Dyes and Pigments 7 (1986) 161–169

Synthesis and Properties of Some Alkyl Esters of *N*-Benzyl-*N*-phenyl-β-alanine and *N*-(β-Phenylethyl)-*N*-phenyl-β-alanine

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(Received: 1 August, 1985)

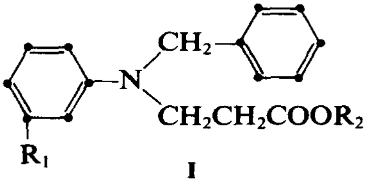
SUMMARY

The synthesis of some alkyl esters of N-benzyl-N-phenyl-β-alanine and N-(β-phenylethyl)-N-phenyl-β-alanine is described. The structure of the derivatives has been confirmed by elemental analysis and by IR and ^1H*-NMR spectroscopy.*

1. INTRODUCTION

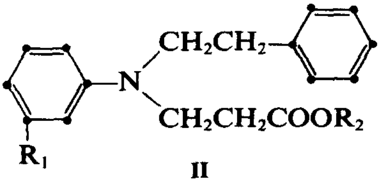
During our investigations of disperse dyes derived from 3-amino-5-nitro[2,1]benzisothiazole[1] we observed that the use as coupling components of derivatives of alkyl esters of acrylic acid resulted in the formation of dyes which had good fastness properties on polyester fibres.

In recent years a significant use in the synthesis of disperse dyes has been made of derivatives of *N*-(β-cyanoethyl)-*N*-benzylaniline[2,3] and *N*-(β-cyanoethyl)-*N*-(β-phenylethyl)aniline.[3] In respect of this, we have now prepared analogues of the above amines which contain the acrylic acid



I

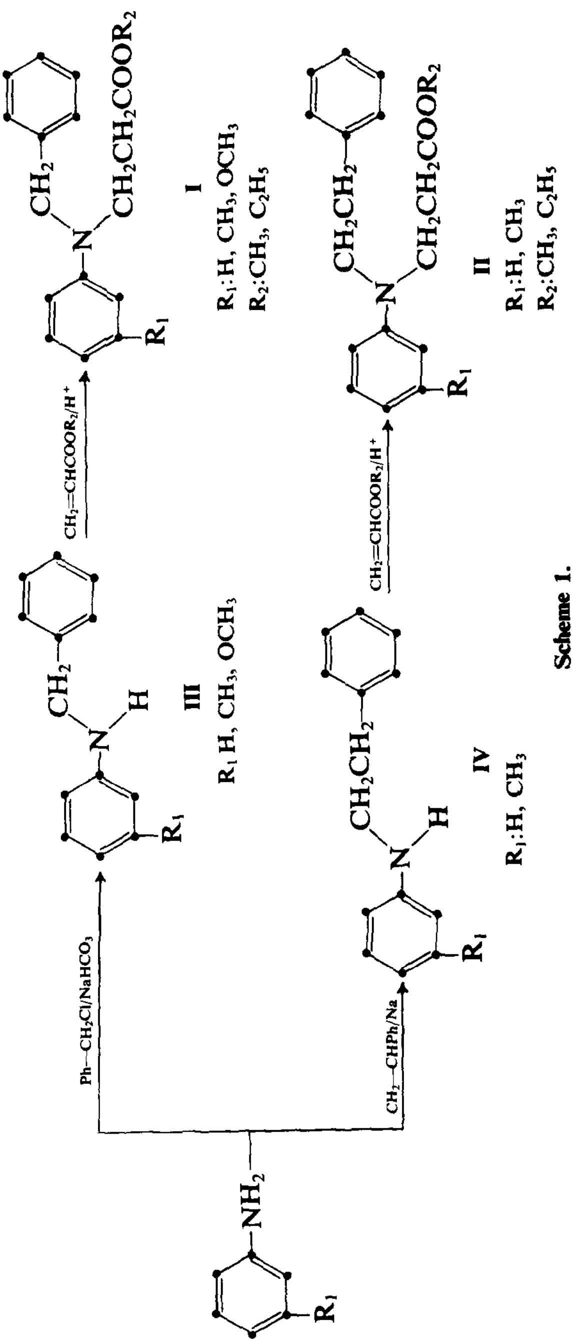
R_1:H, CH_3, OCH_3
R_2:CH_3, C_2H_5



II

R_1:H, CH_3
R_2:CH_3, CH_3, C_2H_5

Dyes and Pigments 0143-7208/86/$03·50 © Elsevier Applied Science Publishers Ltd, England, 1986. Printed in Great Britain


NH2
R1
Ph—CH2Cl/NaHCO3
CH2═CHPh/Na
CH2
N
H
III
R1 H, CH3, OCH3
CH2CH2
IV
R1:H, CH3
CH2═CHCOOR2/H+
CH2CH2COOR2
I
R1:H, CH3, OCH3
R2:CH3, C2H5
II
R1:H, CH3
R2:CH3, C2H5

Scheme 1.

ester group instead of the β-cyanoethyl moiety, and in particular the coupling components represented by formulae **I** and **II**.

2. RESULTS AND DISCUSSION

The amines **I** and **II** were prepared by the two-stage synthesis shown in Scheme 1.

The derivatives of *N*-benzylaniline **III** were prepared according to methods described in the literature,[4] i.e. by treatment of primary aromatic amines such as aniline, *m*-toluidine and *m*-anisidine with benzyl chloride in the presence of sodium bicarbonate at 90–95 °C. Analytically pure products were isolated by vacuum distillation. The second stage of the synthesis of the derivatives **I** involved the addition of amines to α,β-unsaturated carbonyl compounds in the presence of acidic catalyst.[5] This reaction was carried out by heating under reflux the secondary aromatic amine with a 50 % molar excess of methyl or ethyl acrylate in the presence of acetic acid and hydroquinone. The use of a larger excess of acrylate had no marked influence on the yield of the product. However, hydroquinone played a very important role. In its absence, we observed the formation of large amounts of polymeric by-products which caused a significant decrease in the yield of the required reaction products. Analytically pure amines **I** were isolated in 55–70 % yield by vacuum distillation.

The derivatives of *N*-(β-phenylethyl)aniline **IV** were synthesised according to the method described by Wegler and Pieper[6] involving reaction of a primary aromatic amine, e.g. aniline or *m*-toluidine, with a catalytic amount of sodium in the presence of ferrous sulphate. The products obtained in this way were treated with styrene under reflux. Analytically pure amines **IV** were isolated by vacuum distillation. Amines **II**, the derivatives of *N*-(β-phenylethyl)aniline **IV**, were prepared in the same way as described for amines **I** with 55–60 % yield.

The physical constants, yields and elemental analysis data of compounds **I** and **II** are summarised in Table 1.

The chemical structure of compounds **I** and **II** was established by IR and ^{1}H-NMR spectroscopy.

The IR spectra of all amines showed two groups of absorption bands arising from their aromatic structure, the first at 3040–3030 cm^{-1} and the

TABLE 1

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

Amine	R_1	R_2	*Yield* (%)	*B.p.* (°*C/mm Hg*)	n_D^{20}	*Elemental analysis* (%)					
						C		*H*		*N*	
						Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
I	H	CH_3	70	167–172/1	1·5814	75·81	76·36	7·11	7·12	5·19	5·43
I	H	C_2H_5	70	172–178/1	1·5681	76·32	75·77	7·42	7·43	4·94	4·87
I	CH_3	CH_3	55	160–162/0·4	1·5735	76·32	76·37	7·42	7·70	4·94	5·31
I	CH_3	C_2H_5	60	190–193/2	1·5649	76·74	76·63	7·79	7·50	4·71	5·00
I	OCH_3	CH_3	65	209–210/3	1·5785	72·22	73·10	7·07	7·20	4·67	4·86
I	OCH_3	C_2H_5	65	216–218/4	1·5695	72·82	72·70	7·39	7·30	4·46	4·81
II	H	CH_3	65	165–167/0·4	1·5704	76·30	76·40	7·46	7·50	4·94	5·16
II	H	C_2H_5	56	159–164/0·3	1·5617	76·73	76·80	7·79	8·02	4·71	5·03
II	CH_3	CH_3	60	201–203/3	1·5614	76·73	76·56	7·79	7·90	4·71	4·76
II	CH_3	C_2H_5	60	172–176/0·5	1·5576	77·14	77·65	8·08	8·25	4·49	4·39

second at 900–700 cm^{-1}, due to stretching ν_{CH} and bending δ_{CH} vibrations respectively, in the aromatic ring. The strong absorption band in the range 1740–1730 cm^{-1}, which was assigned to stretching vibrations $\nu_{C=O}$ of the carbonyl group, and the band in the range 1190–1180 cm^{-1} (stretching vibration ν_{C-O}) confirmed the presence of the ester group. In the IR spectra of amines **I** and **II** the alkyl stretching bands ν_{CH} in the range 2990–2980 cm^{-1} were also observed. Infrared spectroscopy data of compounds **I** and **II** are given in Table 2.

TABLE 2

Characteristic IR Absorption Maxima of Amines I and II

Amine	R_1	R_2	ν_{CH} (cm^{-1})	ν_{CH} (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	ν_{C-O} (cm^{-1})	δ_{CH} (cm^{-1})
I	H	CH_3	3 040	2 980	1 740	1 190	900–700
I	H	C_2H_5	3 030	2 990	1 730	1 180	900–700
I	CH_3	CH_3	3 040	2 980	1 730	1 190	900–700
I	CH_3	C_2H_5	3 040	2 980	1 730	1 190	900–700
I	OCH_3	CH_3	3 030	2 980	1 740	1 180	900–700
I	OCH_3	C_2H_5	3 040	2 980	1 730	1 180	900–700
II	H	CH_3	3 030	2 980	1 730	1 190	900–700
II	H	C_2H_5	3 030	2 980	1 740	1 190	900–700
II	CH_3	CH_3	3 030	2 980	1 740	1 180	900–700
II	CH_3	C_2H_5	3 030	2 980	1 740	1 190	900–700

In the ^{1}H-NMR spectra, analysis of the chemical shifts, multiplicity and integration of the relevant groups of protons provided unambiguous arguments in support of the proposed structures. The ^{1}H-NMR data of compounds **I** and **II** are presented in Table 3.

3. EXPERIMENTAL

All reagents were purified by conventional methods.

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

TABLE 3

H-NMR Spectral Assignments of Amines **I** and **II**[a]

Amine	R_1	R_2	^{1}*H-NMR* [CCl_4, *TMS int.*, δ (*ppm*), *J* (*Hz*)]
I	H	CH_3	2·475t (2H, $J = 7{\cdot}0$, $-CH_2\underline{CH_2}COOCH_3$), 3·475s (3H, $—COO\underline{CH_3}$), 3·625t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·31bs (2H, $—Ph\underline{CH_2}$), 6·375–7·375m (10H, arom.).
I	H	C_2H_5	1·11t (3H, $J = 7{\cdot}0$, $—OCH_2\underline{CH_3}$), 2·51t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·69t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·01q (2H, $J = 7{\cdot}0$, $—COO\underline{CH_2}CH_3$), 4·47bs (2H, $—Ph\underline{CH_2}$), 6·45–7·30m (10H, arom.).
I	CH_3	CH_3	2·187s (3H, $Ph—\underline{CH_3}$), 2·5t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_3$), 3·51s (3H, $—CH_2COO\underline{CH_3}$), 3·625t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·43bs (2H, $—Ph\underline{CH_2}$), 6.175–7·375m (9H, arom.).
I	CH_3	C_2H_5	1·125t (3H, $J = 7{\cdot}0$, $—COOCH_2\underline{CH_3}$), 2·175s (3H, $Ph—\underline{CH_3}$), 2·5t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOC_2H_5$), 3·625t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 3·975q (2H, $J = 7{\cdot}0$, $—COO\underline{CH_2}CH_3$), 4·425bs (2H, $—Ph\underline{CH_2}$), 6·175–7·412m (9H, arom.).
I	OCH_3	CH_3	2·46t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_3$), 3·46s (3H, $—CH_2CH_2COO\underline{CH_3}$), 3·55s (3H, $Ph—O\underline{CH_3}$), 3·60t (2H, partly overlapped, $—N\underline{CH_2}CH_2$), 4·38bs (2H, $—Ph\underline{CH_2}$), 5·95–7·26m (9H, arom.).
I	OCH_3	C_2H_5	1·06t (3H, $J = 7.0$, $—COOCH_2\underline{CH_3}$), 2·46t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·53s (3H, $Ph—O\underline{CH_3}$), 3·54t (2H, partly overlapped, $—N\underline{CH_2}CH_2$), 3·93q (2H, $J = 7{\cdot}0$, $—CH_2COO\underline{CH_2}CH_3$), 4·38bs (2H, $—Ph\underline{CH_2}$), 6·00–7·28m (9H, arom.).

II	H	CH_3	2·38t (2H, $J = 7{\cdot}0$, $-CH_2\underline{CH_2}COOCH_3$), 2·74t (2H, $J = 7{\cdot}0$, $-Ph\underline{CH_2}CH_2$), 3·45t $\left(4H, J = 7{\cdot}0, -N{<}\begin{smallmatrix}\underline{CH_2}\\ \underline{CH_2}\end{smallmatrix}\right)$, 3·51s (3H, $-COO\underline{CH_3}$), 6·37–7·25m (10H, arom.).
II	H	C_2H_5	1·13t (3H, $J = 7{\cdot}0$, $-COOCH_2\underline{CH_3}$), 2·39t (2H, $J = 7{\cdot}0$, $-CH_2\underline{CH_2}COOCH_2CH_3$), 2·76t (2H, $J = 7{\cdot}0$, $-Ph\underline{CH_2}CH_2$), 3·47t $\left(4H, J = 7{\cdot}0, -N{<}\begin{smallmatrix}\underline{CH_2}\\ \underline{CH_2}\end{smallmatrix}\right)$, 4·00q (2H, $J = 7{\cdot}0$, $-COOCH_2CH_3$), 6·42–7·35m (10H, arom.).
II	CH_3	CH_3	2·23s (3H, $Ph-\underline{CH_3}$), 2·37t (2H, $J = 7{\cdot}0$, $-CH_2\underline{CH_2}COOCH_3$), 2·72t (2H, $J = 7{\cdot}0$, $-Ph\underline{CH_2}CH_2$), 3·45t 4H, $-N{<}\begin{smallmatrix}\underline{CH_2}\\ \underline{CH_2}\end{smallmatrix}\Big)$, 3·68s (3H, $-COO\underline{CH_3}$), 6·17–7·40m (9H, arom.).
II	CH_3	C_2H_5	1·15t (3H, $J = 7{\cdot}0$, $-COOCH_2\underline{CH_3}$), 2·25s (3H, $Ph-\underline{CH_3}$), 2·37t (2H, $J = 7{\cdot}0$, $-CH_2\underline{CH_2}COOCH_2CH_3$), 2·75t (2H, $-Ph\underline{CH_2}CH_2$), 3·47t $\left(4H, -N{<}\begin{smallmatrix}\underline{CH_2}\\ \underline{CH_2}\end{smallmatrix}\right)$, 4·00q (2H, $-COO\underline{CH_2}CH_3$), 6·20–7·35m (9H, arom.).

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

3.1. Synthesis of the methyl ester of *N*-benzyl-*N*-(*m*-methylphenyl)-β-alanine (I; $R_1 = CH_3$; $R_2 = CH_3$)

m-Toluidine (142·3 g; 1·33 mol), 35 ml water and 35 g sodium bicarbonate were heated on a steam bath to 90–95 °C and freshly distilled benzyl chloride (42 g; 0·33 mol) was then added over 1 h. Reaction was continued for a further 3 h at 95 °C. The precipitate was filtered off and from the filtrate the organic layer was separated. This was washed with saturated salt solution, dried with anhydrous magnesium sulphate and distilled under reduced pressure at 190 °C/13 mm Hg (b.p. 165–166 °C/4 mm Hg).[7] *N*-Benzyl-*m*-toluidine (III; $R_1 = CH_3$) was obtained (36 g; 54 % yield).

Calc.: C, 85·27; H, 7·61; N, 7·10 %.
Found: C, 85·30, H, 7·80; N, 7·25 %.

N-Benzyl-*m*-toluidine (19·7 g; 0·1 mol) was heated under reflux with 13·5 ml freshly distilled methyl acrylate in the presence of 4 ml acetic acid and 0·2 g hydroquinone. After reacting for 20 h, the reaction mixture was distilled under reduced pressure at 160–162 °C/0·4 mm Hg to give 15·56 g (55 %) *N*-benzyl-*N*-(*m*-methylphenyl)-β-alanine (I; $R_1 = CH_3$; $R_2 = CH_3$).

3.2. Synthesis of the methyl ester of *N*-benzyl-*N*-(*m*-methoxyphenyl)-β-alanine (I; $R_1 = OCH_3$; $R_2 = CH_3$)

N-Benzyl-*m*-anisidine (III; $R_1 = OCH_3$; b.p. 214–216 °C/13 mm Hg) and its acrylate derivatives were obtained according to the procedure described in Section 3.1 above. The structure of *N*-benzyl-*m*-anisidine was confirmed by elemental analysis.

Calc.: C, 78·87; H, 7·04; N, 6·57 %.
Found: C, 78·90; H, 7·50; N, 7·01 %.

3.3. Synthesis of the methyl ester of *N*-(β-phenylethyl)-*N*-(*m*-methylphenyl)-β-alanine

Sodium (9·0 g) was dissolved under reflux in 64·3 g (0·6 mol) freshly distilled *m*-toluidine with a small amount of ferrous sulphate. Freshly distilled styrene (52 ml, 0·45 mol) was then added slowly over 1 h and the reaction continued for a further 3 h at 198–200 °C. After cooling the mixture to 20 °C, 500 ml water was added. The organic layer was separated, dried with anhydrous magnesium sulphate and distilled under reduced pressure at 208–212 °C/215 mm Hg to give 48·4 g (50 %) of *N*-(*β*-phenylethyl)-*m*-toluidine (IV; $R_1 = CH_3$).

Calc.: C, 85·30; H, 8·05; N, 6·63 %.
Found: C, 85·12; H, 8·05; N, 6·50 %.

The methyl ester of *N*-(*β*-phenylethyl)-*N*-(*m*-methylphenyl)-*β*-alanine was prepared in the same way as the ester described in Section 3.1.

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