serve as conjugated acids.[5]

In conclusion, the selective synthesis of isoindoles, such as **2** and **4**, was performed by the reaction of **1** with alcohols in the presence of various acid or base catalysts.



Scheme 5.

Experimental

All melting points were uncorrected. IR spectra were obtained on a Hitachi 295 spectrophotometer and ^{1}H NMR spectra were obtained on a Hitachi R-22 spectrometer using tetramethylsilane as an internal standard. Mass spectra were taken with a Hitachi RMU-6M mass spectrometer. Elemental analyses were carried out with a Yanagimoto MT-3. All reactions were monitored by TLC (Merck Kiesel gel 60-GF 254).

Materials. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., or Aldrich Chemical Co. The reagents used were further purified by usual methods such as recrystallization or distillation. The silica gel used as an acidic catalyst (Wako gel G) was employed without drying, but Wako gel C-300 was dried under vacuum at 150 °C for 5 h.

General Procedure for Synthesis of 2 by Reactions of 1 with Alcohols in the Presence of Silica Gel. To a solution of **1** (66 mg, 0.5 mmol) in 4 ml of an alcohol was added silica gel (60 mg, Wako gel G) and the mixture was refluxed for 16—75 h. After filtration and evaporation of the alcohol, the residue obtained was chromatographed on silica gel using the mixture of chloroform and methyl alcohol (8/1, v/v) as an eluent to give **2a—e.**

2,3-Dihydro-1-hydroxy-3,3-dimethoxy-1*H*-isoindole (2a): Colorless crystals ($CHCl_3$); mp 97 °C; IR (KBr) 3175 and 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.37 (6H, s, CH_3×2), 5.66 (1H, s, CH), 6.15 (1H, br, OH), 6.90 (1H, br, NH), and 7.30—7.70 (m, 4H, arom); MS *m/z* 164 (M^+—OMe). Found: C, 61,48; H, 6.73; N, 7.15%. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%.

3,3-Diethoxy-2,3-dihydro-1-hydroxy-1*H*-isoindole (2b): Colorless crystals (CH_2Cl_2); mp 99 °C; IR (KBr) 3180 and 3375 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (6H, t, *J*=7.0 Hz, CH_3×2), 3.62 (4H, q, *J*=7.0 Hz, CH_2×2), 5.83 (1H, s, CH), 6.00 (1H, br, OH), 7.10 (1H, br, NH), and 7.23—7.80 (4H, m, arom); MS *m/z* 178 (M^+—OCH_2CH_3). Found: C, 64.55; H, 7.65; N, 6.34%. Calcd for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.67; N, 6.27%.

2,3-Dihydro-1-hydroxy-3,3-dipropoxy-1*H*-isoindole (2c): Colorless crystals ($CHCl_3$); mp 70 °C; IR (KBr) 3175 and 3370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.94 (6H, t, *J*=7.0 Hz, CH_3×2), 1.65 (4H, quint, *J*=7.0 Hz, CH_2×2), 3.55 (4H, dt, *J*=7.0 and 3.1 Hz, CH_2×2), 5.78 (1H, s, CH), 6.10 (1H, br, OH), 7.22 (1H, br, NH), and 7.33—7.83 (4H, m, arom); MS *m/z* 192(M^+—OPr). Found: C, 67.26; H, 8.23; N, 5.83%. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57%.

3,3-Dibutoxy-2,3-dihydro-1-hydroxy-1*H*-isoindole (2d): Colorless crystals ($CHCl_3$); mp 72 °C; IR (KBr) 3180 and 3325 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (6H, t, *J*=7.5 Hz, CH_3×2), 1.20—1.76 (8H, m, CH_2×4), 3.45—3.73 (4H, m, CH_2×2), 5.78 (1H, s, CH), 6.03 (1H, br, OH), and 7.28—7.82 (5H, m, NH and arom); MS *m/z* 206 (M^+—OBu). Found: C, 68.87; H, 8.85; N, 5.27%. Calcd for $C_{16}H_{15}NO_3$: C, 68.79; H, 9.02; N, 5.27%.

2,3-Dihydro-1-hydroxy-3,3-diisobutoxy-1*H*-isoindole (2e): Colorless crystals ($CHCl_3$); mp 93 °C; IR(KBr) 3180 and 3395 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (12H, d, *J*=7.0 Hz, CH_3×4), 1.75—2.15 (2H, m, *J*=7.0 Hz, CH×2), 3.36 (4H, dd, *J*=7.0 and 1.5 Hz, CH_2×2), 5.81 (1H, s CH), 6.10 (1H, br, OH), and 7.31—7.90 (4H, m, arom and NH); MS *m/z* 206 (M^+—OBu-i). Found: C, 68.89; H, 9.26; N, 5.02%. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01%.

General Procedure for Synthesis of 3 and 4 by Reactions of 1 with Alcohols in the Presence of Base Catalyst. To a solution of **1** (66 mg, 0.5 mmol) in 4 ml of an alcohol was added triethylamine, DBU, DABCO, or TMEDA (0.1—0.5 mmol, respectively) and the mixture was stirred at 15—60 °C for 0.5—16 h. After evaporation of the alcohol, the residue obtained was chromatographed on silica gel using the mixture of chloroform and methyl alcohol (8/1, v/v) as eluent, to give **3** and **4**.

1,3-Dihydro-1-imino-3-methoxyisobenzofuran (3a): Colorless crystals ($CHCl_3$); mp 129 °C; IR (KBr) 1640 and 3200 cm^{-1}; ^{1}H NMR ($CHCl_3$) δ=4.10 (3H, s, CH_3), 6.10 (1H, s, CH), and 7.30—7.90 (5H, m, arom and NH); MS *m/z* 132(M^+—OMe). Found: C, 65.82; H, 5.53; N, 8.49%. Calcd for $C_9H_9NO_2$: H, 66.25; H, 5.56; N, 8.58%.

3-Ethoxy-2,3-dihydro-1-iminoisobenzofuran (3b): Colorless crystals ($CHCl_3$); mp 112 °C; IR (KBr) 1620 and 3140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48 (3H, t, *J*=7.0 Hz, CH_3), 4.51 (2H, q, *J*=7.0 Hz,-CH_2-), 6.15 (1H, s, CH), and 7.30—7.73 (5H, m, NH and arom); MS *m/z* 177 (M^+). Found: C, 67.69; H, 6.15; N, 7.96%. Calcd for $C_{10}H_{11}NO_2$: C, 67.76; H, 6.26; N, 7.90%.

3-Butoxy-2,3-dihydro-1-iminoisobenzofuran (3d): Colorless crystals ($CHCl_3$); mp 63 °C; IR (KBr) 1620 and 3100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (3H, t, *J*=7.0 Hz, CH_3), 1.02—2.03 (4H, m, -CH_2CH_2-), 4.46 (2H, t, CH_2), 6.16 (1H, s, CH), and 7.30—7.72 (5H, m, NH and arom); MS *m/z* 205 (M^+). Found: C, 70.04; H, 7.49; N, 6.64%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%.

4a: Colorless crystals ($CHCl_3$); mp 100 °C (lit, 99 °C[3]).

4b: Colorless crystals ($CHCl_3$); mp 105 °C (lit, 108 °C[3]).

4d: Colorless crystals ($CHCl_3$); mp 92 °C; IR (KBr) 1720 and 3170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.88 (3H, t, *J*=7.0 Hz, CH_3), 1.13—1.76 (4H, m, -CH_2CH_2-), 3.18—3.66 (2H, m, CH_2), 5.96 (1H, s, CH), and 7.36—8.04 (5H, m, NH and arom); MS *m/z* 205 (M^+). Found: C, 70.25; H, 7.45; N, 6.80%. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%.

Reaction of 3a with Methanol in the Presence of DBU. To a solution of **3a** (82 mg, 0.5 mmol) in methanol (4 ml) was added DBU (15 mg, 0.1 mmol) and the solution was stirred at 20 °C for 3 h. After evaporation of methanol, the residue was chromatographed on silica gel using mixture of chloroform and ether (8/1, v/v), to give **4a** (81 mg, ca. 100%).

Reaction of 1 with Water in the Presence of DBU. To a solution of **1** (66 mg, 0.5 mmol) in water (4 ml) was added DBU (45 mg, 0.3 mmol) and the solution was heated at 50 °C for 3 h with stirring. After evaporation of water under vacuum, the residue was chromatographed on silica gel using the mixture of chloroform and methanol (10/1, v/v), to give **6** (70 mg, 93%) and **5** (5 mg, 7%).

Reaction of 1 with 6 in the Presence of DBU. To a solution of **1** (33 mg, 0.25 mmol) and DBU (30 mg, 0.2 mmol) in ethanol (4 ml) was added **6** (37 mg, 0.25 mmol) and the mixture was heated at 50 °C for 3 h with stirring. After evaporation of ethanol the residue was chromatographed on silica gel using the mixture of chloroform and methanol (10/1, v/v), to give **5** quantitatively (70 mg, 100%).

5: Colorless crystals (MeOH); mp 225 °C; IR (KBr) 1700 and 3220 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=5.74 (1H, d, *J*=9.1 Hz, CH), 6.45 (1H, s, CH), 6.63 (1H, d, *J*=9.1 Hz,

OH), 7.40—7.80 (8H, m, arom), and 8.77 (1H, s, NH); MS *m/z* 148 and 132. Found: C, 68.30; H, 4.29; N, 9.76%. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.32; N, 9.99%.

6: Colorless crystals (MeOH); mp 165 °C (lit, 178,[3] 184[6] °C); IR (KBr) 1700 and 3450 cm^{-1}; ^1H NMR (DMSO-d_6) δ=5.86 (1H, d, J=9.1 Hz, CH), 6.29 (1H, d, J=9.1 Hz, OH), 7.40—7.80 (4H, m, arom), and 8.70—9.00 (1H br, NH); MS *m/z* 149 (M^+). Found: C, 64.22; H, 9.36; N, 4.67%. Calcd for $C_8H_7NO_2$: C, 64.42; H, 9.39; N, 4.73%.

7: This compound was synthesized by alkylation of phthalimide followed by reduction with sodium borohydride according to the method as shown in the literature.[6] Colorless crystals ($CHCl_3$); mp 130 °C (lit, 129 °C[7]).

References

1) Fujimoto, Japan Kokai Tokkyo Koho, 188567 (1982) [*Chem. Abstr.*, **98**, 179215x (1983)]; P. N. Giraldi and G. Nannini, Ger. Offen, 2154525 (1971) [*Chem. Abstr.*, **77**, 88292v (1972)]; P. N. Giraldi and V. Mariotti, S. Afr. Patent., 3624206 (1971) [*Chem. Abstr.*, **70**, 68156f (1969)]; G. Sacchetti, Farmaco ED Prat., **27**, 708 (1972) [*Chem. Abstr.*, **78**, 119448c (1973)]; M. Takeda, *Oyo Yakuri.*, **7**, 903, 1073 (1973); T. Mukai, *Jpn. T. Phatmacol.*, **31**, 1073 (1973); P. Aeberli and J. Houlihan, *J. Org. Chem.*, **34**, 165 (1969); C. A. Demerson and I. L. Jikovsky, U. S. Patent., 4355031 (1982) [*Chem. Abstr.*, **98**, 160738y (1983)]; M. Los, Eur. Pat. Appl. EP., 135711 (1985) [*Chem. Abstr.*, **103**, 87875f (1985)]; M. Los, Eur. Pat. Appl. EP., 519603 (1985) [*Chem. Abstr.*, **103**, 87872c (1985)]; M. Waniak, H. C. van der Plas, and S. Haskema, *J. Org. Chem.*, **50**, 3435 (1985).

2) R. Sato, T. Senzaki, T. Goto, and M. Saito, *Chem. Lett.*, **1984**, 1599; R. Sato,T. Senzaki, T. Goto, and M. Saito, *Bull. Chem. Soc. Jpn.*, **59**, 2950 (1986).

3) B. Sakurai, *Bull. Chem. Soc. Jpn.*, **5**, 184 (1930); M. M. Dunet and A. Willemart, *Bull. Soc. Chim. Fr.*, **1948**, 887 and 889.

4) Y. Kamitori, M. Hojo, R. Masuda, and T. Yoshida, *Tetrahedron Lett.*, **27**, 4767 (1986); Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, and T. Yoshida, *J. Org. Chem.*, **51**, 1427 (1986). As review: D. W. Young, *Synthesis*, **1979**, 481; M. Hojo and R. Masuda, *Yuki Gosei Kagaku Kyokai Shi*, **37**, 689 (1979)

5) F. Toda and K. Tanaka, *Chem. Lett.*, **1986**, 1905.

6) D. A. Burnett, J. K. Choi, D. J. Hart, and Y. M. Tsai, *J. Am. Chem. Soc.*, **106**, 8201 (1984); A. O. Stewart and R. M. Williams, *ibid.*, **107**, 4289 (1985).

7) F. Englaender, H. Funten, P. Rieger, K-D. Steffen, G. Weigerber, and G. Zoche, *Chem.-Ztg.*, **103**, 9 (1979).