Electrophilic Substitution of Indole on the Benzene Moiety: A Synthesis of 5-Acyl- and 5-Aroylindoles

Vassilis J. Demopoulos,* Ioannis Nicolaou

Department of Pharmaceutical Chemistry, School of Pharmacy, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece
Fax +30(31)997622, E-mail: vdem@pharm.auth.gr
Received 11 September 1997; revised 2 March 1998

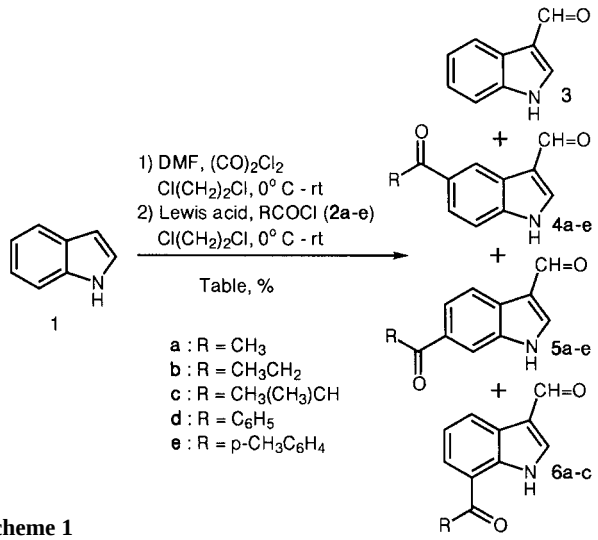
Abstract: The Vilsmeier-Haack intermediate of indole is acylated, in the presence of a certain excess of $AlCl_3$, exclusively at the benzene ring and especially at position-5. The formed acylindolecarboxaldehydes are readily decarbonylated on heating with Pd/C in mesitylene. Thus, 5-acylindoles and 5-aroylindoles are synthesized in a two step sequence from indole with overall yield of 30–46%.

Key words: indole Vilsmeier-Haack intermediate, Friedel-Crafts acylation, Pd/C decarbonylation, 5-acylindoles, 5-aroylindoles

The addition of electrophiles to the C-3 position of the indole ring is perhaps the most characteristic reaction of this class of heterocycles.[1] Acylation of indoles has been widely used and Friedel–Crafts acylation is one of the best methods for introducing an acyl group at the 3-position of 1-phenylsulfonylindole.[2,3] 1-Acylindoles are also acylated at the 3-position. However, their reaction with excess of halogenacyl chlorides in the presence of excess aluminum chloride gives the corresponding 1,6-diacylindoles.[4] The acylation of indoles bearing electron withdrawing groups (ethoxycarbonyl or acetyl) at positions 2 or 3, under certain conditions, leads to substitution of the benzene part of the heterocycle, especially at the C-5 position.[5–7] Analogous electrophilic reactions have also been studied with pyrroles deactivated with electron withdrawing functionalities, and it has been shown that the Vilsmeier–Haack intermediate of pyrrole readily reacts, under Friedel–Crafts acylation conditions, leading to a one-pot synthesis of 4-acylpyrrole-2-carboxaldehydes.[8] The latter could be decarbonylated with the action of Raney Ni or on heating with Pd/C.

In the present study, we investigated the Friedel–Crafts acylation of the Vilsmeier–Haack intermediate of indole **(1)** (Scheme 1) and the subsequent decarbonylation of the formed acylindole-3-carboxaldehydes **4–5** (Scheme 2). The target 5-substituted indoles **7** are of interest as, for example, in the synthesis of serotonin receptor agonists or antagonists.[9,10]

The results of these Friedel–Crafts reactions are presented in the Table. We found that the reaction of the Vilsmeier–Haack intermediate of indole **(1)** with acetyl chloride and a certain excess of $AlCl_3$ (entry 2) leads to the formation of the isomeric acylindoles **4a**, **5a** and **6a**. The isomer **4a** substituted at the 5-position was the major product and could be isolated in 42% yield from indole in this one-pot reaction. Smaller amounts of the Lewis acid catalyst (entry 1) resulted in insignificant acetylation. Larger amounts of $AlCl_3$ (entry 4) or the use of nitromethane (entry 3) did not change the preferred position of electrophilic attack. $AlCl_3$ was the catalyst of choice in this type of reaction. The use of $FeCl_3$ resulted in extensive decomposition and isolation of only low yields of acylated product. It is worth noting that the selectivity in this case is reversed, giving rise to a predominant substitution at the 6-position (entry 5). $SnCl_4$, $TiCl_4$ and BCl_3 were all ineffective catalysts, resulting in no acetylation products. We noted that with the addition of the excess $AlCl_3$ (entries 2–4), and after approximately 10 minutes, the Vilsmeier–Haack intermediate of indole insoluble in 1,2-dichloroethane had dissolved. This did not happen in the cases of the unsuccessful reactions (entries 1 and 5–8). Increasing the length of the side chain or introducing a branching in the acylating agent (e.g., propionyl and isobutyryl chlorides, entries 9 and 10) did not substantially affect the overall yield or the ratio of the formed products. On the other hand, attempts to acetylate directly indole-3-carboxaldehyde resulted in a low yield (20%) of almost equimolar quantities of **4a** and **5a** along with 4% of **6a** and a 62% recovery of the starting aldehyde.



Scheme 1

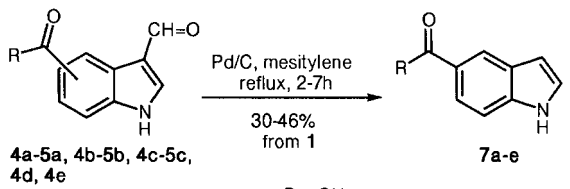
The use of an aroyl halide (eg. benzoyl or *p*-toluoyl chloride, entries 11 and 12) as the acylating agent, resulted in the formation of the corresponding aroylindole isomers, **4d–5d** and **4e–5e**. In these reactions, for reproducible results, we found it necessary to use a greater excess of the Lewis acid catalyst. Again, the 5-substituted isomers (**4d** and **4e**) were the predominant products and could be isolated in 59% and 46% yield, respectively.

Table. Friedel-Crafts Reactions of the Vilsmeier-Haack Intermediate of Indole

Entry	Acylating Chloride	Lewis Acid	Ratio **1** : **2** : Lewis Acid	Yield (%)		
				3	**4** and **5** % (ratio **4** : **5**)	**6**
1	**2a** (Me)	$AlCl_3$	1 : 1.12 : 1.22	79	2	0
2	**2a** (Me)	$AlCl_3$	1 : 1.12 : 2.44	0	80 (75 : 25)[a]	12
3	**2a** (Me)	$AlCl_3$	1 : 1.12 : 2.44[b]	0	64 (75 : 25)[a]	13
4	**2a** (Me)	$AlCl_3$	1 : 1.12 : 3.66	0	77 (70 : 30)[a]	9
5	**2a** (Me)	$FeCl_3$	1 : 1.12 : 2.44	7	14 (20 : 80)[a]	6
6	**2a** (Me)	$SnCl_4$	1 : 1.12 : 2.44	–[c]	0	0
7	**2a** (Me)	$TiCl_4$	1 : 1.12 : 2.44	–[c]	0	0
8	**2a** (Me)	BCl_3	1 : 1.12 : 2.44	–[c]	0	0
9	**2b** (Et)	$AlCl_3$	1 : 1.12 : 2.44	0	70 (80 : 20)[a]	11
10	**2c** (*i*-Pr)	$AlCl_3$	1 : 1.12 : 2.44	0	76 (75 : 25)[a]	7
11	**2d** (Ph)	$AlCl_3$	1 : 1.12 : 3.66	0	79 (75 : 25)[d]	0
12	**2e** (4-MeC_6H_4)	$AlCl_3$	1 : 1.12 : 3.66	0	63 (73 : 27)[d]	0

[a] The ratio is based on the ^1H NMR spectrum of the mixture. The peak at $\delta = 10$ (which corresponds to the CHO of both **4a–c** and **5a–c**) was compared with the peak at $\delta = 8.79$ (which corresponds to the H-4 of **4a–c**).
[b] Nitromethane (equimolar to $AlCl_3$) was added.
[c] Sole product based on TLC.
[d] The ratio is based on the isolated isomers.

Deformylation or deacylation of the C-3 substituent of certain indoles has been reported by the action of ethylene glycol and *p*-toluenesulfonic acid in refluxing benzene[11,12] or on heating in strongly basic solutions for extended periods.[13] However, under these conditions only small amounts of the desired product from **4a** were formed. It has been shown that ethyl 5-formylpyrrole-3-glyoxylate is decarbonylated by the action of Pd/C in refluxing mesitylene.[14] We found that **4a** is readily decarbonylated under similar conditions. Also, it could be decarbonylated in refluxing xylene, but this reaction requires extended periods of time for completion. For preparative purposes, it is not necessary to separate **4a** from **5a**. Deformylation of this mixture of isomers resulted in the isolation of 5-acetylindole (**7a**) in 46% overall yield from indole in a two step sequence. In a similar manner **7b** and **7c** were formed in 37 and 41% overall yield from indole, respectively. This represents a facile methodology and compares favorably with previously reported procedures which either involve substitution of 1-potassio-5-lithioindole[9] or are roundabout routes via *N*-acetylindoline.[15,16] 5-Benzoylindole-3-carbaldehyde (**4d**) was also readily decarbonylated to **7d** in 62% yield. Thus, the overall yield of formation of 5-benzoylindole is 37% from indole. To the best of our knowledge, **7d** has been previously reported[17] only as a minor product in the photo-Fries rearrangement of 1-benzoylindole; no physicochemical properties were presented. Finally, decarbonylation of **4e** afforded **7e** in 65% yield (30% from indole).



Scheme 2

Melting points are uncorrected and were determined in open glass capillaries using a Mel-Temp II apparatus. IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer and ^1H NMR spectra on a Bruker AW-80 spectrometer with internal TMS as reference. Elemental analyses were performed using a Perkin-Elmer 2400 CHN analyzer. Flash chromatography was carried out using Merck 9385 silica gel. Petroleum ether refers to the fraction with bp 40–60°C. For all isolated compounds (**4a, 4d,e, 5d,e, 6a–c, 7a–e** and **8a**) satisfactory microanalyses were obtained: C±0.34, H±0.33, N±0.40.

Formation and Friedel–Crafts Reaction of the Vilsmeier–Haack Intermediate of Indole (1) (Entries 2 and 9–12, Table); General Procedure:

Oxalyl chloride (0.7 g, 5.5 mmol) in 1,2-dichloroethane (10 mL) was added dropwise over a period of 5 min into a stirred, ice cold solution of DMF (0.41 g, 5.6 mmol) in 1,2-dichloroethane (10 mL) under a N_2 atmosphere, and then the mixture was allowed to warm to r.t. for 15 min. The mixture was cooled (ice bath) and a solution of indole (0.59 g, 5 mmol) in 1,2-dichloroethane (10 mL) was rapidly added. The resulting mixture was warmed to r.t. for 15 min and then cooled (ice bath). $AlCl_3$ (12.2 or 18.3 mmol) was rapidly added and the mixture was allowed to warm to r.t. for 15 min. The mixture was cooled (ice bath), a solution of the appropriate acyl or aroyl chloride (5.6 mmol) in 1,2-dichloroethane (5 mL) was rapidly added and the reaction was allowed to proceed overnight at r.t.

1. Acylation Reactions: The reaction mixture was poured into ice/water, basified with solid NaOH, stirred vigorously for 2 h, cooled (ice bath) and acidified with concd HCl. It was filtered (if necessary), the two phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, filtered through a pad of anhyd $MgSO_4$ and evaporated under reduced pressure. The residue, combined with the precipitate, was flash chromatographed on silica gel with petroleum ether/EtOAc (2:1 to 0:1) as eluent to afford the products as described below.

7-Acetyl-1H-indole-3-carboxaldehyde (**6a**); yield: 0.112 g (12%); mp 162–164 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3320, 1640 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 2.69 (s, 3H, CH_3), 7.34 (t, 1H, *J* = 8 Hz, H-5), 7.81–7.93 (m, 2H, H-2,6), 8.56 (d, 1H, *J* = 8 Hz, H-4), 10.08 (s, 1H, CHO), 11 (br s, 1H, NH).
A mixture (75:25) of 5-acetyl-1*H*-indole-3-carboxaldehyde (**4a**) and 6-acetyl-1*H*-indole-3-carboxaldehyde (**5a**); yield: 0.745 g (80%). This mixture was twice recrystallized from absolute EtOH to afford *5-acetyl-1H-indole-3-carboxaldehyde* (**4a**) which was homogeneous by TLC (silica gel) (CH_2Cl_2/Et_2O,1:1); yield: 0.39 g (42%); mp 238–240 °C .
IR (nujol): ν = 3150, 1635 cm^{-1}.
^1H NMR (1:1 $CDCl_3$/DMSO-d_6): δ = 2.62 (s, 3H, CH_3), 7.51 (d*AB*, 1H, *J* = 8.6 Hz, H-7), 7.87 (d*AB*, 1H, *J* = 8.6 Hz, H-6), 8.08 (s, 1H, H-2), 8.79 (s, 1H, H-4), 10 (s, 1H, CHO).

7-Propionyl-1H-indole-3-carboxaldehyde (**6b**); yield: 0.11 g (11%); mp 132–133 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3320, 1640 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.25 (t, 3H, *J* = 7.3 Hz, CH_3), 3.13 (q, 2H, *J* = 7.3 Hz, CH_2), 7.32 (t, 1H, *J* =7.6 Hz, H-5), 7.8–7.98 (m, 2H, H-2,6), 8.54 (d, 1H, *J* = 7.6 Hz, H-4), 10.08 (s, 1H, CHO), 11.2 (br s, 1H, NH).
A mixture (80:20) of 5-propionyl-1*H*-indole-3-carboxaldehyde (**4b**) and 6-propionyl-1*H*-indole-3-carboxaldehyde (**5b**); yield: 0.704 g (70%).

7-Isobutyroyl-1H-indole-3-carboxaldehyde (**6c**); yield: 0.07 g (7%); mp 134–135 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3340, 1660, 1640 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.29 (d, 6H, *J* = 6.6 Hz, CH_3), 3.85 (q, 1H, *J* = 6.6 Hz, CH), 7.36 (t, 1H, *J* = 7.4 Hz, H-5), 7.85–8.00 (m, 2H, H-2,6), 8.58 (d, 1H, *J* = 7.4 Hz, H-4), 10.1 (s, 1H, CHO), 11.1 (br s, 1H, NH).
A mixture (75:25) of 5-isobutyroyl-1*H*-indole-3-carboxaldehyde (**4c**) and 6-isobutyroyl-1*H*-indole-3-carboxaldehyde (**5c**); yield: 0.813 g (76%).

Aroylation Reactions: The reaction mixture was poured into ice/water, stirred vigorously for 4 h, the two phases were separated and the aqueous phase was extracted with CH_2Cl_2. The aqueous phase was basified with solid NaOH, stirred briefly (30 min), acidified with concd HCl and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was flash chromatographed on silica gel with petroleum ether/EtOAc (2:1 to 0:1) as the eluent to afford the products as given below.

6-Benzoyl-1H-indole-3-carboxaldehyde (**5d**); yield: 0.25 g (20%); mp 157–159 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3160, 1635, 1615 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 7.4–7.66 (m, 3H, phenyl H), 7.7–7.87 (m, 3H, H-2 and phenyl H), 7.93–8.08 (m, 2H, H-5,7), 8.32 (d, 1H, *J* = 8 Hz, H-4), 10.04 (s, 1H, CHO), 10.2 (br s, 1H, NH).

5-Benzoyl-1H-indole-3-carboxaldehyde (**4d**); yield: 0.739 g (59%); mp 202–204 °C (EtOAc/petroleum ether).
IR (nujol): ν = 3100, 1640, 1605 cm^{-1}.
^1H NMR (1:1 $CDCl_3$/DMSO-d_6): δ = 7.48–7.59 (m, 4H, H-7 and phenyl H), 7.75–7.97 (m, 4H, H-2,6 and phenyl H), 8.66 (s, 1H, H-4), 10 (s, 1H, CHO).

6-(4-Methylbenzoyl)-1H-indole-3-carboxaldehyde (**5e**); yield: 0.224 g (17%); mp 223–224 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3160, 1660, 1625 cm^{-1}.
^1H NMR (1:1 $CDCl_3$/DMSO-d_6): δ = 2.42 (s, 3H, CH_3), 7.28 (d, 2H, *J* = 7.6 Hz, phenyl H), 7.57–8.09 (m, 5H, H-2,5,7 and phenyl H), 8.26 (d, 1H, *J* = 8.4 Hz, H-4), 10.02 (s, 1H, CHO), 12.05 (br s, 1H, NH).

5-(4-Methylbenzoyl)-1H-indole-3-carboxaldehyde (**4e**); yield: 0.6 g (46%); mp 206–207 °C (toluene).
IR (nujol): ν = 3170, 1630 cm^{-1}.
^1H NMR (1:1 $CDCl_3$/DMSO-d_6): *d* = 2.41 (s, 3H, CH_3), 7.27 (d, 2H, *J* = 7 Hz, phenyl H), 7.52–8.07 (m, 5H, H-2,6,7 and phenyl H), 8.6 (s, 1H, H-4), 9.98 (s, 1H, CHO).

5-Acylindoles 7a–c; General Procedure:
To a stirred suspension of the mixtures of isomers **4a–5a**, **4b–5b** and **4c–5c** (1.6 mmol) in mesitylene (10 mL) under a nitrogen atmosphere was added Pd/C (10%, 0.06 g) and the mixture was refluxed for 4–7 h. It was cooled to r.t., diluted with CH_2Cl_2, filtered through celite and concentrated under reduced pressure.

1-(1H-Indol-5-yl)ethanone **(7a)**:
The residue was flash chromatographed on silica gel with petroleum ether/EtOAc (1:0 to 5:1) as the eluent to afford **7a**; yield: 0.128 g (46% from indole); mp 72–74 °C (CH_2Cl_2/petroleum ether) (Lit.[9] 73–75 °C).
IR (nujol): ν = 3230, 1645 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 2.65 (s, 3H, CH_3), 6.63 (m, 1H, H-3, after addition of D_2O changes to d, *J* = 3 Hz), 7.26 (m, 1H, H-2, after addition of D_2O changes to d, *J* = 3 Hz), 7.36 (d, 1H, *J* = 9 Hz, H-7), 7.84 (dd, 1H, *J* = 1.6, 9 Hz, H-6), 8.32 (s, 1H, H-4), 9.00 (br s, 1H, NH).

1-(1H-Indol-6-yl)ethanone (**8a**); yield: 0.01 g (4% from indole); mp 120–121 °C (CH_2Cl_2/petroleum ether) (Lit.[18] mp 122–122.5 °C).
IR (nujol): ν = 3350, 1655 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 2.6 (s, 3H, CH_3), 6.6 (m, 1H, H-3, after addition of D_2O changes to d, *J* = 3 Hz), 7.38 (m, 1H, H-2, after addition of D_2O changes to d, *J* = 3 Hz), 7.55–7.84 (m, 2H, H-4,5), 8.1 (s, 1H, H-7), 8.8 (br s, 1H, NH).

1-(1H-Indol-5-yl)propan-1-one **(7b)**:
The residue was flash chromatographed on silica gel with petroleum ether/CH_2Cl_2 (1:0 to 1:2) to afford **7b**; yield: 0.146 g (37% from indole); mp 111–112 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3280, 1650 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.23 (t, 3H, *J* = 6.4 Hz, CH_3), 3.06 (q, 2H, *J* = 6.4 Hz, CH_2), 6.62 (m, 1H, H-3, after addition of D_2O changes to d, *J* = 3.3 Hz), 7.25 (m, 1H, H-2, after addition of D_2O changes to d, *J* = 3.3 Hz), 7.4 (d, 1H, *J* = 8.4 Hz, H-7), 7.87 (d, 1H, *J* = 8.4 Hz, H-6), 8.33 (s, 1H, H-4), 8.87 (br s, 1H, NH).
No attempt was made to isolate and characterize the corresponding C-6 isomer.

1-(1H-Indol-5-yl)2-methylpropan-1-one **(7c)**:
The residue was flash chromatographed on silica gel with petroleum ether/CH_2Cl_2 (1:0 to 1:2) to afford **7c**; yield: 0.162 g (41% from indole); mp 70 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3280, 1655 cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.23 (d, 6H, *J* = 6.6 Hz, CH_3), 3.67 (q, 1H, *J* = 6.6 Hz, CH), 6.63 (m, 1H, H-3, after addition of D_2O changes to d, *J* = 3 Hz), 7.4 (d, 1H, *J* = 8.4 Hz, H-7), 7.89 (d, 1H, *J* = 8.4 Hz, H-6), 8.33 (s, 1H, H-4), 8.8 (br s, 1H, NH).
No attempt was made to isolate and characterize the corresponding C-6 isomer.

5-Aroylindoles 7d and **7e; General Procedure:**
A mixture of **4d** or **4e** (1.6 mmol) and Pd/C (10%, 0.06 g) in mesitylene (10 mL) was refluxed under a N_2 atmosphere for 2 h. Workup as above and flash chromatography on silica gel with petroleum ether/EtOAc (1:0 to 4:1) afforded **7d** and **7e**.
(1H-Indol-5-yl)phenylmethanone (**7d**); yield: 0.22 (62% or 37% from indole); mp 151–152 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3275, 1605 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 6.6 (m, 1H, H-3, after addition of D_2O changes to d, J = 3.2 Hz), 7.2 (m, 1H, H-2, after addition of D_2O changes to d, J = 3.2 Hz), 7.3–7.56 (m, 4H, H-7 and phenyl H), 7.67–7.88 (m, 3H, H-6 and phenyl H), 8.12 (s, 1H, H-4), 8.95 (br s, 1H, NH).

(1H-Indol-5-yl)-p-tolylmethanone (**7e**); yield: 0.243 g (65 or 30% from indole); mp 165–166 °C (CH_2Cl_2/petroleum ether).
IR (nujol): ν = 3220, 1620 cm^{-1}.
^{1}H NMR (1:1 $CDCl_3$/DMSO-d_6): δ = 2.41 (s, 3H, CH_3), 6.56 (m, 1H, H-3, after addition of D_2O changes to d, J = 3.3 Hz), 7.15–7.82 (m, 7H, H-2,6,7 and phenyl H), 8.06 (s, 1H, H-4), 10.6 (br s, 1H, NH).

(1) Sundberg, R.J. *Indoles*; Academic Press: London, 1996; p 105.
(2) Ketcha, D.M.; Gribble, G.W. *J. Org. Chem.* **1985**, *50*, 5451.
(3) Wenkert, E.; Moeller, P.D.R.; Piettre, S.R.; McPhail, A.T. *J. Org. Chem.* **1988**, *53*, 3170.
(4) Nakatsuka, S.; Teranishi, K.; Goto, T. *Tetrahedron Lett.* **1994**, *35*, 2699.
(5) Hino, T.; Torisawa, Y.; Nakagawa, M. *Chem. Pharm. Bull.* **1982**, *30*, 2349.
(6) Murakami, Y.; Tani, M.; Tanaka, K.; Yokoyama, Y. *Chem. Pharm. Bull.* **1988**, *36*, 2023.
(7) Tani, M.; Aoki, T.; Ito, S.; Matsumoto, S.; Hideshima, M.; Fukushima, K.; Nozawa, R.; Maeda, T.; Tashiro, M.; Yokoyama, Y.; Murakami, Y. *Chem. Pharm. Bull.* **1990**, *38*, 3261.
(8) Anderson, H.J.; Loader, C.E.; Foster, A. *Can. J. Chem.* **1980**, *58*, 2527.
(9) Yang, Y.; Martin, A.R.; Nelson, D.L.; Regan, J. *Heterocycles* **1992**, *34*, 1169.
(10) Agarwal, A.; Pearson, P.P.; Taylor, E.W.; Li, H.B.; Dahlgren, T.; Herslöf, M.; Yang, Y.; Lambert, G.; Nelson, D.L.; Regan, J.W.; Martin, A.R. *J. Med. Chem.* **1993**, *36*, 4006.
(11) Kametani, T.; Kigawa, Y.; Takahashi, K.; Nemoto, H.; Fukumoto, K. *Chem. Pharm. Bull.* **1978**, *26*, 1918.
(12) Nagarathnam, D. *J. Heterocyclic Chem.* **1992**, *29*, 1371.
(13) Powers, J. C. *Tetrahedron Lett.* **1965**, 655.
(14) Demopoulos, B.J.; Anderson, H.J.; Loader, C.E.; Faber, K. *Can. J. Chem.* **1983**, *61*, 2415.
(15) Akagi, M.; Ozaki, K. *Heterocycles* **1987**, *26*, 61.
(16) Terent'ev, A.P.; Preobrazhenskaya, M.N.; Sorokina, G.M. *Zhur. Obshchei Khim*. **1959**, *29*, 2875; *Chem. Abstr*. **1960**, *54*, 12098f.
(17) Oldroyd, D.L.; Weedon, A.C. *J. Photochem. Photobiol., A* **1991**, *57*, 207.
(18) Somei, M.; Natsume, M. *Tetrahedron Lett.* **1973**, *27*, 2451.