Stereospecific Synthesis of (*Z*/*E*)-Isomers of 2-Benzoylamino-3-phenyl-2-butenoic Acids

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The chemistry of 5-oxo-4,5-dihydro-1,3-oxazoles has been the subject of several reviews[1-7]. Recently, interest has been shown in oxazolones derived from methyl ketones[8,9]. We have previously reported[10] on the synthesis and physical characteristics of (*E*/*Z*)-isomers of 2-phenyl-4-(arylmethylmethylene)-5-oxo-4,5-dihydro-1,3-oxazoles **3**. The pure isomers were obtained by suitable isomerization procedures.

In continuation of this investigation on the reactivity of 5-oxo-4,5-dihydro-1,3-oxazoles, we now report on the synthesis and physical characteristics of (*E*/*Z*)-isomers of 2-benzoylamino-3-phenyl-2-butenoic acids (α-benzamido-β-methylcinnamic acids; **4**). These compounds were prepared by alkaline hydrolysis from the corresponding (*E*/*Z*)-isomers of 2-phenyl-4-(arylmethylmethylene)-5-oxo-4,5-dihy-

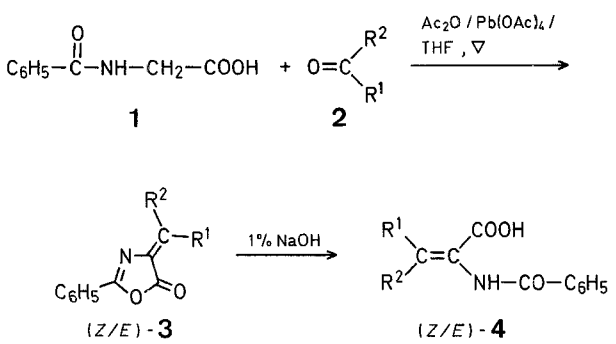

Table. 2-Benzoylamino-3-phenyl-2-butenoic Acids **4**

Product No.	R^1	R^2	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (nujol) ν [cm^{-1}] NH, C=O$_{acid}$, C=O$_{amide}$	^{1}H-N.M.R. (DMSO-d_6) δ [ppm]	U.V. (C_2H_5OH) λ_{max} [nm] (log ε)
(*Z*)-**4a**	CH_3	C_6H_5	85	198°	$C_{17}H_{15}NO_3$ (281.3)	3280, 1690, 1640	2.34 (s, 3H); 7.0–7.7 (m, 10H); 9.48 (s, 1H)	204 (4.35); 222 (4.21); 250 (4.06)
(*E*)-**4a**	C_6H_5	CH_3	86	186°	$C_{17}H_{15}NO_3$ (281.3)	3200, 1700, 1630	2.04 (s, 3H); 7.1–8.2 (m, 10H); 9.85 (s, 1H)	202 (4.45); 223 (4.18); 266 (4.11)
(*Z*)-**4b**	CH_3	4-O_2N—C_6H_4	94	208°	$C_{17}H_{14}N_2O_5$ (326.3)	3400, 1715, 1650	2.36 (s, 3H); 7.3–8.5 (m, 9H); 9.56 (s, 1H)	202 (4.48); 224 (4.25)
(*Z*)-**4c**	CH_3	3-O_2N—C_6H_4	83	195°	$C_{17}H_{14}N_2O_5$ (326.3)	3220, 1690, 1640	2.36 (s, 3H); 7.2–8.2 (m, 9H); 9.53 (s, 1H)	202 (4.45); 224 (4.31); 257 (4.23)
(*E*)-**4c**	3-O_2N—C_6H_4	CH_3	72	208°	$C_{17}H_{14}N_2O_5$ (326.3)	3260, 1695, 1635	2.08 (s, 3H); 7.3–8.2 (m, 9H); 9.95 (s, 1H)	202 (4.47); 220 (4.27); 262 (4.27)
(*Z*)-**4d**	CH_3	4-Cl—C_6H_4	87	203°	$C_{17}H_{14}ClNO_3$ (315.8)	3290, 1690, 1640	2.3 (s, 3H); 7.1–7.8 (m, 9H); 9.4 (s, 1H)	202 (4.45); 222 (4.25); 260 (4.08)
(*Z*)-**4e**	CH_3	4-H_3C—C_6H_4	82	194°	$C_{18}H_{17}NO_3$ (295.3)	3295, 1690, 1640	2.18 (s, 3H); 2.3 (s, 3H); 7.0–7.8 (m, 9H); 9.4 (s, 1H)	204 (4.35); 220 (4.22); 265 (4.06)
(*E*)-**4e**	4-H_3C—C_6H_4	CH_3	96	188°	$C_{18}H_{17}NO_3$ (295.3)	3200, 1710, 1625	2.05 (s, 3H); 2.28 (s, 3H); 7.1–8.2 (m, 9H); 9.94 (s, 1H)	202 (4.44); 220 (4.23); 272 (4.14)

[a] All compounds gave satisfactory elemental analyses (C ±0.3%, H ±0.2%, N ±0.3%).

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dro-1,3-oxazoles **3**. It should be pointed out that basic hydrolysis of the oxazoles **3** gave isomeric acids, with retention of configuration, and the yields were substantially better than those obtained under acid conditions.

Structural assignments for the products **4** have been made on the basis of the N.M.R. spectral data. The methyl group of (*Z*)-isomer gives rise to a low field signal as it is in a *cis* position with respect to the carboxylic group.

2-Benzoylamino-3-phenyl-2-butenoic Acids 4; General Procedure: A suspension of the corresponding (*Z*)- or (*E*)-2-phenyl-4-(arylmethylmethylene)-5-oxo-4,5-dihydro-1,3-oxazole[10] **3** (0.01 mol) in 1% sodium hydroxide solution (250 ml) is heated under reflux till complete dissolution occurs. The solution is then cooled to room temperature and filtered, after which 3 normal hydrochloric acid (30 ml) is added to precipitate the *N*-benzoyl derivative, which is crystallized by dissolving in 5% sodium hydroxide solution and reprecipitating with hydrochloric acid. The precipitate is filtered, washed free of acid with water, and dried. A single recrystallization from ethanol/water gives an analytically pure sample (Table).

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