Preparation of *N*-Benzoylamines by Photodecarboxylation of *N*-Benzoyl-α-amino Acids[1]

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Reactions leading to the cleavage of carbon-carbon bonds are often of preparative importance, although generally less than that of those leading to the formation of such bonds. In the majority of cases, the thermal cleavage of carbon-carbon bonds involves the decarboxylation of carboxylic acids having certain structural requirements[2]. For example, *p*-methylaminophenol is industrially prepared by decarboxylation of *N*-substituted glycines[3].

During the course of photochemical studies on imides[4], we have observed that *N*-phthaloyl-α-amino acids undergo facile decarboxylation on exposure to ultraviolet irradiation[5]. In an extension of this work, we now report that *N*-benzoyl-α-amino acids are better substrates for such photolysis, and this process can be used for an easy synthesis of *N*-benzoylamines.

Results of the photolysis of a series of *N*-benzoyl-α-amino acids **1** are summarized in the Table. Corresponding *N*-ben-

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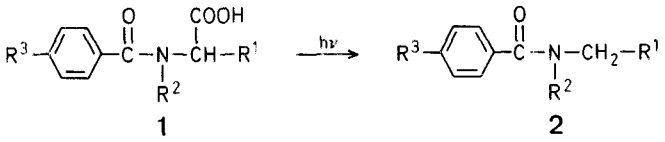
zoylamines **2** were prepared mostly in moderate yields. With tryptophan and tyramine derivatives, the yields were low, but still better than those obtained with the phthaloyl counterparts[5].



1 **2**

α-Amino carboxylic acids sometimes give the next lower amine when heated at high temperature (200–250 °C)[6], but this reaction is of no general preparative use. The present method provides perhaps one of the rare examples of a photodecarboxylation reaction employed for a preparative purpose. Amines with another functional group can be prepared **(2f, 2g, 2i, 2j)**. Although nitrobenzoyl derivatives are ineffective, the *p*-methoxybenzoyl derivative gave a good result, suggestive of some electron-transfer mechanism. Variation in the acyl groups could extend the scope of this reaction.

All melting points were determined with a Yanagimoto capillary melting point apparatus (Model MP-1) and are uncorrected. I.R. spectra were recorded on a Hitachi IR-215 spectrophotometer. ^{1}H-N.M.R. spectra were determined on a JEOL Model ME60 instrument with tetramethylsilane as internal standard. Mass spectra were measured on a Hitachi RMS-4 mass spectrometer.

N-Methylbenzamide (2a); Typical Procedure:

A solution of *N*-benzoylglycine (**1a**; 1.22 g, 6.8 mmol) in acetone (300 ml) is irradiated with a 400 W high pressure mercury lamp at room temperature for 3 h in an atmosphere of argon. After removal of the solvent under reduced pressure, the residual oil is subjected to silica gel preparative thin-layer chromatography (chloroform) to give **2a** as colorless prisms from benzene/petroleum ether; yield: 910 mg (99%); m.p. 75–76 °C (Ref.[8], m.p. 78–79 °C). This compound was identical with an authentic sample on mixture m.p. test and spectral comparison.

N-(3-Methylbutyl)-benzamide (2c):

The title compound is prepared from *N*-benzoyl-L-leucine (**1c**) in essentially the same manner as described above; yield: 815 mg (81%); b.p. 144–145 °C/1.0 torr.

$C_{12}H_{17}NO$	calc.	C 75.35	H 8.96	N 7.32
(191.2)	found	75.55	8.99	7.48

I.R. (neat): ν = 3300, 1627, 1600, 1574, 1540 cm^{-1}.

M.S.: m/e = 191 (M^+).

^{1}H-N.M.R. ($CDCl_3$): δ = 0.84 (s, 3H); 0.98 (s, 3H); 1.2–1.9 (m, 3H); 3.2–3.65 (m, 2H); 6.50–7.20 (broad, 1H); 7.25–7.6 (m, 3H); 7.7–8.05 ppm (m, 2H).

N-[3-(Methylthio)-propyl]benzamide (2g):

A solution of *N*-benzoyl-DL-methionine (**1g**) in acetone is irradiated in a manner similar to that described for **2a**. The desired compound is obtained as a pale yellow oil; yield: 441 mg (42%); b.p. 184–185 °C/1.0 torr.

$C_{11}H_{15}NOS$	calc.	C 63.14	H 7.23	N 6.69	S 15.29
(209.2)	found	63.39	7.28	6.88	15.17

I.R. (neat): ν = 3340, 1630, 1602, 1578, 1535 cm^{-1}.

M.S.: m/e = 209 (M^+).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.6–2.15 (m, 2H); 2.00 (s, 3H); 2.50 (t-like, J = 6 Hz, 2H); 3.47 (q-like, J = 6 Hz, 2H); 7.0–7.3 (m, 1H); 7.3–7.5 (m, 3H); 7.6–7.9 ppm (m, 2H).

N-Benzoyltyramine (2i):

A solution of *N*-benzoyl-L-tyrosine (**1i**) in acetone is treated in a manner similar to that described above. The crude product is recrystallized from ethanol as colorless needles; yield: 332 mg (33%); m.p. 159–160 °C.

$C_{15}H_{15}NO_2$	calc.	C 74.66	H 6.27	N 5.81
(241.3)	found	74.80	6.23	5.99

I.R. (nujol): ν = 3310, 1628, 1601, 1574, 1540 cm^{-1}.

M.S.: m/e = 241 (M^+).

^{1}H-N.M.R. ($CDCl_3$/DMSO-d_6): δ = 2.80 (t, J = 6.5 Hz, 2H); 3.4–3.75 (m, 2H); 6.75, 7.02 (q, AB type, J = 9.0, 4 Hz); 7.3–7.5 (m, 3H); 7.65–7.8 (m, 2H); 8.4–8.7 ppm (m, 1H).

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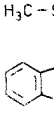
Table. Preparation of *N*-Benzoylamines **2** by Photodecarboxylation of Benzoyl-α-amino Acids **1**

Compound No.	R^1	R^2	R^3	Amount of **1** used [g (mmol)]	Solvent (300 ml)	Concentration (millimolar)	Time [h]	Yield[a] [%]	m.p. [°C] or b.p. [°C]/torr found	reported[b]
a	H	H	H	1.22 (6.8)	acetone	22.7	3	99	75–76°	78–79°[8]
				1.35 (7.5)	acetonitrile	25.0	3	94		
				1.22 (6.8)	*t*-butanol	22.7	3	84		
b		H	H	1.24 (4.6)	acetone	15.3	3	80	113–114°	114–115°[9]
c		H	H	1.24 (5.3)	acetone	17.7	3	82	144–145°/1.0	—
d	H	H_3C	H	1.36 (5.9)	acetone	19.7	3	62	190–191°/12	40–41°[10]
e			H	1.21 (5.5)	acetone	18.3	3	23	46–47°	46–47°[11]
f	$HOOC-CH_2-$	H	H	1.40 (5.9)	acetone	19.7	3	80	117–118°	118–120°[12]
g	$H_3C-S-(CH_2)_2-$	H	H	1.27 (5.0)	acetone	16.7	1.5	42	184–185°/1.0	—
h		H	H	1.04 (3.4)	acetone	11.3	3	16	135–137°	141–142°[13]
i		H	H	1.20 (4.2)	acetone	14.0	3	33	159–160°	—
j		H	H	1.40 (4.0)	acetone	13.3	3	81	130–131°	130–131°[14]
k	H	H	H_3CO	1.19 (5.7)	acetone	19.0	3	91	114–115.5°	119.5–120°[15]

[a] Yield of pure isolated product.

[b] The I.R. and N.M.R. spectra were identical with those of authentic samples[8–15].

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