Reaction of *N*-(4-Pyridylmethyl)benzamide *N*-Oxides and *N*-[(α-Acetoxy)-4-pyridylmethyl]benzamides with 1,3-Diphenyl-1,3-propanedione

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Reaction of *N*-(4-pyridylmethyl)benzamide *N*-oxides **2** with 1,3-diphenyl-1,3-propanedione in the presence of acetic anhydride afforded 1,1-dibenzoyl-2-(4-pyridyl)-2-(benzoylamino)ethanes **4** in low yield. Treatment of *N*-[(α-acetoxy)-4-pyridylmethyl]benzamides **3** with 1,3-diphenyl-1,3-propanedione in the presence of triethylamine and chloroform as a solvent provided **4** in high yield. Reaction of **4** with nucleophiles as hydrazine, methyl and phenylhydrazine gave the corresponding pyrazoles **5**.

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Picobenzide **1a** [1] is a potent pharmacological agent. During the last few years, we have obtained new derivatives [2-13] of **1a** by various modifications of its skeleton. As a part of our program, we have shown that there are two methods to functionalize the methylene group of **1a**. The first consists of the reaction of the *N*-oxide **2a** with active methylene compounds in the presence of the acetic anhydride. The second method utilises the *N*-[(α-acetoxy)-4-pyridylmethyl] derivative **3a** with acidic compounds.

These facts, and our continuing interest in the chemistry of Picobenzide, prompted us to investigate the reactivity of a series of *N*-(4-pyridylmethyl)benzamide *N*-oxides **2** and *N*-[(α-acetoxy)-4-pyridylmethyl]benzamides **3** with 1,2-diphenyl-1,3-propanedione.

The starting *N*-(4-pyridylmethyl)benzamide *N*-oxides **2** were prepared by oxidation of the corresponding benzamides with hydrogen peroxide in acetic acid [5]. Benzamides **1** were obtained by the direct reaction of the apropiate acids with 4-aminomethylpyridine in the presence of dicyclohexylcarbodiimide [14].

Reaction of *N*-(4-pyridylmethyl)-3,5-dimethylbenzamide *N*-oxide **2a** with 1,3-diphenyl-1,3-propanedione in the presence of acetic anhydride afforded 1,1-dibenzoyl-2-(4-pyridyl)-2-(3,5-dimethylbenzoylamino)ethane **4a** in 20% yield. This structure was established on the basis of elemental analysis and spectral data (Tables I-III).

Similarly, the *N*-oxides **2b-f** react with 1,3-diphenyl-1,3-propanedione to give the corresponding ethane derivatives **4b-f** in low yield (< 20% in all cases, method A). The synthetic results and various spectral data are summarized in Tables I-III.

Table I

1,1-Dibenzoyl-2-(4-pyridyl)-2-(benzoylamino)ethanes **4a-f**.

Compound	R	Yield % Method A	Yield % Method B	Mp [a]	Formula	Analyses % Calcd./Found C	H	N
4a	3,5(CH_3)$_2$	20	84	204-205°	$C_{30}H_{26}N_2O_3$	77.89 78.11	5.66 5.41	6.05 6.21
4b	H	19	88	211-212°	$C_{28}H_{22}N_2O_3$	77.39 77.40	5.10 4.80	6.45 6.64
4c	2-CH_3	15	49	200-202° [b]	$C_{29}H_{24}N_2O_3$	77.65 77.51	5.39 5.47	6.24 6.34
4d	4-OCH_3	17	72	216-217°	$C_{29}H_{24}N_2O_4$	74.97 75.10	5.20 5.29	6.03 6.32
4e	4-NO_2	12	40	215-216°	$C_{28}H_{21}N_3O_5$	70.13 70.24	4.41 4.45	8.76 8.61
4f	4-Cl	17	77	214-215°	$C_{28}H_{21}ClN_2O_3$	77.71 71.79	4.51 4.39	5.97 6.03

[a] From ethanol. [b] From benzene.

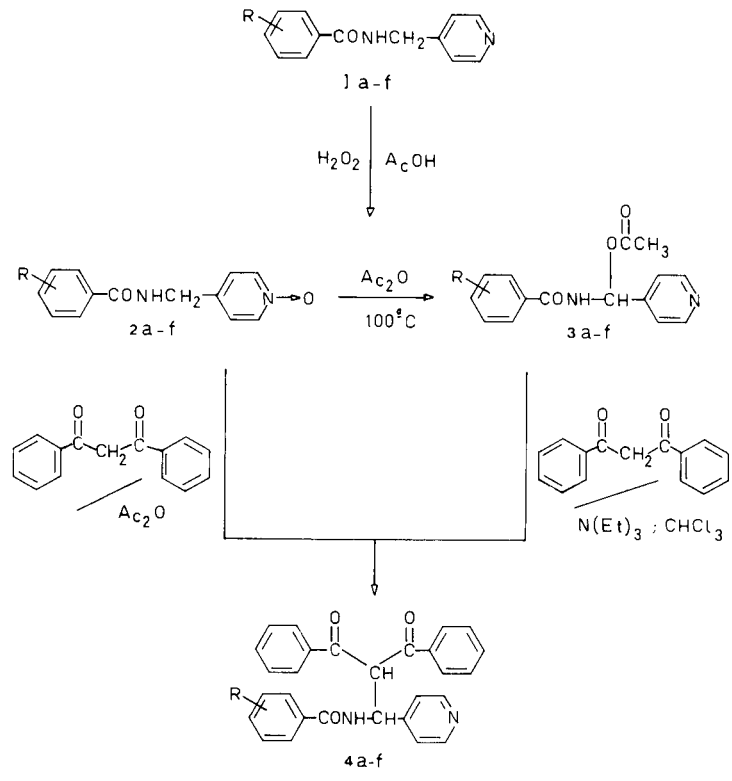
Table II

IR [a] and ^{1}H NMR [b] Spectral Data of Compounds **4a-f**

Compound	R	IR, cm^{-1} ν NH	ν CO	^{1}H NMR, δ
4a	3,5-$(CH_3)_2$	3300	1680, 1660, 1640	2.2 (s, 6H, $2CH_3$), 5.9 (t, 1H, CH), 6.6 (d, 1H, CHO), 6.8-7.6 (m, 11H, $2H_3$, $2H_4$, $2H_5$-PhCO, H_2, H_4, H_6-PhCONH, H_3, H_5-Py), 7.6-8.1 (m, 4H, $2H_2$, $2H_6$-PhCO), 8.2 (d, 2H, H_2, H_6-Py), 8.6 (d, 1H, NH)
4b	H	3360	1690, 1670, 1640	6.1 (t, 1H, CH), 6.7 (d, 1H, CHCO), 7.1-7.6 (m, 13H, $2H_3$, $2H_4$, $2H_5$-PhCO, 5H-PhCONH, H_3, H_5-Py), 7.7-8.2 (m, 4H, $2H_2$, $2H_6$-PhCO), 8.4 (d, 2H, H_2, H_6-Py), 8.9 (d, 1H, NH)
4c	2-CH_3	3300	1680, 1660, 1630	2.0 (s, 3H, CH_3), 5.9 (t, 1H, CH), 6.4 (d, 1H, CHCO), 6.8-7.4 (m, 12H, $2H_3$, $2H_4$, $2H_5$-PhCO, 4H-PhCONH, H_3, H_5-Py), 7.5-7.9 (m, 4H, $2H_2$, $2H_6$-PhCO), 8.2 (d, 2H, H_2, H_6-Py), 8.6 (d, 1H, NH)
4d	4-OCH_3	3320	1690, 1660, 1630	3.6 (s, 3H, OCH_3), 5.9 (t, 1H, CH), 6.5 (d, 1H, CHCO), 6.6-7.5 (m, 12H, $2H_3$, $2H_4$, $2H_5$-PhCO, 4H-PhCONH, H_3, H_5-Py), 7.6-8.0 (m, 4H, $2H_2$, $2H_6$-PhCO), 8.2 (d, 2H, H_2, H_6-Py), 8.5 (d, 1H, NH)
4e	4-NO_2	3340	1970 (overlapped)	5.9 (t, 1H, CH), 6.5 (d, 1H, CHCO), 7.2-7.5 (m, 8H, $2H_3$, $2H_4$, $2H_5$-PhCO, H_3, H_5-Py), 7.6-8.4 (m, 10H, $2H_2$, $2H_6$-PhCO, 4H-PhCONH, H_2, H_6-Py), 9.0 (d, 1H, NH)
4f	4-Cl	3320	1680, 1660, 1630	5.9 (t, 1H, CH), 6.5 (d, 1H, CHCO), 7.0-7.5 (m, 12H, $2H_3$, $2H_4$, $2H_5$-PhCO, 4H-PhCONH, H_3, H_5-Py), 7.6-8.0 (m, 4H, $2H_2$, $2H_6$-PhCO), 8.2 (d, 2H, H_2, H_6-Py), 8.8 (d, 1H, NH)

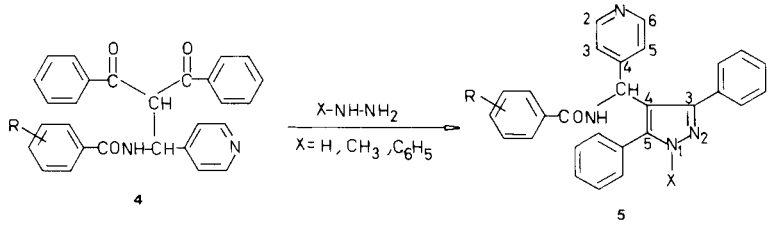
[a] Potassium Bromide. [b] DMSO-d_6.

Scheme 1



a, R = 3,5 $(CH_3)_2$
b, R = H
c, R = 2-CH_3
d, R = 4-OCH_3
e, R = 4-NO_2
f, R = 4-Cl

Scheme 2



a, R = 3,5(CH$_3$)$_2$

c, R = 2 CH$_3$

f, R = 4 Cl

a, R = 3,5 (CH$_3$)$_2$ X = H

a', R = 3,5 (CH$_3$)$_2$ X = C$_6$H$_5$

c, R = 2 CH$_3$ X = CH$_3$

c', R = 2 CH$_3$ X = C$_6$H$_5$

f, R = 4 Cl X = C$_6$H$_5$

Table III

^{13}C NMR of **4a-f** (DMSO-d$_6$, δ)

Compound	R	CH_3	CH	C_3 and C_5 pyridine	Ph	C_4 pyridine	C_2 and C_6 pyridine	CONH	C=O
4a	3,5-$(CH_3)_2$	20.7	52.9, 58.4	122.9	124.9, 128.5, 128.8, 129.0, 132.7, 134.1, 135.5, 136.2, 137.4	149.1	149.6	166.3	193.6
4b	H	—	52.9, 58.5	122.8	127.1, 128.3, 128.5, 128.6, 129.0, 131.5, 133.9, 134.1, 135.4, 136.1	148.9	149.5	165.9	193.4 193.7
4c	2-CH_3	19.0	52.6, 58.7	122.8	125.5, 128.5, 128.7, 129.0, 129.5, 130.5, 134.1, 135.5, 136.1, 136.5	149.0	149.6	168.4	193.3 193.7
4d	4-OCH_3	55.4	52.9, 58.6	122.9	113.6, 126.1, 128.7, 129.1, 134.1, 134.2, 135.5, 136.1, 161.9	149.2	149.6	165.4	193.5 193.7
4e	4-NO_2	—	53.1, 58.5	123.5	122.9, 128.5, 128.7, 129.0, 134.1, 135.4, 136.0, 139.5, 139.6	148.5	149.2	164.4	193.4 193.7
4f	4-Cl	—	53.0, 58.5	122.9	128.4, 128.7, 129.0, 129.1, 132.6, 134.1, 135.5, 136.1, 136.5	148.8	149.6	165.0	193.4 193.7

Table IV

4-[(Benzoylamino)(4-pyridyl)]methyl-3,5-diphenylpyrazoles **5**

Compound	R	X	Yield %	Mp [a]	Formula	Analyses, % Calcd./Found C	H	N
5a	3,5-$(CH_3)_2$	H	60	220-221° [b]	$C_{30}H_{26}N_4O$	78.57 78.82	5.71 5.74	12.21 11.98
5a'	3,5-$(CH_3)_2$	C_6H_5	87	162-163°	$C_{30}H_{30}N_4O$	80.87 80.61	5.65 5.63	10.48 10.36
5c	2-CH_3	CH_3	83	138-139°	$C_{30}H_{26}N_4O$	78.57 78.31	5.71 5.77	12.22 12.13
5c'	2-CH_3	C_6H_5	77	204-205°	$C_{35}H_{28}N_4O$	80.74 80.59	5.42 5.40	10.76 10.77
5f	4-Cl	C_6H_5	78	183-184°	$C_{34}H_{25}ClN_4O$	75.47 75.36	4.65 4.63	10.35 10.23

[a] From ethanol-water. [b] From benzene.

Table V

IR [a] and ^{1}H NMR [b] Spectral Data for Compounds **5**

Compound	R	X	IR, cm^{-1} ν NH	ν CO	^{1}H NMR, δ
5a	3,5-$(CH_3)_2$	H	2800-3300	1640	2.2 (s, 6H, $2CH_3$), 6.5-7.4 (m, 18H, CH, 13H-Ph, H_3, H_5-Py, 2NH), 8.2 (d, 2H, H_2, H_6-Py)
5a'	3,5-$(CH_3)_2$	C_6H_5	3300	1660	2.3 (s, 6H, $2CH_3$), 6.7-7.6 (m, 22H, CH, 18H-Ph, H_3, H_5-Py, NH), 8.5 (d, 2H, H_2, H_6-Py)
5c	2-CH_3	CH_3	3300	1660	2.2 (s, 3H, CH_3), 3.7 (s, 3H, CH_3N), 6.3-7.5 (m, 18H, CH, 14H-Ph, H_3, H_5-Py, NH), 8.1 (d, 2H, H_2, H_6-Py)
5c'	2-CH_3	C_6H_5	3300	1660	2.2 (s, 3H, CH_3), 6.2-7.4 (m, 23H, CH, 19H-Ph, H_3, H_5-Py, NH), 8.2 (d, 2H, H_2, H_6-Py)
5f	4-Cl	C_6H_5	3200	1660	6.4-7.4 (m, 23H, CH, 19H-Ph, H_3, H_5-Py, NH), 8.3 (d, 2H, H_2, H_6-Py)

[a] Potassium Bromide. [b] Deuteriochloroform.

Table VI

^{13}C NMR of **5** (DMSO-d_6, δ)

Compound	R	X	CH_3	CH	C_4 pyrazole	C_3 and C_5 pyridine	Ph	C_4 pyridine	C_2 and C_6 pyridine	C_3 and C_5 pyrazole	CONH
5a [b]	3,5-$(CH_3)_2$	H	20.9	48.8	113.9	122.2	122.5, 128.4, 128.6, 132.9, 133.9, 137.5	148.9	150.0	151.1	166.6
5a'	3,5-$(CH_3)_2$	C_6H_5	20.8	47.2	117.4	121.4	124.1, 124.5, 127.0, 128.3, 128.5, 128.6, 128.8, 128.9, 129.3, 129.7, 132.9, 133.1, 137.9, 139.1, 141.7	150.7	149.7	151.4	166.1
5c	2-CH_3	CH_3	19.4 36.6	47.5	115.3	121.0	125.0, 126.0, 127.8, 128.2, 128.4, 128.8, 129.2, 129.6, 130.6, 132.7, 134.7, 135.9, 142.6	148.8	148.8	150.5	168.3
5c'	2-CH_3	C_6H_5	19.7	47.4	117.3	121.3	124.5, 125.3, 126.2, 127.0, 128.3, 128.5, 128.6, 128.9, 129.2, 129.3, 129.7, 130.0, 131.0, 132.8, 134.6, 136.5, 139.2, 142.1	150.8	149.6	150.9	168.4
5f	4-Cl	C_6H_5	—	47.5	117.0	121.4	124.9, 127.0, 127.8, 128.3, 128.6, 128.7, 128.9, 129.3, 129.6, 131.4, 132.9, 137.6, 139.0, 141.7	150.6	149.6	150.8	164.7

[b] Deuteriochloroform.

We have previously shown [7-11] that the *N*-[(α-acetoxy)-4-pyridylmethyl)-3,5-dimethylbenzamide **3a** is the intermediate in the reaction of the *N*-oxide **2a** with hydrogen acidic compounds. So, in order to get **4a-f** in better yield, we have carried out the reaction of **3a-f** with 1,3-diphenyl-1,3-propanedione in the presence of triethylamine using chloroform as a solvent. This procedure afforded **4a-f** in high yield (method B) (Tables I-III).

The starting *N*-[(α-acetoxy)-4-pyridylmethyl]benzamides **3a-f** were obtained by the direct reaction of the corresponding *N*-oxides **2a-f** with acetic anhydride at 100° [4].

Finally, owing to our interest in the synthesis of heterocyclic systems related to Picobenzide, we have carried out the reaction of **4** with nucleophiles as hydrazine, methyl and phenylhydrazine. These reactions lead to the formation of the corresponding pyrazoles **5**. The synthetic results and various spectral data are summarized in Tables IV-VI.

EXPERIMENTAL

Melting points were determined on a Büchi 510D apparatus in open capillaries and are uncorrected. The ir spectra were measured on a Perkin-Elmer 781 spectrophotometer. The ^{1}H nmr spectra were recorded on a Varian T-60A spectrometer using TMS as an internal standard. The

^{13}C nmr spectra were obtained on a Varian FT-80A spectrometer. Mass spectrometry was performed with a Varian MAT-711 apparatus. Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas, Madrid..

N-(4-Pyridylmethyl)benzamides **1a-f** [14] and *N*-(4-pyridylmethyl)-benzamides *N*-oxides **2a-f** [5] were obtained according to literature methods.

General Procedure for *N*-[(α-Acetoxy)-4-pyridylmethyl]benzamides **3a-f.**

A solution of the corresponding *N*-(4-pyridylmethyl)benzamide *N*-oxide **2a-f** (0.02 mole) in 50 ml of acetic anhydride was heated at 100° for 20 minutes. The solution was cooled to room temperature and compounds **3** were isolated by crystallization of the precipitate formed or by evaporation under reduced pressure and trituration of the residual oil with ether.

N-[(α-Acetoxy)-4-pyridylmethyl]-3,5-dimethylbenzamide **3a** [4] was prepared according to the previously reported procedure.

N-[(α-Acetoxy)-4-pyridylmethyl]benzamide (**3b**).

This compound was obtained in a yield of 40%, mp 104-105° (benzene); ir (potassium bromide): 3260 (NH), 1730 (C=O, ester), 1640 (C=O, amide); ^1H nmr (DMSO-d_6): δ 2.2 (s, 3H, $COCH_3$), 6.7 (d, 1H, CH), 7.0-8.0 (m, 7H, 5H-phenyl, H_3 and H_5-pyridine), 8.5 (d, 2H, H_2 and H_6-pyridine, J = 5 Hz), 9.6 (d, 1H, NH).

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.36. Found: C, 66.48; H, 5.16; N, 10.46.

N-[(α-Acetoxy)-4-pyridylmethyl]-2-methylbenzamide (**3c**).

This compound was obtained in a yield of 80%, mp 101-102° (ether-petroleum ether); ir (potassium bromide): 3300 (NH), 1730 (C=O, ester), 1640 (C=O, amide); ^1H nmr (deuteriochloroform): δ 2.1 (s, 3H, $COCH_3$), 2.3 (s, 3H, CH_3), 6.9-7.4 (m, 7H, CH, 4H-phenyl, H_3 and H_5-pyridine), 7.9 (d, 1H, NH), 8.2 (d, 2H, H_2 and H_6-pyridine, J = 5 Hz).

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.63; H, 5.56; N, 9.80.

N-[(α-Acetoxy)-4-pyridylmethyl]-4-methoxybenzamide (**3d**).

This compound was obtained in a yield of 88%, mp 108-109° (benzene); ir (potassium bromide): 3260 (NH), 1730 (C=O, ester), 1650 (C=O, amide); ^1H nmr (DMSO-d_6): δ 2.1 (s, 3H, $COCH_3$), 3.7 (s, 3H, OCH_3), 6.4 (d, 1H, CH), 6.8 (d, 2H, H_3 and H_5-phenyl J = 9 Hz), 7.3 (d, 2H, H_3 and H_5-pyridine J = 5 Hz), 7.8 (d, 2H, H_2 and H_6-phenyl J = 9 Hz), 8.4 (d, 2H, H_2 and H_6-pyridine J = 5 Hz), 9.3 (d, 1H, NH).

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.90; H, 5.53; N, 9.45.

N-[(α-Acetoxy)-4-pyridylmethyl]-4-nitrobenzamide (**3e**).

This compound was obtained in a yield of 85%, mp 107-108° (ether); ir (potassium bromide): 3280 (NH), 1740 (C=O, ester), 1660 (C=O, amide); ^1H nmr (deuteriochloroform): δ 2.1 (s, 3H, $COCH_3$), 7.0-7.4 (m, 3H, CH, H_3 and H_5-pyridine), 7.6-8.1 (m, 5H, 4H-phenyl, NH), 8.2 (d, 2H, H_2 and H_6-pyridine, J = 5 Hz).

Anal. Calcd. for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.15; N, 13.32. Found: C, 57.22; H, 4.38; N, 13.48.

N-[(α-Acetoxy)-4-pyridylmethyl]-4-chlorobenzamide (**3f**).

This compound was obtained in a yield of 82%, mp 124-125° (chloroform-petroleum ether); ir (potassium bromide): 3260 (NH), 1730 (C=O, ester), 1660 (C=O, amide); ^1H nmr (DMSO-d_6): δ 2.2 (s, 3H, $COCH_3$), 7.2-7.6 (m, 5H, CH, H_3 and H_5-phenyl, H_3 and H_5-pyridine), 7.9 (d, 2H, H_2 and H_6-phenyl J = 9 Hz), 8.5 (d, 2H, H_2 and H_6-py-ridine, J = 5 Hz), 9.7 (d, 1H, NH).

Anal. Calcd. for $C_{15}H_{13}ClN_2O_3$: C, 59.12; H, 4.29; N, 9.19; Cl, 11.63. Found: C, 59.10; H, 4.08; N, 9.15; Cl, 11.49.

General Procedures for 1,1-Dibenzoyl-2-(4-pyridyl)-2-(benzoylamino)ethanes **4a-f.**

Method A.

A solution of the corresponding *N*-oxide **2a-f** (0.02 mole) and 1,3-diphenyl-1,3-propanedione (0.02 mole) in 50 ml of acetic anhydride was heated at 100° until the completion of the reaction (determined by tlc). The solvent was evaporated under reduced pressure to yield the compounds.

Method B.

To a solution of the corresponding *N*-[(α-acetoxy)-4-pyridylmethyl]-benzamide **3a-f** (0.005 mole) in 25 ml of chloroform was added 1,3-diphenyl-1,3-propanedione (0.005 mole) and 5 ml of triethylamine. The mixture was refluxed until the completion of the reaction (determined by tlc) and the solvent was evaporated under reduced pressure to yield the compounds.

Reaction of 1,1-Dibenzoyl-2-(4-pyridyl)-2-(3,5-dimethylbenzoylamino)-ethane (**4a**) and Hydrazine.

A suspension of **4a** (0.924 g, 0.0002 mole) and 80% hydrazine (0.08 g, 0.002 mole) in 30 ml of ethanol was refluxed until the completion of the reaction (determined by tlc). After being cooled, the precipitate was filtered off and crystallized to give 4-[(3,5-dimethylbenzoylamino)(4-pyridyl)]methyl-3,5-diphenylpyrazole **5a**; ms: m/z (relative intensity %) 458 (M^+, 85), 380 (M^+-C_5H_4N, 22), 325 (M^+-$C_9H_9O^+$, 77), 133 ($C_9H_9O^+$, 100), 105 ($C_6H_9^+$, 44).

Reaction of 1,1-Dibenzoyl-2-(4-pyridyl)-2-(benzoylamino)ethanes **4a,c,f** with Methyl and Phenylhydrazine.

To a suspension of **4** (0.004 mole) in 40 ml of ethanol was added 98% methyl or phenylhydrazine (4 ml) and acetic acid (4 ml). The mixture was refluxed until the completion of the reaction (determined by tlc), and then basified with 10% sodium hydroxide to give **5**.

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