**L-1-(Chlorocarbonyl)proline Methyl Ester (L-15a) and Ethyl Ester (L-15b).** (a) L-**14a** (1.0 g, 5.3 mmol) in 20 mL of dioxane was hydrogenated with 1.0 g of Pd/C E 10 R (10 wt.% relative to L-**14a**) and 100 bar of $H_2$ pressure for 30 h at 40 °C as described above. LGC analysis of the reaction mixture gave ≥99% L-**15a**/≤1% L-**14a**.

(b) A solution of L-proline methyl ester hydrochloride (828.1 g, 5.0 mol) in 2 L of chloroform was saturated with gaseous $NH_3$ at 0 °C, the precipitated ammonium chloride filtered off, and the filtrate concentrated in vacuo. The crude L-**2a** residue was added (45 min) to a stirred solution of 1 L of phosgene in 2 L of chloroform at 0 °C. The mixture was stirred for 12 h at 25 °C, chloroform and excess phosgene were removed, and the residue was fractionated in vacuo (0.01 torr) to yield 896.1 g (93%) of L-**15a**; bp 90–95 °C; $[\alpha]^{20}_D$ −50.3° (*c* 2.262, ethyl acetate); $^1$H NMR ($CDCl_3$) δ 4.53 (mc, 1 H, 2-H), 3.97–3.53 (m, 2 H, 5-H), 3.83 (s, 3 H, $CH_3$), 2.19 (mc, 4 H, 3-H and 4-H). Anal. Calcd for $C_7H_{10}ClNO_3$ ($M_r$ 191.6): C, 43.88; H, 5.26; Cl, 18.50; N, 7.31. Found: C, 44.16; H, 5.46; Cl, 17.93; N, 7.38.

(c) A solution of L-proline ethyl ester hydrochloride (179.6 g, 1.0 mol) in 500 mL of chloroform was saturated with gaseous $NH_3$ at 0 °C and worked up as described above. The crude L-**2b** was added (45 min) to the stirred solution of 200 mL of phosgene in 500 mL of chloroform at 0 °C. Stirring was continued for 12 h at 5 °C, for 5 h at 25 °C, and for 12 h at 40 °C. Workup as in b yielded ($10^{-3}$ torr) 196.4 g (95%) of L-**15b**: bp 90 °C; $[\alpha]^{20}_D$ −54.03° (*c* 2.362, ethyl acetate); $^1$H NMR ($CDCl_3$) δ 4.47 (mc, 1 H, 2-H), 4.27, 4.23 (q, 2 H, $J$ = 7 Hz, $CH_2CH_3$), 3.75 (mc, 2 H, 5-H), 2.13 (mc, 4 H, 3-H and 4-H), 1.33 (t, 3 H, $J$ = 7 Hz, $CH_3$). Anal. Calcd for $C_8H_{12}ClNO_3$ ($M_r$ 205.6): C, 46.73; H, 5.88; Cl, 17.24; N, 6.81. Found: C, 46.80; H, 6.03; Cl, 17.20; N, 7.21.

**Hydrolysis of L-15.** Aqueous HCl (200 mL, 10%) was vigorously stirred at 73 °C and 0.10 mol of L-**15** (19.2 g of L-**15a** and 20.6 g of L-**15b**, respectively) added within 45 min. Stirring was continued at 73 °C until $CO_2$ evolution subsided and then for 5 h at 25 °C. Excess HCl was evaporated in vacuo and the residue dehydrohalogenated with a weak basic ion exchanger (MP 62). Evaporation of the eluate yielded L-proline (L-**17**). From L-**15a**: 11.2 g (97%); mp 222–229 °C dec; $[\alpha]^{20}_D$ −83.6° (*c* 1, $H_2O$). From L-**15b**: 11.3 g (98%); mp 224–230 °C dec; $[\alpha]^{20}_D$ −83.7° (*c* 1, $H_2O$) (lit.[15] mp 224–226 °C, $[\alpha]^{20}_D$ −84 ±2° (*c* 0.1, $H_2O$).

**L-Proline (L-17).** (a) L-**6a**, prepared from L-**2a** (0.25 mol) and phosgene as described above, was dehydrogenated as in b. The L-**7a** thus obtained was dehydrogenated and hydrogenated catalytically in 300 mL of dioxane (Table I). The catalyst and triethyl-, tripropyl- or tributylammonium chloride, respectively, were filtered off, the filtrate was concentrated under reduced pressure. The resulting L-**15a** was hydrolyzed in 500 mL of 10% aqueous HCl as described above. The percentage of L-**17** and of glutamic acid in the reaction product was determined with an amino analyzer.

(b) Liquid phosgene (52.0 g, 0.525 mol) was added to the stirred solution of 35.8 g (0.25 mol) of L-**2a** in 250 mL of dichloromethane at −10 °C. Stirring was continued at 25 °C for 3 h, phosgene evaporated, and the residue stirred with 350 mL of tributylamine (under nitrogen, 70 °C, 4 h). The solution was hydrogenated for 30 h at 50 °C in a hastelloy autoclav with 32.6 g of Pd/C E 10 R catalyst/180 bar of $H_2$ pressure. The catalyst was filtered off, excess tributylamine evaporated in vacuo, and the solution added dropwise at 75 °C to 400 mL of vigorously stirred 10% aqueous HCl. Stirring was continued for 5 h at 25 °C, until $CO_2$ evolution had subsided, excess HCl removed in vacuo, and the remaining solution neutralized with aqueous NaOH. Tributylamine was separated and the filtrate acidified with 10% aqueous HCl, treated with activated charcoal, and concentrated. The residue was worked up by column chromatography (basic ion exchanger MP62). The eluate was concentrated and the residue recrystallized from $H_2O$/isopropyl alcohol to yield 22.6 g (78%) of L-**17**: mp 227–229 °C; $[\alpha]^{20}_D$ 83° (*c* 1, $H_2O$), optical purity 99.7% (HPLC).

**Acknowledgment.** We gratefully acknowledge preparation of the acylated compounds L-**12** and L-5-oxo-1-(trimethylsilyl)proline methyl ester (L-**11**) by Dr. Wolfgang Müller.

**Registry No.** L-**1**, 98-79-3; L-**2a**, 4931-66-2; L-**2b**, 7149-65-7; (*S*)-**5a**, 103322-10-7; (*S*)-**5b**, 103322-11-8; L-**6a**, 86050-91-1; L-**6b**, 86042-46-8; L-**7a**, 86042-45-7; L-**7b**, 86042-47-9; L-**11**, 96105-69-0; L-**12a**, 75857-93-1; L-**12b**, 103322-12-9; L-**14a**, 103322-13-0; L-**15a**, 85665-59-4; L-**15b**, 86050-92-2; L-**17**, 147-85-3; AcCl, 75-36-5; BaCl, 98-88-4; $Me_3SiCl$, 75-77-4; L-proline methyl ester hydrochloride, 2133-40-6; L-proline ethyl ester hydrochloride, 33305-75-8.

# Kinetics and Mechanism of Aminolysis of Carbamates

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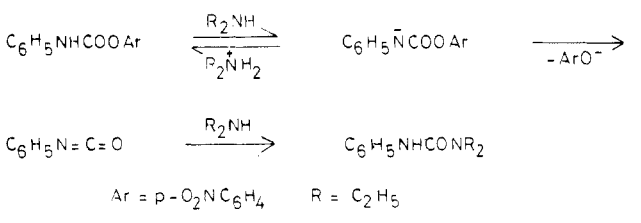
The kinetics of the *n*-butylaminolysis of three series of mono- and disubstituted phenyl *N*-phenylcarbamates **1–3** have been studied spectrophotometrically under pseudo-first-order conditions in dioxane. The relation $k_{obsd} = k_2[n\text{-BuNH}_2] + k_3[n\text{-BuNH}_2]^2$ was found applicable for all esters. The rate constants $k_2$ and $k_3$ were correlated by the Hammett equation, and the corresponding activation parameters were determined. The reaction was found to be much more sensitive to a substituent on the leaving group (OAr) than to a substitutent on the amine portion (NHAr) of the esters. Results from crossover experiments revealed the absence of isocyanate intermediate. The mechanism of the aminolysis of carbamates is discussed in terms of these facts.

A fairly large amount of information exists about the kinetics and mechanism of hydrolysis of aryl carbamates.[1-4] However, not too much is known about the aminolysis of such esters. At present, there are two conflicting reports concerning the mechanism of aminolysis of carbamates. Menger and Glass[5] proposed an E1cB mechanism (Scheme I) for the reaction of *p*-nitrophenyl *N*-phenylcarbamate

**Scheme I**




with diethylamine in toluene, while Stohandl and Vecera[6] assigned a $B_{Ac}2$ path (Scheme II) for the aminolysis of

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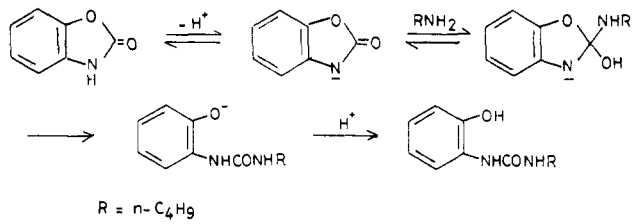
0022-3263/86/1951-3498$01.50/0 

**Scheme II**



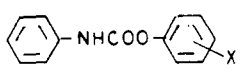
R = n-$C_4H_9$

**Table I. Second- and Third-Order Rate Constants of the Reactions of Aryl Carbamates 1–3 with *n*-Butylamine in Dioxane at 31 °C**

| ester | $10^6k_2$, L mol$^{-1}$ s$^{-1}$ | $10^6k_3$, L$^2$ mol$^{-2}$ s$^{-1}$ | ester | $10^6k_2$, L mol$^{-1}$ s$^{-1}$ | $10^6k_3$, L$^2$ mol$^{-2}$ s$^{-1}$ |
|---|---|---|---|---|---|
| **1a** | 1.06 | 4.57 | **2c** | 20.43 | 74.10 |
| **1b** | 3.80 | 7.52 | **2d** | 91.90 | 525.00 |
| **1c** | 4.05 | 16.49 | **3a** | 1.32 | 27.82 |
| **1d** | 7.47 | 25.14 | **3b** | 4.97 | 36.50 |
| **1e** | 34.39 | 213.70 | **3c** | 47.02 | 110.40 |
| **1f** | 35.50 | 283.00 | **3d** | 33.60 | 157.60 |
| **1g** | 101.95 | 812.10 | **3e** | 123.20 | 468.30 |
| **1h** | 1441.00 | 17565.00 | **3f** | 92.70 | 810.40 |
| **1i** | 6737.00 | 66300.00 | **3g** | 338.70 | 1882.00 |
| **2a** | 2.32 | 19.92 | **3h** | 1452.00 | 66520.00 |
| **2b** | 7.47 | 25.14 | **3i** | 2484.00 | 69520.00 |

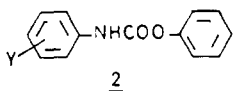
2-benzoxazolone with *n*-butylamine and piperidine in aqueous medium.

We report here a study of the kinetics of the reactions of three series of aryl *N*-arylcarbamates **1–3** with *n*-butylamine in dioxane. The study aims at elucidation of the mechanism of aminolysis of carbamates. The knowledge of the exact degradation pathway of carbamates by nitrogen nucleophiles will cast light on their metabolism by different life forms as these esters are widely used as agrochemicals.[7]



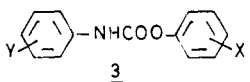
**1**

**1** a, X = 4-$CH_3O$ e, X = 4-Cl
b, X = 4-$CH_3$ f, X = 4-Br
c, X = 3-$CH_3$ g, X = 3-Cl
d, X = H h, X = 3-$NO_2$
i, X = 4-$NO_2$



**2**

**2** a, Y = 4-$CH_3O$ c, Y = 4-Cl
b, Y = H d, Y = 4-$NO_2$



**3**

**3** a, X = 4-$CH_3$; Y = 4-Cl
b, X = 4-$CH_3$; Y = 3-Cl
c, X = 4-Cl; Y = 4-$CH_3$
d, X = 4-Cl; Y = 3-$CH_3$
e, X = 4-Cl; Y = 4-Cl
f, X = 4-Cl; Y = 3-Cl
g, X = 3-Cl; Y = 4-Cl
h, X = 3-$NO_2$; Y = 4-$CH_3$
i, X = 4-$NO_2$ Y = 4-$CH_3$

## Results and Discussion

For all esters **1–3** the kinetic data, in the temperature range 31–51 °C, fit eq 1, where $k_{obsd}$ is the pseudo-first-order rate constant. A plot of $k_{obsd}/[n\text{-BuNH}_2]$ vs. $[n\text{-BuNH}_2]$ yielded, in each case, a straight line with intercept $k_2$ and slope $k_3$ (Figure 1). The values of $k_2$ and $k_3$ were calculated from linear least-squares fit of the data to eq 1 and are given in Tables I and II. Activation parameters were also calculated from the linear least-squares fit of the data at different temperatures using eq 2 and 3 and the values are given in Table III.

$$k_{obsd} = k_2[n\text{-BuNH}_2] + k_3[n\text{-BuNH}_2]^2 \quad (1)$$

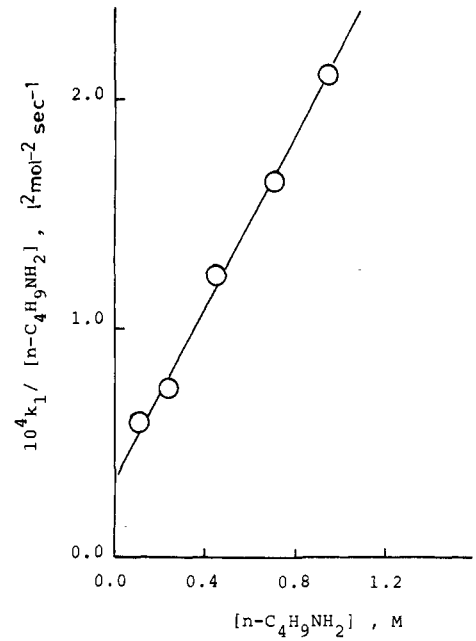
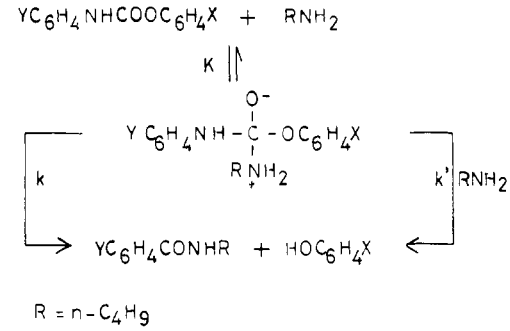



**Figure 1.** Plot of $k_1/[n\text{-}C_4H_9NH_2]$ against *n*-butylamine concentration for the aminolysis of 3-chlorophenyl *N*-(4-chlorophenyl)carbamate in anhydrous dioxane at 31 °C.

**Scheme III**



R = n-$C_4H_9$

Equation 1 indicates two concurrent overall second-order and third-order paths are available for *n*-butylaminolysis of aryl carbamates **1–3** in dioxane. In the third-order process, the second amine molecule obviously acts as a catalyst. A sequence consistent with eq 1 is presented in Scheme III. This sequence leads to expression 4, which is kinetically equivalent to eq 1.

$$k_{obsd} = k'K[n\text{-BuNH}_2] + k''K[n\text{-BuNH}_2]^2 \quad (4)$$

The basic difference between Menger's E1cB mechanism (Scheme I) and the present sequence (Scheme III) lies in the proposal of an isocyanate intermediate by Menger.[5] There are strong evidences that exclude the presence of isocyanate intermediate in the reactions studied. Thus, recording the infrared spectrum of dioxane solution of **1d** and *n*-butylamine with time reveals only the disappearance of the ester CO near 1720 cm$^{-1}$ and the appearance of urea CO near 1655 cm$^{-1}$. No isocyanate band in the region

$$k_i = (RT/Nh)e^{-\Delta H^*/RT}e^{\Delta S^*/R} \quad (2)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (3)$$

(1) Mindl, J.; Sterban, V. *Collect. Czech. Chem., Commun.* **1982**, *98*, 900.
(2) Bergon, M.; Calmon, J. P. *Bull. Soc. Chim. Fr.* **1976**, 797.
(3) Stankovicova, M.; Kucarova, M.; Pesak, M. *Chem. Zvesti* **1985**, *29*, 227.
(4) Christenson, I. *Acta Pharm. Suec.* **1969**, *6*, 287.
(5) Menger, F. M.; Glass, L. E. *J. Org. Chem.* **1974**, *39*, 2469.
(6) Stohandl, J.; Vecera, M. *Collect. Czech. Chem. Commun.* **1979**, *44*, 1790.
(7) Kaufman, D. D. *J. Agric. Food Chem.* **1967**, *15*, 582.

**Table II. Summary of the Kinetic Data for *n*-Butylaminolysis of Aryl *N*-Phenylcarbamates in Dioxane at Different Temperatures[a]**

| | $T$ = 31 °C | | $T$ = 41 °C | | $T$ = 51 °C | |
|---|---|---|---|---|---|---|
| ester | $10^6k_2$ | $10^6k_3$ | $10^6k_2$ | $10^6k_3$ | $10^6k_2$ | $10^6k_3$ |
| 1a | 1.06 | 4.57 | 3.55 | 8.90 | 8.92 | 12.05 |
| 1d | 7.47 | 25.14 | 24.56 | 32.08 | 42.13 | 56.16 |
| 1e | 34.39 | 213.70 | 65.70 | 309.10 | 147.70 | 424.60 |
| 1i | 6737.00 | 66300.00 | 123500.00 | 81630.00 | 20390.00 | 134690.00 |

[a] $k_2$, L mol$^{-1}$ s$^{-1}$; $k_3$, L$^2$ mol$^{-2}$ s$^{-1}$.

**Table III. Activation Parameters for the Second- and Third-Order Processes of *n*-Butylaminolysis of Aryl *N*-Phenylcarbamates in Dioxane[a]**

| | second-order process | | | third-order process | | |
|---|---|---|---|---|---|---|
| ester | $\Delta G^*$ | $\Delta H^*$ | $\Delta S^*$ | $\Delta G^*$ | $\Delta H^*$ | $\Delta S^*$ |
| 1a | 22.91 | 20.43 | −8.25 | 15.96 | 8.95 | −23.39 |
| 1d | 20.12 | 16.47 | −12.16 | 14.59 | 7.28 | −24.38 |
| 1e | 18.17 | 13.70 | −14.89 | 14.76 | 6.15 | −28.73 |
| 1i | 14.83 | 10.28 | −15.17 | 12.04 | 6.40 | −18.79 |

[a] $\Delta G^*$, kcal mol$^{-1}$; $\Delta H^*$, kcal mol$^{-1}$; $\Delta S^*$, cal deg$^{-1}$ mol$^{-1}$.

**Table IV. Results of Linear Free Energy Correlations of the Rate Constants at 31 °C[a]**

| series | $\log k_i = \rho\sigma + \log k_0$ | $r$ | $s_{est}$ | $n$ |
|---|---|---|---|---|
| 1 | $\log k_2 = 3.36\sigma_X - 5.10$ | 0.991 | 0.169 | 9 |
| | $\log k_3 = 3.95\sigma_X - 4.47$ | 0.996 | 0.126 | 9 |
| 2 | $\log k_2 = 1.50\sigma_Y - 5.15$ | 0.991 | 0.088 | 4 |
| | $\log k_3 = 1.43\sigma_Y - 4.44$ | 0.983 | 0.120 | 4 |
| 1–3 | $\log k_2 = 5.45[(\sigma_X/1.50) + (\sigma_Y/3.36)] - 5.26$ | 0.977 | 0.229 | 22 |
| | $\log k_3 = 6.02[(\sigma_X/1.43) + (\sigma_Y/3.95)] - 4.49$ | 0.986 | 0.241 | 22 |

[a] $r$, correlation coefficient; $s_{est}$, standard deviation of the estimate value; $n$, number of points.

2275–2240 cm$^{-1}$ was observed. Also, the infrared spectrum of the product obtained from the reaction of **1d** with a mixture of *n*-butylamine and *p*-chloroaniline was identical with that of *N*-phenyl-*N'*-*n*-butylurea (**4**). However, the spectrum of the product obtained from the reaction of phenyl isocyanate with the same mixture of amines in dioxane under the same conditions was similar to that of an authentic mixture of **4** and *N*-phenyl-*N'*-(*p*-chlorophenyl)urea (**5**). In addition, the results of the conductivity[8] and spectral[9] measurements on solutions of carbamate esters and triethylenediamine in dioxane excluded the formation of isocyanate intermediate.

The overall second-order and third-order rate constants ($k_2$ and $k_3$, respectively) were correlated with Hammett substituent constant $\sigma$.[10] The results of such correlations are summarized in Table IV. The relatively large substituent effect observed for the *O*-aryl ring is consistent with the proposed mechanism (Scheme III). In terms of the latter pathway, the values of $\rho$ are composite as $k_2 = k'K$ and $k_3 = k''K$. Electron withdrawal in the *O*-aryl group would be expected to favor both $K$ and $k'$ (and $k''$), resulting in large positive $\rho$ values (as observed). The small substituent effect for **2** observed for the *N*-aryl group is also compatible with the mechanism in Scheme III. In this case electron withdrawal in the *N*-aryl group would change $K$ and $k'$ (or $k''$) in opposite directions, leading to small positive $\rho$ value (as observed).

The negative values of $\Delta S^*$ (Table III) indicate a loss in the degrees of freedom of the system when the reactants pass into the transition states. This fact provides an additional evidence against the intermediacy of isocyanate in the *n*-butylaminolysis of **1–3** in dioxane. This is mainly due to the fact that alkaline hydrolysis of aryl N-monosubstituted carbamates, following an E1cB path, exhibits positive values of $\Delta S^*$,[2,11,12] whereas hydrolysis of aryl N,N-disubstituted carbamates, following a $B_{Ac}2$ mechanism, has negative $\Delta S^*$ values.[13]

## Experimental Section

Melting points were determined on electrothermal capillary apparatus and are uncorrected. Infrared spectra were measured with a Pye-Unicam SP3-100 spectrophotometer. Elemental analyses were carried out at the Microanalytical laboratory of the National Research Center, Giza, Egypt. Dioxane was BDH AnalaR grade, used without further purification. *n*-Butylamine was BDH reagent and purified before use as previously described.[14]

**Substrates.** Aryl *N*-phenylcarbamates **1a–i** and aryl *N*-arylcarbamates **3a–i** were prepared from the appropriate phenol and aryl isocyanate as previously described.[15] Phenyl *N*-arylcarbamates **2a–f** were prepared from the appropriate arylamine and phenyl chloroformate following a previous method.[15] All esters were crystallized from chloroform–pentane to constant mp (Table V). In each case, satisfactory combustion analytical data for C, H, and N were obtained.

**Kinetics.** A Pye-Unicam SP8-100 ultraviolet recording spectrophotometer with a jacketed cell compartment was used for the kinetic measurements. Water at the required temperature (31, 41, or 51 ± 0.1 °C) was circulated through the cell compartment by means of a circulating pump of a constant temperature bath unit, Haake Circulator Series De-L. A small thermometer placed in the cell compartment showed that the temperature remained constant within the range ±0.1 °C. The reactions were carried out in 1-cm, ground-glass stoppered fused silica absorption cells. The reference solution was that of dioxane

(8) Furuya, Y.; Ito, S. K.; Vrasaki, I.; Morita, A. *Tetrahedron* **1967**, *24*, 2367.
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(12) Christenson, I. *Acta Chem. Scand.* **1964**, *18*, 904.
(13) Mindl, J.; Salcarek, P.; Silar, L.; Vecera, M. *Collect. Czech. Chem. Commun.* **1980**, *45*, 3130.
(14) Shawali, A. S.; Beichler, S. S.; *J. Am. Chem. Soc.* **1967**, *89*, 3020.
(15) Hegarty, A. F.; Frost, L. N. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1719.

**Table V. Aryl *N*-Arylcarbamates 1-3**

| ester | mp, °C (lit.[17] mp, °C) | molec formula | ester | mp, °C (lit.[17] mp, °C) | molec formula |
|---|---|---|---|---|---|
| **1a** | 135–136 (136–137) | $C_{14}H_{13}NO_3$ | **2a** | 154–155 | $C_{14}H_{13}NO_3$ |
| **1b** | 111–112 (108–110) | $C_{14}H_{13}N_2$ | **2c** | 149–150 (148–150) | $C_{13}H_{10}ClNO_2$ |
| **1c** | 120–122 | $C_{14}H_{13}NO_2$ | **2d** | 153–155 (152–154) | $C_{13}H_{10}N_2O_4$ |
| **1d** | 123–124 (121–124) | $C_{13}H_{11}NO_2$ | **3a** | 184–186 | $C_{14}H_{12}ClNO_2$ |
| **1e** | 148–149 (148–150) | $C_{13}H_{10}ClNO_2$ | **3b** | 95–96 | $C_{14}H_{12}ClNO_2$ |
| **1f** | 138–139 | $C_{13}H_{10}BrNO_2$ | **3c** | 166–168 | $C_{14}H_{12}ClNO_2$ |
| **1g** | 123–124 (123–125) | $C_{13}H_{10}ClNO_2$ | **3d** | 116–117 | $C_{14}H_{12}ClNO_2$ |
| **1h** | 133–134 (132–133) | $C_{13}H_{10}N_2O_4$ | **3e** | 175–176 | $C_{13}H_9Cl_2NO_2$ |
| **1i** | 147–148 (146–149) | $C_{13}H_{10}N_2O_4$ | **3f** | 113–114 | $C_{13}H_9Cl_2NO_2$ |
| | | | **3g** | 114–116 | $C_{13}H_9Cl_2NO_2$ |
| | | | **3h** | 133–135 | $C_{14}H_{12}N_2O_4$ |
| | | | **3i** | 135–136 | $C_{14}H_{12}N_2O_4$ |

**Table VI. Characteristic Ultraviolet Maxima for Phenol and Its Substituted Derivatives**

| $XC_6H_4OH$, X | $\lambda_{max}$, nm | $XC_6H_4OH$, X | $\lambda_{max}$, nm |
|---|---|---|---|
| 4-$CH_3O$ | 290 | 4-$CH_3$ | 282 |
| 3-$CH_3$ | 278 | H | 274 |
| 4-Cl | 282 | 3-Cl | 278 |
| 4-Br | 282 | 3-$NO_2$ | 330 |
| 4-$NO_2$ | 314 | | |

containing an equal amine concentration to that being used in the particular run.

Stock solutions of carbamate esters, usually about $10^{-2}$ M were prepared and the concentrations checked by comparing the optical densities with those calculated from Beer's law at the characteristic wavelength. Stock *n*-butylamine solution was prepared and the concentration was determined by acid–base titration. Appropriate concentrations of amine and ester were prepared by dilution of the stock solutions with dioxane. All ester concentrations were $5.0 \times 10^{-4}$ M.

The reactions were followed by rate of appearance of the phenol peak (Table VI). The corresponding ureas and carbamates showed no absorption in the 290–320-nm region. Complete spectra taken for several mixtures of *N*-phenyl-*N'*-*n*-butylurea and phenol in dioxane corresponded to the spectra of pure phenol solutions having the same concentration of phenol. Also, complete spectra taken at the end of each kinetic run corresponded to the spectra of phenol solutions of the same concentration. Beer's law was found to be obeyed within the concentration and wavelength range employed.

Reactions were followed up to 95% completion under pseudo-first-order conditions in which at least 10-fold excess of *n*-butylamine over ester was used. Duplicate or triplicate runs were performed for each concentration and readings taken in any kinetic run covered a range of 85% transmittance units. The observed pseudo-first-order rate constants ($k_{obsd}$) were calculated from log $(A_\infty - A_t)$ vs. $t$ data ($A_t$ and $A_\infty$ are the absorbances of the solution at times $t$ and infinity, respectively) by using a least-squares program. The plots were linear for at least five half-lives.

**Identification of the Products.** *n*-Butylamine (7.3 g, 0.1 mol) was added to a solution of phenyl *N*-phenylcarbamate (4.26 g, 0.02 mol) in dioxane (30 mL). The reaction flask was immersed in a constant temperature bath at 31 ± 0.1 °C. After 24 h, the white solid that separated out was filtered, and upon crystallization from chloroform–pentane mxiture, it gave *N*-*n*-butyl-*N'*-phenylurea in an 85% yield, mp 130–131 °C (lit.[16] mp 130–131 °C), not depressed when mixed with an authentic sample prepared from the reaction of phenyl isocyanate and *n*-butylamine in dioxane. The spectral data of both the product and the authentic sample were identical in all respects.

The filtrate, left after separation of the crude *N*-*n*-butyl-*N'*-phenylurea from the reaction mixture, was distilled under reduced pressure to remove the solvent and the excess of *n*-butylamine. The residue left was dissolved in ether, and the ether layer was collected and throughly extracted with 10% sodium hydroxide solution. The sodium hydroxide extract was found to give violet color with ferric chloride solution, indicating the presence of phenol. The latter was separated from its solution as benzoate derivative as follows. Benzoyl chloride (2.6 g, 0.02 mol) was added portionwise to the sodium hydroxide extract with continuous stirring. After 30 min, the precipitated phenyl benzoate was collected and crystallized from ethanol. Pure phenyl benzoate was obtained in 85% yield, mp 71 °C (lit.[17] mp 68 °C): IR (KBr) 1735 (CO) $cm^{-1}$.

**Trapping Experiments.** To a solution of **1d** (0.02 mol) in dioxane (30 mL) was added a mixture of *n*-butylamine and *p*-chloroaniline (0.1 mol each), and the reaction mixture was stirred at 31 °C. After 24 h, the solid that precipitated was filtered off and identified as **4** by comparison with an authentic sample (IR, mp, and mixed mp). Workup of the filtrate in the usual way yielded phenol and *p*-chloroaniline. The total recovery of the latter represents 82% and 95%, respectively, of the theoretical quantities.

Repitition of the above experiment using phenyl isocyanate instead of **1d** and workup of the reaction mixture yielded a mixture of **4** and **5** (IR, mp, and TLC).

**Registry No.** **1a**, 19219-48-8; **1b**, 16323-13-0; **1c**, 33274-94-1; **1d**, 4930-03-4; **1e**, 16323-15-2; **1f**, 16323-16-3; **1g**, 16400-09-2; **1h**, 35289-89-5; **1i**, 6320-72-5; **2a**, 20950-96-3; **2c**, 50882-28-5; **2d**, 6465-01-6; **3a**, 92290-74-9; **3b**, 93535-10-5; **3c**, 102736-20-9; **3d**, 96445-19-1; **3e**, 99514-47-3; **3f**, 102736-21-0; **3g**, 102736-22-1; **3h**, 102736-23-2; **3i**, 3848-42-8; **5**, 1967-26-6; *N*-butyl-*N'*-phenylurea, 3083-88-3; phenyl benzoate, 93-99-2; *p*-chloroaniline, 106-47-8; phenyl isocyanate, 103-71-9; *n*-butyamine, 109-73-9.

**Supplementary Material Available:** Tables of melting points, molecular formulas, and elemental analyses data for **1–3** and IR spectra of **4** and **5** and the products from the reactions of phenyl isocyanate and phenyl *N*-phenylcarbamate with a mixture of *n*-butylamine and *p*-chloroaniline (4 pages). Ordering information is given on any current masthead page.

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