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KINETICS AND MECHANISM OF THE AMINOLYSIS OF *p*-NITROPHENYL *N*-PHENYLCARBAMATES

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Kinetic studies of the reactions of *p*-nitrophenyl *N*-phenylcarbamates with benzylamines were carried out in acetonitrile at 25·0 °C. Second-order (k_2) and third-order (k_3) rate constants were observed for all the Y-substituted carbamates except for Y = *m* − Cl. The relatively large magnitude of ρ_X (for X-substituted benzylamines) and ρ_Y together with a positive cross-interaction constant ρ_{XY} supports a stepwise mechanism involving rate-limiting breakdown of the zwitterionic tetrahedral intermediate $T^{\pm}$. Kinetic isotope effect studies with deuterated benzylamine ($XC_6H_4CH_2ND_2$) indicate that in the base-catalyzed path, k_3, rate-limiting deprotonation occurs at the amino group of benzylamine within the $T^{\pm}$ intermediate. The low $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for the k_3 process are in accord with the proposed mechanism. © 1997 John Wiley & Sons, Ltd.

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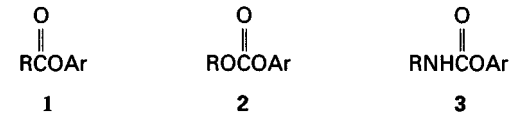
INTRODUCTION

Although the mechanism of the aminolysis of aryl esters[1] (**1**) and carbonates[2] (**2**) have been investigated extensively, reports on the aminolysis mechanism of *N*-phenylcarbamates (**3**) are scarce. These three classes of carbonyl compounds differ only in the acyl part , R, RO and RNH, where R is alkyl or aryl, with a similar phenoxy leaving group, OAr. The aminolysis mechanism of the carbamates is therefore expected to be similar to the relatively well known aminolysis mechanisms of the esters **1** and carbonates **2**. Shawali *et al.*[3] proposed a stepwise mechanism with rate-limiting breakdown of a tetrahedral intermediate, $T^{\pm}$, for the reactions of aryl *N*-arylcarbamates, R = Ar in **3**, with *n*-butylamine in dioxane. Their kinetic results were compatible with the stepwise mechanism involving two reaction pathways, an overall second-order, k_2, and an overall third-order, k_3, process (Scheme 1), which is similar to the aminolysis mechanisms proposed for some of **1** and **2**, but is in contrast to an ElcB mechanism proposed by Menger and Glass[4] for the reaction of *p*-nitrophenyl *N*-phenylcarbamate with diethylamine in toluene. In this latter mechanism, an isocyanate is formed instead of a zwitterionic tetrahedral intermediate $T^{\pm}$ (Scheme 2). We extend here our series of kinetic studies on the effects of acyl group on the mechanism of the aminolysis of carbonyl compounds to the reactions of *p*-nitrophenyl *N*-phenylcarbamates with benzylamines in acetonitrile [equation (1)].



1 **2** **3**

$$YC_6H_4NHCOOC_6H_4Z + XC_6H_4CH_2NH_2 \xrightarrow[25\cdot0\ ^{\circ}C]{MeCN} YC_6H_4NHC(=O)NHCH_2C_6H_4X + HOC_6H_4Z \quad (1)$$

X = *p* − CH_3, H, *p*-Cl or *m* − Cl
Y = *p* − CH_3, H, *p*-Cl or *m* − Cl
Z = *p* − NO_2

In this work, we apply the mechanistic criteria based on the cross-interaction constants, ρ_{ij} in equations (2), where *i* and *j* denote the substituents in the nucleophile (X), substrate (Y) and leaving group (Z).[5] The simple second-order expression

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (2a)$$

is obtained by a Taylor series expansion of log k_{ij} around $\sigma_i = \sigma_j = 0$ and neglecting pure second-order (ρ_{ii} and ρ_{jj}) and higher-order (ρ_{iij}, etc.) terms. The cross-interaction constant, ρ_{ij}, can be alternatively defined as[5]

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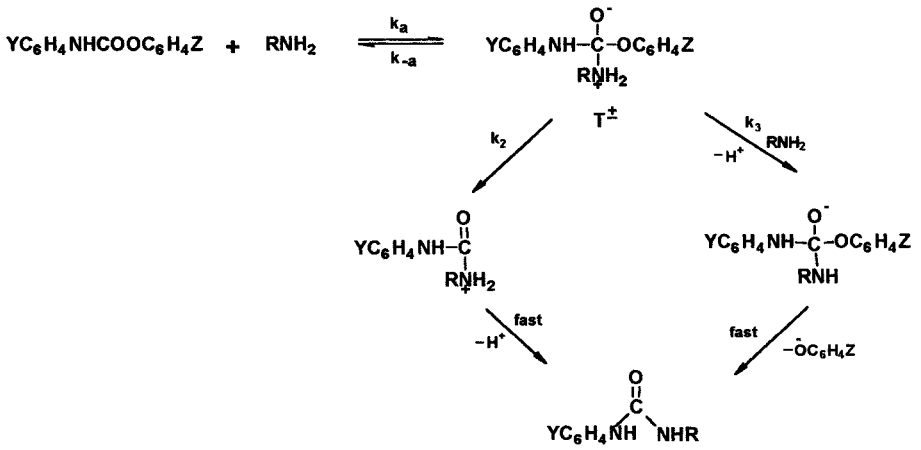


Scheme 1

$$\rho_{ij}=\frac{\partial\rho_j}{\partial\sigma_i}=\frac{\partial\rho_i}{\partial\sigma_j} \quad (2b)$$

RESULTS AND DISCUSSION

The reactions of *p*-nitrophenyl *N*-phenylcarbamates (PCB) with benzylamines (BA) in acetonitrile at 25·0 °C obey a third-order rate law:

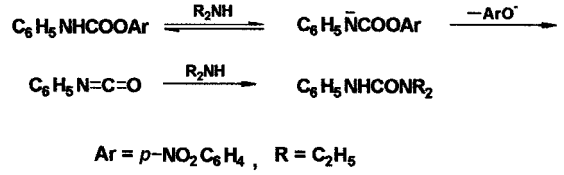
$$\text{rate}=k_{obs}[\text{PCB}] \quad (3)$$

$$k_{obs}=k_2[\text{BA}]+k_3[\text{BA}]^2 \quad (4)$$

except for Y = *m*-Cl, for which k_3=0. The second and third order-rate constants, k_2 and k_3, are obtained from a straight line plot of k_{obs}/[BA] vs [BA] (Figure 1) as the intercept and slope, respectively. For the case of Y = *m*-Cl, the slope of a plot of k_{obs} vs [BA] yielded k_2. The values of k_2 and k_3 are summarized in Tables 1 and 2. The k_3 values are in general greater than the corresponding k_2 values as noted for the similar reaction of esters[1a] (**1**), halides,[1h] carbonates[6] (**2**) and carbamates[3] (**3**).

An isocynate intermediate proposed by Menger and Glass[4] was not found in the analysis of the infrared spectrum (2275–2240 cm^{-1}). The product studies and the third-order kinetics [equation (4)] observed lead us to a likely mechanism for the present reactions as shown in Scheme 1, where Z = *p*-NO_2 and R = $XC_6H_4CH_2$. The k_3 step is deprotonation by benzylamine of the tetrahedral intermediate, $T^{\pm}$, to yield the anionic intermediate T^-. The k_3 step is the rate-determining step for the right-hand side path of Scheme 1 since breakdown of $T^{\pm}$ to products should be fast.[6] The proton transfer is fast in water but not in MeCN. As a result, the k_3 step may become competitive with k_2.[1k, l]

The Hammett (ρ_X and ρ_Y) and Brønsted (β_X) coefficients determined are given in Table 1 for the k_2 step. The exceptionally large magnitudes of these selectivity parameters are consistent with the stepwise mechanism with rate-limiting breakdown of $T^{\pm}$;[1, 2] both ρ_X and ρ_Y should be



Scheme 2

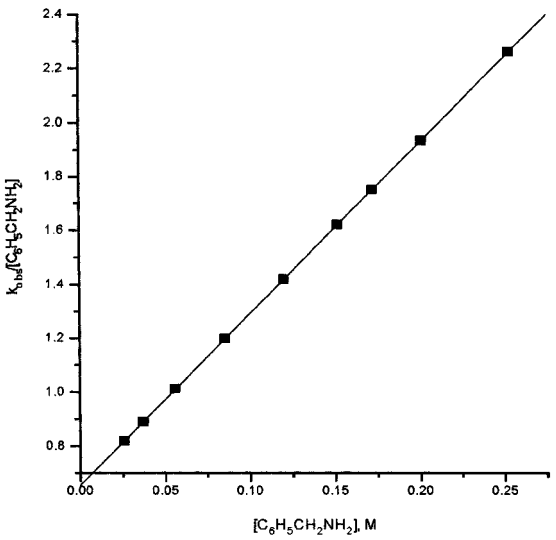


Figure 1. The plot of $k_{obs}/[C_6H_5CH_2NH_2]$ vs [benzylamine] for the reaction of *p*-nitrophenyl *N*-phenylcarbamate with benzylamine in acetonitrile at 25·0 °C

Table 1. Second-order rate constants, k_2 ($dm^3\ mol^{-1}\ s^{-1}$), for the reactions of *p*-nitrophenyl *N*-(Y)phenylcarbamates with X-benzylamines in acetonitrile at 25·0 °C

	Y			
X	*p*-CH_3	H	*p*-Cl	*m*-Cl
p-CH_3	0·403[a]			3·57[a]
	0·953	1·23	3·26	8·49
	2·28[b]			20·2[b]
H	0·528	0·655	1·89	5·81
p-Cl	0·201	0·268	0·894	3·20
m-Cl	0·0471[a]			0·962[a]
	0·112	0·161	0·458	2·29
	0·267[b]			5·45[b]
ρ_X[c]	−1·73	−1·63	−1·55	−1·06
β_X[d]	1·75	1·65	1·56	1·07

[a] At 15·0 °C.
[b] At 35·0 °C.
[c] The σ values were taken from Ref. 7. Correlation coefficients were better than 0·997 in all cases.
[d] The pK_a (H_2O, 25·0 °C) values were taken from Ref. 8. Correlation coefficients were better than 0·997 in all cases.

compared with other corresponding values after taking into account of a non-conjugating intervening group, CH_2 and NH, present in the benzylamine nucleophile and in the *N*-phenylcarbamate substrate respectively, which are known to reduce the ρ values by a factor of *ca* 2·8.[9] The large β_X values are also in line with the proposed mechanism,[1,2] but they are less reliable since the pK_a values used are those in water, not in acetonitrile. However, it is well known that although the absolute pK_a values are different in H_2O and MeCN, the $\Delta pK_a = (pK_a)_{MeCN} - (pK_a)_{H_2O}$ values for the structurally similar amines are nearly the same.[10] Thus the β_X values should be nearly the same in both H_2O and MeCN.[10c]

The 16 k_2 values in Table 1 are subjected to multiple regression using equation (2a) with *i*, *j*=X, Y. The result (correlation coefficient = 0·974):

$$\log(k_{XY}/k_{HH}) = -1{\cdot}62\sigma_X + 1{\cdot}94\sigma_Y + 1{\cdot}10\sigma_X\sigma_Y \qquad (5)$$

indicates that ρ_{XY} is positive and relatively large, which is again in line with the proposed stepwise mechanism; it has been shown both experimentally and theoretically that the sign of ρ_{XY} should be positive in contrast to the negative ρ_{XY} for the S_N2 processes.[5,11] In the bond-making step, a stronger electron acceptor substituent in the substrate ($\delta\sigma_Y > 0$) invariably leads to a tighter bond with the nucleophile in the TS ($\delta\rho_X < 0$) so that ρ_{XY} ($= \delta\rho_X/\delta\sigma_Y$) is negative.[5,11] The values of ρ_X ($-1{\cdot}62$) and ρ_Y(1·94) are in good agreement with the corresponding values in Table 1 determined independently using the simple (first-order) Hammett equation ($\rho_X = -1{\cdot}63$; $\rho_Y = 1{\cdot}92$).

For the base-catalyzed process, k_3, a similar multiple regression analysis yielded a much worse correlation, probably due to complex effects of the substituents. For example, the effects of substituent in nucleophile, X, on the rate of deprotonation is complex since the effect of the catalyst benzylamine should be opposite to that of benzylamine within $T^{\pm}$.

Kinetic deuterium isotope effects involving amine protons on the second- (k_2) and third-order (k_3) rate constants are studied incorporating deuterium isotopes (i) in the substrate amino group, $YC_6H_4NH(D)COOC_6H_4NO_2$, and (ii) in the nucleophile amino group, $XC_6H_4CH_2NH_2(D_2)$. The results are summarized in Tables 3 and 4. Reference to Table 3 reveals that the isotope effects involving substrate amine protons are small ($k_H/k_D \approx 1{\cdot}10$) for k_2 and negligible (*ca* 1·00) for k_3. The small kinetic isotope effects for k_2 probably arise from the same origin as those found for the deuterated nucleophiles in the stepwise mechanisms of the esters and carbonates; the k_H/k_D values are normally slightly greater than unity for such processes, in contrast to inverse effects ($k_H/k_D < 1{\cdot}0$) observed for the rate-limiting attack process, i.e. for S_N2 or rate-limiting formation of $T^{\pm}$.[5c] The negligible effects for k_3 suggest that the substrate amine proton is not involved in the deprotonation step, k_3. This is in contrast to the kinetic deuterium isotope effects observed with the deuterated nucleophiles in Table 4. Again for k_2, the k_H/k_D values are similar to those for the deuterated substrate amine in Table 3. However, for the k_3 step, we observe strong primary isotope effects ($k_H/k_D \approx 1{\cdot}7$–$1{\cdot}8$), which can be taken as clear evidence that in the base-catalyzed process, k_3, deprotonation takes place at the amino group of the nucleophile in the TS. This supports our proposed mechanism presented in Scheme 1 for the reactions of *p*-nitrophenyl *N*-phenylcarbamates with benzylamines in acetonitrile.

A relatively strong acceptor in the substrate (Y = *m*-Cl) seems to stabilize the TS (k_2) for the uncatalyzed pathway so that the k_2 path becomes predominant over the base-catalyzed process, k_3. This is reasonable since in the TS (k_2) negative charge develops ($\rho_Y > 0$) at the carbonyl carbon, which can be delocalized by a stronger acceptor Y.

Table 2. Third-order rate constants, k_3 ($dm^6\ mol^{-2}\ s^{-1}$), for the reactions of *p*-nitrophenyl *N*-(Y)phenylcarbamates with X-benzylamines in acetonitrile at 25·0 °C

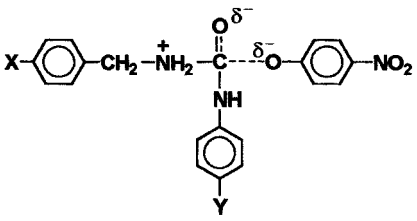
	Y		
X	*p*-CH_3	H	*p*-Cl
p-CH_3	8·59[a]		
	9·45		
	10·4[b]	10·2	32·3
H	5·61	6·37	27·5
p-Cl	1·51	2·50	7·04
m-Cl	1·14[a]		
	1·28		
	1·43[b]	1·38	4·98

[a] At 15·0 °C.
[b] At 35·0 °C.

Table 3. Kinetic isotope effects on the second- (k_2) and the third-order rate constants (k_3) for the reactions of deuterated *p*-nitrophenyl *N*-(Y)phenylcarbamates [$YC_6H_4NH(D)C(O)OC_6H_4$-*p*-NO_2] with X-benzylamines in acetonitrile at 25·0 °C

X	Y	$k_{2(H)}$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k_{2(D)}$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_H/k_D
H	H	0·655±0·002[a]	0·585±0·003	1·12±0·03[b]
H	*m*-Cl	5·80±0·03	5·60±0·02	1·04±0·02
m-Cl	H	0·161±0·004	0·460±0·004	1·10±0·05
n-Cl	*m*-Cl	2·29±0·02	2·14±0·04	1·07±0·03
X	Y	$k_{3(H)}$ ($dm^6\ mol^{-2}\ s^{-1}$)	$k_{3(D)}$ ($dm^6\ mol^{-2}\ s^{-1}$)	k_H/k_D
H	H	6·37±0·03[a]	6·34±0·06	1·01±0·04[b]
m-Cl	H	1·38±0·02	1·16±0·02	1·19±0·03

[a] Standard deviation.
[b] Standard error.



TS (k_2)

From the k_2 and k_3 values at three temperatures, we determined the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for each pathways. The results in Table 5 indicate that the $\Delta H^{\neq}$ and $-\Delta S^{\neq}$ values are relatively small for the k_2 processes, but the $\Delta H^{\neq}$ values are very small and the $-\Delta S^{\neq}$ values are fairly large for the k_3 processes. These are in good accord with the trends found for the corresponding activation parameters for the uncatalyzed and catalyzed stepwise breakdown processes of the tetrahedral intermediate, $T^{\pm}$, in the aminolysis of the esters, halides and carbonates.[1e,h, 3, 13]

We conclude that the aminolysis of *p*-nitrophenyl *N*-phenylcarbamates in acetonitrile proceeds by a stepwise mechanism with rate-limiting breakdown of the zwitterionic tetrahedral intermediate, $T^{\pm}$. The breakdown step can be either base-catalyzed (k_3) or uncatalyzed (k_2).

EXPERIMENTAL

Materials. The solvent, acetonitrile, was of HPLC grade (Aldrich), and was further distilled over phosphorus pentoxide. The benzylamine nucleophiles, of GR grade (Aldrich), were used without further purification. Preparations of deuterated benzylamines were as described previously.[14] The analysis (NMR and GC–mass spectrometry) of the deuterated benzylamines showed more than a 99% deuterium content, so no corrections to kinetic effects for incomplete deuterium content were made.[15]

Table 4. Kinetic isotope effects on the second- (k_2) and the third-order rate constants (k_3) for the reactions of *p*-nitrophenyl *N*-(Y)phenylcarbamates with deuterated X-benzylamines [$XC_6H_4CH_2NH_2(D_2)$] in acetonitrile at 25·0 °C

X	Y	$k_{2(H)}$ ($dm^3\ mol^{-1}$)	$k_{2(D)}$ ($dm^3\ mol^{-1}$)	k_H/k_D
p-CH_3	*p*-CH_3	0·958±0·007[a]	0·855±0·008	1·12±0·01[b]
p-CH_3	*m*-Cl	8·49±0·06	7·19±0·05	1·18±0·02
m-Cl	*p*-CH_3	0·112±0·004	0·102±0·004	1·10±0·05
m-Cl	*m*-Cl	2·29±0·02	2·01±0·04	1·14±0·04
X	Y	$k_{3(H)}$ ($dm^6\ mol^{-2}\ s^{-1}$)	$k_{3(D)}$ ($dm^6\ mol^{-2}\ s^{-1}$)	k_H/k_D
p-CH_3	*p*-CH_3	9·45±0·06[a]	5·59±0·06	1·69±0·03[b]
p-CH_3	*p*-Cl	32·3±0·8	19·9±0·6	1·62±0·04
m-Cl	*p*-CH_3	1·28±0·04[a]	0·703±0·007	1·82±0·04
m-Cl	*p*-Cl	4·98±0·08	2·80±0·06	1·78±0·03

[a] Standard deviation.
[b] Standard error.

Table 5. Activation parameters[a] for the reactions of *p*-nitrophenyl *(N*-(Y)phenylcarbamates with X-benzylamines in acetonitrile

X	Y	Reaction	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
p-CH_3	*p*-CH_3	k_2	14·3	11
p-CH_3	*m*-Cl	k_2	14·2	9
m-Cl	*p*-CH_3	k_2	14·8	15
m-Cl	*m*-Cl	k_2	14·2	15
p-CH_3	*p*-CH_3	k_3	1·1	53
m-Cl	*p*-CH_3	k_3	1·4	53

[a] Calculated values at 25·0 °C.

Substrates. *p*-Nitrophenyl *N*-phenylcarbamate. A solution of *p*-nitrophenol (0·01 mol) in dry benzene (10 ml) was added to a solution of phenyl isocyanate (0·01 mol). A catalytic quantity (0·5 ml) of pyridine was added and the solution refluxed for 1 h. On evaporation of the solvent *in vacuo*, the carbamate precipitated and was recrystallized from chloroform–pentane. The other substituted phenyl *N*-phenylcarbamates were prepared in an analogous manner and recrystallized from chloroform–pentane. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

***p*-$CH_3C_6H_4NHC(=O)OC_6H_4$-*p*-NO_2:** m.p. 135–136 °C; δ_H ($CDCl_3$), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH), 2·3 (3H, s, CH_3); ν_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m/z* 272 (M^+). Calc. for $C_{14}H_{12}N_2O_4$: C, 61·8; H, 4·4. Found: C, 61·8; H, 4·3%.

$C_6H_5NHC(=O)OC_6H_4$-*p*-NO_2: m.p. 146–148 °C; δ_H ($CDCl_3$), 7·2–8·3 (9H, m, phenyl), 6·8 (1H, s, NH); ν_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m/z* 258 (M^+). Calc. for $C_{13}H_{10}N_2O_4$: C, 60·5; H, 3·9. Found: C, 60·4; H, 3·8%.

***p*-$ClC_6H_4NHC(=O)OC_6H_4$-*p*-NO_2:** m.p. 111–112 °C; δ_H ($CDCl_3$), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH); ν_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m/z* 292 (M^+). Calc. for $C_{13}H_9N_2O_4Cl$: C, 53·4; H, 3·1. Found: C, 53·3; H, 3·1%.

***m*-$ClC_6H_4NHC(=O)OC_6H_4$-*p*-NO_2:** m.p. 111–112 °C; δ_H ($CDCl_3$), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH); ν_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m/z* 292 (M^+). Calc. for $C_{13}H_9N_2O_4Cl$: C, 53·4; H, 3·1. Found: C, 53·3; H, 3·1%.

Deuterated *p*-nitrophenyl *N*-phenyl carbamate [$C_6H_5NDC(=O)OC_6H_4$-*p*-NO_2]. DOC_6H_4-*p*-NO_2: a solution of potassium hydroxide in methanol was added to a solution of *p*-nitrophenol. The reaction mixtures were kept for 2 h and the solvent, methanol, was removed. The salt, KOC_6H_4-*p*-NO_2, was dissolved in excess D_2O under a nitrogen atmosphere and left over 12 h at 25·0 °C. The solution was neutralized with DCl. The deuterated *p*-nitrophenol was extracted with dry diethyl ether and dried again over $MgSO_4$. After expulsion of solvent, the analysis (GC–mass spectrometry) of dried deuterated *p*-nitrophenol had >99% deuterium content.

$C_6H_5NDC(=O)OC_6H_4$-*p*-NO_2: a solution of deuterated *p*-nitrophenol (0·01 mol) in dry benzene (10 ml) was added to a solution of phenyl isocyanate (0·01 mol). A catalytic quantity (0·5 mol) of pyridine was added and the solution was refluxed for 1 h. On evaporation of the solvent *in vacuo*, the carbamate precipitated and was recrystallized from chloroform–pentane. The deuterated substrate synthesized was confirmed by spectral and mass spectrometric analysis as follows. **$C_6H_5NDC(=O)OC_6H_4$-*p*-NO_2:** m.p. 146–148 °C; δ_H ($CDCl_3$), 7·2–8·3 (9H, m, phenyl); ν_{max} (KBr), 2800 (CH, aromatic), 2300 (ND), 1720 (C=O); *m/z* 259 (M^+).

Kinetic procedures. Rates were measured conductimetrically in acetonitrile. The conductivity bridge used in this work was a laboratory-made computer aromatic A/D converter conductivity bridge. Pseudo-first-order rate constants, k_{obs}, were determined by the Guggenheim method[16] with a large excess of benzylamine; [carbamate] = $2·0 \times 10^{-4}$ mol dm^{-3} and [benzylamine = 0·02–0·25 mol dm^{-3}. The rate constants k_2 and k_3 were obtained by plotting k_{obs}/[benzylamine] vs [benzylamine] and determining the intercept and slope of the straight line. The k_2 and k_3 values in Tables 1 and 2 are the averages of more than triplicate runs and were reproducible to within ±3%.

Product analysis. *p*-Nitrophenyl *N*-phenylcarbamate was reacted with excess *p*-methylbenzyl amine with stirring for more than 15 half-lives at 25·0 °C in acetonitrile and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate–*n*-hexane). Analysis of the product gave the following results.

$C_6H_5NHC(=O)NHCH_2C_6H_4$-*p*-$CH_3$: R_F = 0·33 (20% ethyl acetate–*n*-hexane); m.p. 182–184 °C; δ_H($CDCl_3$), 7·2–8·2 (9H, m, C_6H_5, C_6H_4), 6·9 (1H, s, NH), 4·2 (2H, d, CH_2), 2·1 (3H, s, CH_3); ν_{max} (KBr), 3220 (NH), 3050–3100(CH), 2950 (CH, aromatic), 1710 (C=O); *m/z* 285 (M^+). Calc. for $C_{15}H_{16}N_2O$: C, 63·2; H, 5·6. Found: C, 63·1; H, 5·5%.

ACKNOWLEDGEMENTS

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