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A Facile Synthesis of some Alkyl Esters of N-Benzyl-N-Phenyl-β-Alanine

Jolanta Sokołowska-Gajda

Institute of Dyes, Technical University, 90-924 Łódź, Poland

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ABSTRACT

The synthesis of some alkyl esters of N-benzyl-N-phenyl-β-alanine, useful as coupling components in disperse azo dyes, is reported. The structure of the compounds was confirmed by IR and ^{1}*H-NMR.*

1 INTRODUCTION

The use as coupling components of derivatives of alkyl esters of acrylic acid in the synthesis of disperse azo dyes results in the formation of dyes having good fastness properties on polyester.[1–3]

In a previous paper[4] we have described the synthesis of some alkyl esters of N-benzyl-N-phenyl-β-alanine by alkylation of aromatic amines with benzyl chloride and subsequent condensation with acrylates. Herein is reported a synthesis of some analogues of the above coupling components, and which contain in the benzyl residue substituents such as NO_2, CH_3 and OCH_3, viz. compounds **I** and **II**.

2 RESULTS AND DISCUSSION

The amines **I** and **II** were prepared via a three-stage reaction as outlined in Scheme 1.

In the first stage, the appropriate arylamine and substituted benzaldehyde (e.g. *m*-nitrobenzaldehyde, *p*-anisaldehyde, *p*-toluylaldehyde) were refluxed

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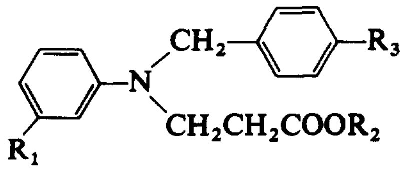
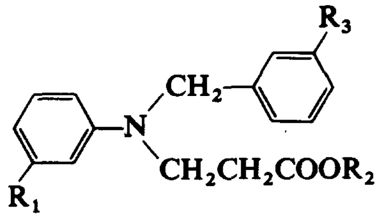


I



II

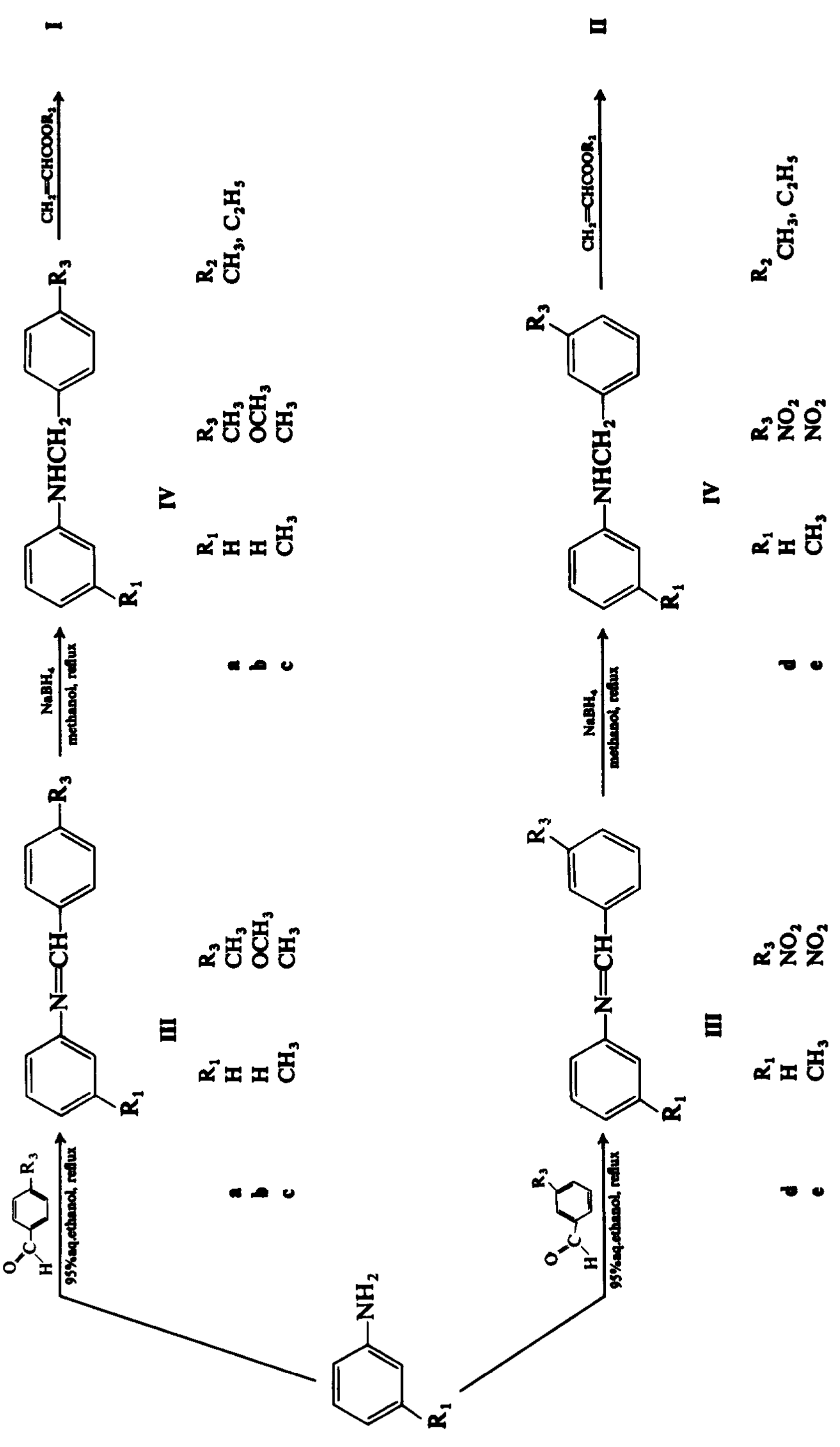
	R_1	R_2	R_3
a	H	CH_3	CH_3
b	H	C_2H_5	CH_3
c	H	CH_3	OCH_3
d	H	C_2H_5	OCH_3
e	CH_3	CH_3	CH_3
f	CH_3	C_2H_5	CH_3

	R_1	R_2	R_3
a	H	CH_3	NO_2
b	H	C_2H_5	NO_2
c	CH_3	CH_3	NO_2
d	CH_3	C_2H_5	NO_2

in 95% aq. ethanol to give the benzylidene anilines[5] **III** (85–90% yield). The crude **III** thus obtained were then converted to the N-benzylanilines **IV** in 85–90% yield by reduction with sodium borohydride[6] in boiling methanol. The final stage involved the addition of **IV** to α,β-unsaturated carbonyl compounds in the presence of an acidic catalyst.[7] This reaction was carried out by refluxing the amines **IV** with a 50% molar excess of methyl acrylate or ethyl acrylate in the presence of acetic acid and hydroquinone. The presence of hydroquinone is very important, since, in its absence, polymeric by-products are formed, resulting in a significant decrease in yield of the required products.

TABLE 1
Physical Constants, Yield and Elemental Analysis Data of Amines I and II

Amine	*Yield (%)*	*B.p. (°C/mm Hg)*	*M.p. (°C) or n_D^{20}*	*Elemental analysis (%)*					
				C		*H*		*N*	
				Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
Ia	52	180–184/0·5	41–43	76·30	76·20	7·41	7·20	4·94	4·90
Ib	52	188–192/2	1·5465	76·73	76·40	7·79	7·52	4·71	4·45
Ic	49	188–193/0·4	71–72	72·21	72·01	7·07	6·85	4·67	4·30
Id	51	204–208/2	32–33	72·81	72·69	7·39	7·14	4·46	4·27
Ie	50	192–195/2	1·5692	76·73	76·44	7·79	7·54	4·71	4·38
If	52	193–196/2	1·5609	77·13	77·02	8·09	7·92	4·49	4·58
IIa	42	200–205/0·4	90	64·95	65·04	5·77	5·98	8·91	9·15
IIb	44	214–220/0·3	67–69	65·83	66·05	6·13	6·27	8·53	8·90
IIc	43	218–220/1	67–68	65·83	66·12	6·13	6·45	8·53	8·75
IId	39	234–237/1	52–53	66·64	66·52	6·47	6·13	8·18	8·00


NH$_2$
R$_1$
95%aq.ethanol, reflux
O
H
C
R$_3$
N=CH
III
R$_1$ H H CH$_3$
R$_3$ CH$_3$ OCH$_3$ CH$_3$
a b c
NaBH$_4$
methanol, reflux
NHCH$_2$
IV
R$_1$ H H CH$_3$
R$_3$ CH$_3$ OCH$_3$ CH$_3$
a b c
CH$_2$=CHCOOR$_2$
I
R$_2$ CH$_3$, C$_2$H$_5$
d e
R$_1$ H CH$_3$
R$_3$ NO$_2$ NO$_2$
II
R$_2$ CH$_3$, C$_2$H$_5$

Scheme 1

TABLE 2

^{1}H-NMR Spectral Assignments of Amines **I** and **II**[a]

Amine	*^1H-NMR [CCl_4, $TMS_{int.}$ δ (ppm), J (Hz)]*
Ia	2·23s (3H, Ph-$\underline{CH_3}$), 2·48t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·51s (3H, —$COO\underline{CH_3}$), 3·63t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 4·40bs (2H, —$Ph\underline{CH_2}$), 6·32–7·21m (9H, arom.)
Ib	1·11t (3H, —$COOCH_2\underline{CH_3}$), *J* = 7·0), 2·23s (3H, Ph-$\underline{CH_3}$), 2·45t (2H, —$CH_2\underline{CH_2}COOCH_2CH_3$, *J* = 7·0), 3·63t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 3·98q (2H, —$COO\underline{CH_2}CH_3$, *J* = 7·0), 4·41bs (2H, —$Ph\underline{CH_2}$), 6·38–7, 11m (9H, arom.)
Ic	2, 48t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·55s (3H, —$COO\underline{CH_3}$), 3·65t (2H, —$N\underline{CH_2}CH_2$, partly overlapped), 3·70s (2H, Ph —$O\underline{CH_3}$), 4·41bs (2H, —$Ph\underline{CH_2}$), 6·42–7·25m (9H, arom.)
Id	1·10t (3H, —$COOCH_2\underline{CH_3}$, *J* = 7·0), 2·44t (2H, —$CH_2\underline{CH_2}COOCH_2CH_3$, *J* = 7·0), 3·63s (3H, $O\underline{CH_3}$), 3·63t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0, partly overlapped), 3·96q (2H, —$COO\underline{CH_2}CH_3$, *J* = 7·0), 4·36bs (2H, —$Ph\underline{CH_2}$), 6·32–7·32m (9H, arom.)
Ie	2·18s (3H, Ph-$\underline{CH_3}$), 2·23s (3H, Ph-$\underline{CH_3}$), 2·48t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·48s (3H, —$COO\underline{CH_3}$), 3·60t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 4·38bs (2H, —$Ph\underline{CH_2}$), 6·18–7·18m (8H, arom.)
If	1·13t (3H, —$COOCH_2\underline{CH_3}$, *J* = 7·0), 2·15s (3H, Ph—$\underline{CH_3}$), 2·21s (3H, Ph-$\underline{CH_3}$), 2·45t (2H, —$CH_2\underline{CH_2}COOCH_2CH_3$, *J* = 7·0), 3·60t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 3·95q (2H, —$COO\underline{CH_2}CH_3$, *J* = 7·0), 4·37bs (2H, —$Ph\underline{CH_2}$), 6·13–7·13m (8H, arom.)
IIa	2·56t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·58s (3H, –$COO\underline{CH_3}$), 3·72t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 4·61bs (2H, —$Ph\underline{CH_2}$), 6·35–8·20m (9H, arom.)
IIb	1·15t (3H, —$COOCH_2\underline{CH_3}$, *J* = 7·0), 2·55t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·73t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 4·04q (2H, —$COO\underline{CH_2}CH_3$, *J* = 7·0), 4·60bs (2H, —$Ph\underline{CH_2}$), 6·38–8·25m (9H, arom.)
IIc	2·19s (3H, Ph—$\underline{CH_3}$), 2·55t (2H, —$CH_2\underline{CH_2}COOCH_3$, *J* = 7·0), 3·55s (3H, —$COO\underline{CH_3}$, *J* = 7·0), 3·69t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 4·56bs (2H, —$Ph\underline{CH_2}$), 6·25–8·25m (8H, arom.)
IId	1·18t (3H, —$COOCH_2\underline{CH_3}$, *J* = 7·0), 2·22s (3H, Ph—$\underline{CH_3}$), 2·55t (2H, —$CH_2\underline{CH_2}COOCH_2CH_3$, *J* = 7·0), 3·70t (2H, —$N\underline{CH_2}CH_2$, *J* = 7·0), 3·90q (2H, —$COO\underline{CH_2}CH_3$, *J* = 7·0), 4·60bs (2H, —$Ph\underline{CH_2}$), 6·15–8·25m (8H, arom.)

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[a] Abbreviations: s, singlet; t, triplet; q, quartet; m, multiplet; b, broad.

Analytically pure **I** and **II** were isolated in 39–52% yields by vacuum distillation. Furthermore, it was observed that the yield in the reaction with methyl or ethyl acrylate depended on the structure of the secondary amines **IV**. The yield was considerably lower when the benzyl residue was substituted by a NO_2 group. This may be related to the electron-attracting character of the nitrobenzyl group, which decreases the nucleophilic character of **IV** in the reaction.

Characterisation data for compounds **I** and **II** are given in Table 1.

The structure of compounds **I** and **II** was established by IR and ^{1}H-NMR. The IR spectra of the amines showed absorption bands at 3040–3030 cm^{-1} and at 900–700 cm^{-1}, corresponding to ν_{CH} stretching and δ_{CH} bending vibrations in the aromatic ring respectively. A strong band in the region 1740–1730 cm^{-1} corresponded to $\nu_{C=O}$ stretching vibrations of the carbonyl group and a band in the region 1190–1180 cm^{-1} to ν_{C-O} stretching vibrations, confirming the presence of the ester group. Alkyl stretching ν_{CH} at 2990–2980 cm^{-1} and ν_{NO_2} at 1530–1520 cm^{-1} were also observed. ^{1}H-NMR data for **I** and **II** (Table 2) also supported the structures.

3 EXPERIMENTAL

IR spectra were recorded (liquid films or KBr pellets) on a Specord 71 IR spectrometer (Zeiss, Jena). ^{1}H-NMR spectra were measured at 80 MHz on a Tesla BS 487c spectrometer (in CCl_4 solutions) using TMS as internal standard.

3.1 Synthesis of the methyl ester of N-(*m*-nitrobenzyl)-N-(phenyl)-β-alanine IIa

A solution of *m*-nitrobenzaldehyde (7·5 g, 0·05 M) and aniline (4·6 g, 0·05 M) in 95% aq. ethanol (20 ml) was refluxed for 20 min. Water (15 ml) was then added and the oil which separated was left to solidify. The precipitate was filtered and washed with ethanol, giving N-(*m*-nitrobenzylidene)aniline **IIId** (10 g, 88%), m.p. = 65°C (lit.[8] m.p. = 66°C).

A solution of N-(*m*-nitrobenzylidene)aniline **IIId** (10 g, 0·044 M) in methanol (100 ml) was heated to 40°C. At this temperature sodium borohydride (1·7 g, 0·044 M) was added portionwise over 30 min. The solution was then refluxed for 15 min, water (15 ml) added, and the mixture cooled to room temperature. The precipitate was filtered and washed with water, giving N-(*m*-nitrobenzyl)aniline **IVd** (9 g, yield 90%), m.p. = 84–85°C (lit.[9] m.p. = 84·5–85·0°C).

N-(*m*-nitrobenzyl)aniline **IVd** (5·7 g, 0·025 M) was refluxed with freshly distilled methyl acrylate (3·38 ml, 0·0375M) in the presence of acetic acid (1 ml) and hydroquinone (0·05 g) for 20 h. The mixture was distilled under reduced pressure at 200–205°C/0·4 mm Hg to give N-benzyl-N-(*m*-nitrophenyl)-β-alanine **IIa** (3·31 g, yield 42%). The crude product was recrystallised from ethanol to give a product of m.p. = 89–90°C.

Other compounds were synthesised in a similar manner.

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