

heptane as an internal standard with the column temperature at 150 °C and 35 psi nitrogen pressure.

Preparations of *endo*-5-(2-Haloethyl)-2-norbornenes 1-3. By use of published procedures,⁵¹ 1 (X = I), 2 (X = Br), and 3 (X = Cl) were obtained. For X = I: bp 83-84 °C (2.5 mmHg); ¹H NMR 0.47-0.54 ppm (1 H, m), 1.0-2.20 (5 H, m), 2.65-2.95 (2 H, m), 3.28-3.60 (2 H, t, *J* = 7 Hz), 5.85-6.14 (2 H, m). For X = Br: bp 71-73 °C (2.5 mmHg); ¹H NMR 0.48-0.54 ppm (1 H, m), 1.0-2.28 (5 H, m), 2.65-2.90 (2 H, m), 3.08-3.40 (2 H, t, *J* = 7 Hz), 5.88-6.17 (2 H, m). For X = Cl: bp 86-87 °C (12 mmHg) (lit.⁵² bp 87-90 °C at 14 mmHg); ¹H NMR 0.45-0.51 ppm (1 H, m), 1.0-2.30 (5 H, m), 2.65-3.08 (2 H, m), 3.50-3.80 (2 H, t, *J* = 7 Hz), 5.85-6.12 (2 H, m).

Preparations of 6-Halo-1-heptenes 8 and 9. 8 (X = Br) and 9 (X = I) were prepared by a previously described method.⁵³

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General Procedure for the Reaction of *t*-BuLi with Alkyl Halides. A solution of 0.1 M of an appropriate halide in pentane/ether was cooled to -78 °C under a blanket of nitrogen or argon and 0.2 M of *t*-BuLi as a solution in pentane was added via syringe over a 5-min period. In cases where complexation reagents were employed (TMEDA, HMPA, 18-crown-6), the solutions of additive were precooled and added to the reaction mixture at -78 °C after the reaction was complete. At the chosen time, reaction mixtures were carefully quenched with D₂O (or EtOD), internal standard was added, and GLC analyzes were performed. Deuterium incorporation was evaluated by GC-MS.

Acknowledgment. We are indebted to the National Science Foundation Grant No. CHE8403024 for support of this work.

(53) Ashby, E. C.; DePriest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* 1984, 49, 3545.

Selective Mono-N-alkylation of Aromatic Amines by Dialkyl Carbonate under Gas-Liquid Phase-Transfer Catalysis (GL-PTC) Conditions

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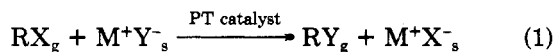
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The reaction between aromatic amines and dialkyl carbonates, carried out in gas phase under gas-liquid phase-transfer catalysis (GL-PTC) conditions, in a continuous-flow process, produces the mono-N-alkylation product and its carboxyalkyl derivative (selectivity > 99%). The catalyst is a polyethylene glycol in the presence of a base (K₂CO₃). The reaction produces CO₂ so it can be carried out indefinitely because the chemical nature of the catalytic bed, at steady conditions, does not change during the time. According to the mechanism discussed, this high selectivity might be due the following: (i) the reaction between the amine and dialkyl carbonate that produces only carboxymethylated compound (ArNHCOOR); (ii) the subsequent reaction of this intermediate with the dialkyl carbonate that exclusively produces N-alkylated products (ArNR₂COOR, from which ArNHR is selectively produced).

Introduction

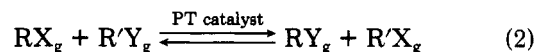
The development of new synthetic methods are of interest because more attention is turned to work safety and to use of reagents less dangerous from an industrial and environmental point of view; so new reactions and new synthetic methods often offer the opportunity to improve productive processes. An example is gas-liquid phase-transfer catalysis (GL-PTC).¹ This new synthetic method, with its theoretical basis in phase-transfer catalysis (PTC),² takes advantage of anionic activation of PTC in processes that are carried out in continuous flow and in gas-phase conditions.

It has been reported that GL-PTC can work in two different ways: (1) with a bed that consumes itself progressively during the reaction (eq 1; the gaseous reagent



RX flows on a solid bed composed of the salt M⁺Y⁻ and a PT catalyst; its transformation into RY then occurs. The

solid reagent M⁺Y⁻ is progressively consumed).^{1c} (2) with a bed that is not consumed during the reaction (eq 2: The



solid bed is composed of a solid supporting a PT catalyst. RX and R'Y can be, in this case, two alkyl halides; they undergo halogen exchange at the outlet of reactor).^{1d}

This second possibility is surely of greater interest because the reaction can be carried out for an indefinite time, making the bed effectively catalytic.

Dimethyl carbonate (DMC) is a well-known reagent which provides carboxymethylation with nucleophiles when the reaction is carried out in liquid phase.³ More-

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(2) (a) Starks, C. M. *J. Am. Chem. Soc.* 1971, 93, 195-199. (b) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* 1982, 101, 147-200. (c) Dehmlow, E. V.; Dehmlow, S. S. *Phase-Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.

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Table I. Reaction between Aniline and DMC Carried Out on Different Beds^a

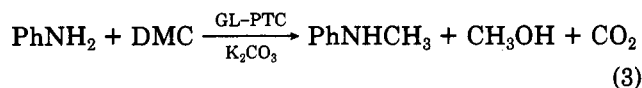
entry	solid bed	composition (%) at equilibrium of the reaction mixture ^b				
		PhNH ₂ ^j	PhNHCH ₃	PhN(CH ₃) ₂	PhNHCOOCH ₃	PhNCH ₃ COOCH ₃
1	glass wool ^c	97.8	1.2	1.0	<i>k</i>	<i>k</i>
2	K ₂ CO ₃ ^d	95.2	2.4		1.8	0.7
3	K ₂ CO ₃ + 5% PEG 6000 ^e	54.3	40.8	1.6	<i>k</i>	3.3
4	silica gel ^f	64.4	20.9	14.7		
5	Alumina 60, basic ^g	46.5	46.1	7.4		
6	α-Alumina/5% Bu ₄ P ⁺ Br ^{-h}	2.8	31.0		0.7	45.7 ⁱ

^a DMC/aniline molar ratio = 4.0; *T* = 180 °C; atmospheric pressure; liquid flow = 24 mL/h. ^b Due to chromatographic factors, the first collected samples are richer in the more volatile compounds. After about 40 mL the composition of the reaction mixture does not change more, reaching steady conditions. See also Figure 1. ^c The column was filled with 2.0 g of glass wool. ^d 95 g. ^e 95 g of K₂CO₃ coated with 5 wt % of PEG 6000 (PEG of *M* = 6000; Merck, 807491). ^f 30 g (Merck, 7734). ^g 30 g (Merck, 1067). ^h 95 g of α-Alumina pellets containing 5 wt % of phosphonium salt. ⁱ This reaction mixture contains also 20% of PhNHCONHPh + PhNHCON(CH₃)Ph + PhN(CH₃)CON(CH₃)Ph; by GLC analysis. ^j Not reacted. ^k Trace.

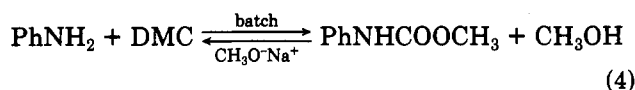
over it appears to be an ideal reagent under GL-PTC conditions: it is not toxic; it is sufficiently volatile (bp 90.4 °C) and provides different results if employed in the gas phase. Under GL-PTC conditions DMC selectively acts as alkylating agent as described here and elsewhere.⁴

We report here a continuous flow reaction that takes place between aromatic primary amines and DMC or a dialkyl carbonate in general. The catalytic bed is composed of a base (K₂CO₃) and a PT catalyst; the latter can be a simple polyethylene glycol (PEG 6000 is a polyethylene glycol of *M_r* = 6000).⁵

The reaction between aniline and DMC will be discussed. In accordance with eq 3, the reaction carried out under GL-PTC conditions is very selective in forming the product of mono-N-alkylation. When the reaction is ex-



ecuted in a batch reactor, on the other hand, the formation of the carboxymethylated product is prevalent (eq 4).^{3d}



Alkylation of primary aromatic amines is a well-known and important problem in organic synthesis because alkylation agents such as alkyl halides are not selective and give a mixture of alkylated amines. According to continuous-flow methods, the mono-N-alkylation of anilines in the gas phase is carried out industrially with methanol (ethylene and dialkyl ethers are also used). The catalytic beds promoting this reaction are alumina/Cu-containing transition-metal oxides. High temperatures (200–400 °C), high pressures, or long contact time are needed.⁶

Results

According to stoichiometric eq 3, the acidity produced during the alkylating process with DMC is removed from reaction environment as CO₂; this behavior allows the reaction to be carried out indefinitely under GL-PTC

conditions; in fact the chemical composition of the catalytic bed, at steady conditions, remains unchanged.

The reactions reported here were carried out at 180 °C and atmospheric pressure; the liquid mixture of the reagents was sent continuously with the aid of a syringe pump to a column containing the catalytic solid bed. The reagents and the products are in gas phase; this was obtained by feeding the reactor (together with more high-boiling aniline) with a low-boiling compound. For this purpose a flow of nitrogen may also be used.

The low-boiling compound acts as a gaseous carrier and is able to hold in the gas phase the high-boiling compound; the necessary relative ratio between them depends, of course, on the respective vapor pressure at that temperature. (Table II shows the influence on the reaction pathway of different carriers).

Dimethyl carbonate itself can be used as carrier. In the reported reactions, the molar ratio between DMC and aniline were 1.2, 4.0, and 10.0. This high quantity of alkylating agent was possible because of the high selectivity of the reaction. The alternative possibility is to operate under reduced pressure; however, this procedure is more complicated and was not used here.

The catalytic beds that promote the reaction were of two different types: just solid potassium carbonate supporting the catalyst and potassium carbonate plus the PT catalyst both supported on an inactive macroporous solid: α-alumina spheres (3 mm in diameter) having surface area of 0.03 m²/g. This latter support (widely used in industry in different type of continuous-flow processes)⁷ allows, with the elimination of preferential ways in the gaseous flow, a more accurate determination of catalytic effectiveness of the solid bed.

Table I shows that the reaction does not proceed in gas phase (entry 1) or on K₂CO₃ alone (entry 2). Classical solid supports such as silica gel and alumina (entries 4 and 5), although able to promote the reaction, are not selective in forming the mono-N-alkylation product. The combination of a basic environment and a PT catalyst allows the reaction between aniline and DMC to occur and give selectively the mono-N-alkylated derivative (Table I, entry 3, and Figure 1).

The reaction is very sensitive to the amount of catalyst present on the basic support. Figure 2 shows that a plateau is quickly reached with 1% of PEG on K₂CO₃. However, without a PT catalyst the reaction is very slow, indicating the need of a liquid film in the reaction environment. This film, increases the local concentration of reagents adsorbed from the gas phase and changes their microenvironment. Working with Bu₄P⁺Br⁻ instead of PEG (entry 6, footnote i), large amounts of ureas are also produced.

(3) (a) Quesada, M. L.; Schlessinger, R. H. *J. Org. Chem.* **43**, 1978, 346–347. (b) Krapcho, A. P.; Jahgen, E. G. E.; Kashdan, D. S. *Tetrahedron Lett.* **32**, 1974, 2721–2723. (c) Hart, W. P.; Maconber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196–1198. (d) Romano, U.; Fornasari, G.; Di Gioacchino, S.; Ger. Offen. DE 3 202 690, 1982.

(4) (a) Trotta, F.; Tundo, P. *Ital. Pat. Appl.* 20661 A/86, 1986. (b) Angeletti, E.; Trotta, F.; Tundo, P.; Venturello, P. *Ital. Pat. Appl.* 19971 A/86, 1986.

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(6) Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1978; Vol. II, p 310 and references therein.

(7) Stinson, S. C. *Chem. Eng. News*, Feb 17, 1986, 27–50.

Table II. Effect of the Carrier on the Reaction between Aniline and DMC under GL-PTC Conditions^a

carrier	composition (%) at steady conditions of reaction mixture ^b				
	PhNH ₂ ^c	PhNHCH ₃	PhN(CH ₃) ₂	HNHCOOCH ₃	PhNCH ₃ COOCH ₃
cyclohexane	52.6	31.6	0.4	0.7	14.6
THF	51.0	31.3	0.5	0.7	16.7
dioxane	55.4	27.8		1.2	15.7
methanol	92.2	4.7	0.1	2.8	0.3

^a DMC/Aniline molar ratio = 1.2; to 39 mL of this mixture 60 mL of solvent was added; 95 g of K₂CO₃ coated with 5 wt % of PEG 6000; T = 180 °C; atmospheric pressure; liquid flow = 24 mL/h. ^b See Table I, footnote b. ^c Not reacted.

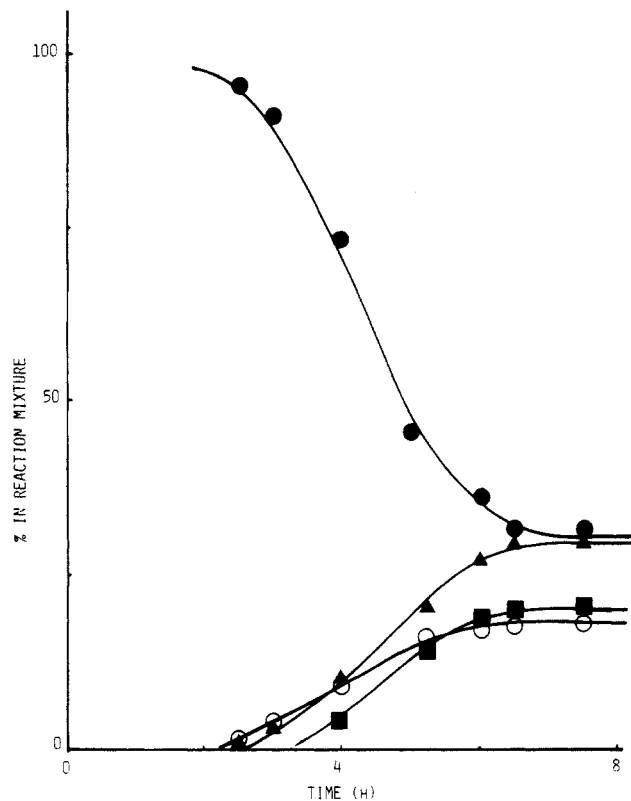


Figure 1. Variation in composition of reactor effluent with time. At the beginning only DMC (and methanol) comes out the column; subsequently, the effluent becomes richer in aniline and then in its reaction products [aniline and DMC (1:10 mol/mol); 180 °C; atmospheric pressure; flow rate, 30 mL/h. Catalytic bed: 40 g of α -Al₂O₃ coated with 5% of K₂CO₃ and 5 wt % of PEG 6000]: (●) % of PhNH₂; (○) % of PhNHCH₃; (▲) % of PhNCH₃COOCH₃; (■) % of PhNHCOOCH₃.

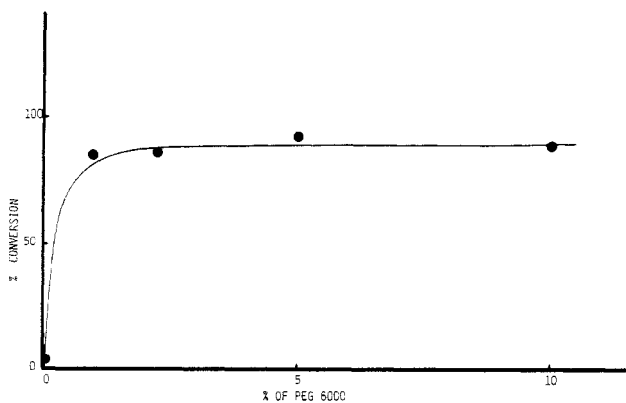


Figure 2. Influence of PEG 6000 on the reaction between aniline and DMC. Conditions were the same as in Figure 1, but liquid flow was 8 mL/h and α -Al₂O₃ pellets were coated with 5 wt % of K₂CO₃.

Several low-boiling compounds were used together with aniline and DMC. Table II shows that cyclohexane, tetrahydrofuran, or dioxane solvents promote the reaction

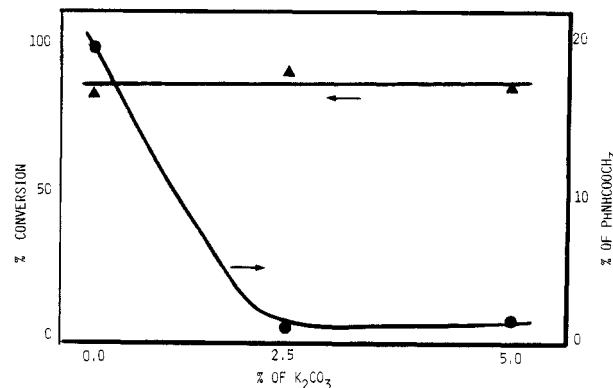


Figure 3. Influence of K₂CO₃ percent (on α -Al₂O₃ pellets coated with 5 wt % of PEG 6000) on the reaction between aniline and DMC. Conditions of Figure 2: (▲) % conversion of aniline (left scale); (●) % of PhNHCOOCH₃ in the reaction products (right scale).

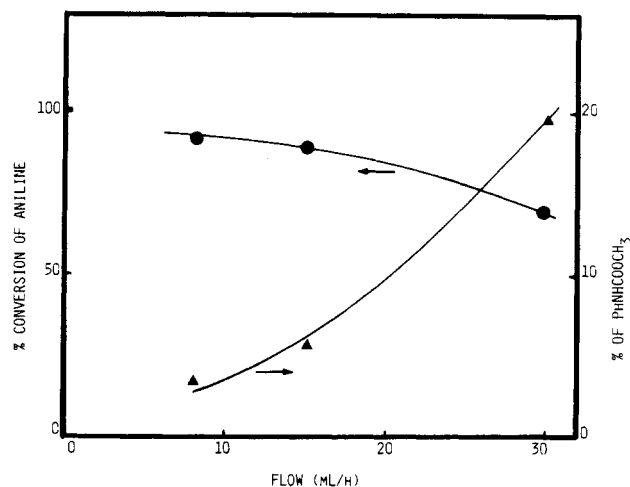


Figure 4. Influence of flow of the reagents in the reaction between aniline and DMC, carried out under the conditions of Figure 2: (●) % conversion of aniline (left scale); (▲) % of PhNHCOOCH₃ in the reaction products (right scale).

and its selectivity, while both are depressed with methanol.

Figure 3 demonstrates the importance of a basic environment. Note that in the absence of K₂CO₃, a higher amount of PhNHCOOCH₃ forms than in the presence of K₂CO₃.

N-(carboxymethyl)aniline is a reactive intermediate of the reaction: in fact as shown in Figure 4, increasing the reagents' flow (and then lowering the permanence of compounds in the reactor) increases the percent of *N*-(carboxymethyl)aniline; the decreased reaction time lowers, of course, the conversion of aniline.

As reported in the Experimental Section, the reactions of aniline with DMC and diethyl carbonate carried out under optimized conditions allow selective and high-yield synthesis of mono-*N*-alkylanilines. In fact, the only major byproduct, urethane PhNRCOOR, by hydrolysis also gives the corresponding amine.

Table III. Reactions of Aromatic Primary Amines with DMC under GL-PTC Conditions^a

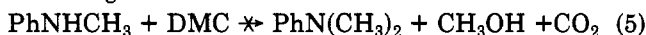
amine	composition (%) at equilibrium of the reaction mixture ^b				
	ArNH ₂	ArNHCH ₃	ArN(CH ₃) ₂	ArNHCOOCH ₃	ArNCH ₃ COOCH ₃
aniline ^c	54.3	40.8	1.6	<i>e</i>	3.3
<i>o</i> -toluidine ^d	27.7	47.0	0.3		25.0
<i>o</i> -chloroaniline ^d	14.6	62.7			22.7
<i>p</i> -chloroaniline ^e	10.1	70.0			19.9

^a 95 g of K₂CO₃ coated with 5 wt % of PEG 6000; *T* = 180 °C; atmospheric pressure; liquid flow = 24 mL/h. ^b See Table I, footnote b. ^c DMC/aniline molar ratio = 4.0. ^d DMC/aniline molar ratio = 10.0. ^e Trace.

Discussion

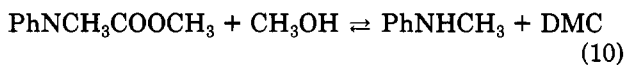
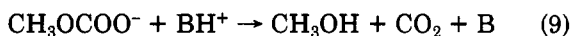
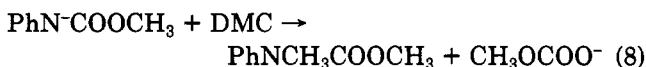
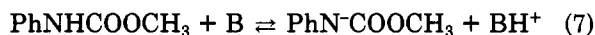
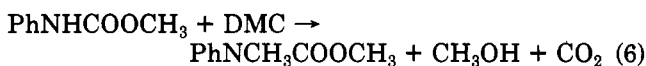
Mechanistic Aspects. PhNHCOOCH₃ is an intermediate of reaction since it is present in higher amount when the reaction mixture remains shorter in column (Figure 4). It is easy to suppose that this intermediate is produced by a transamination reaction of the aromatic amine on DMC (eq 4). As occurs under batch conditions,^{3d} this compound is the sole product of the reaction between aniline and DMC.

Actually PhNHCH₃ is not produced by a nucleophilic substitution of aniline on DMC, because, if so, it is difficult to explain why at the same time the double methylation (shown in eq 5) does not occur; it should have to take place according to the same mechanism.



The fact that the reaction shows a high selectivity even with a large excess of alkylating agent (up to 10 molar equiv were used; Table III, footnote d, and Figures 1–4) does not agree with a simple nucleophilic substitution. Therefore, mono-N-alkylaniline might be produced via its carboxyalkyl derivative, in accordance with eq 6–10 (Scheme I).

Scheme I



Equation 6, describing an overall reaction, is catalyzed by bases as show in Figure 3: it proceeds much slower in their absence. The need for a base is explained in eq 7, where the formation of the anion is favored by the presence of the carboxymethyl group. This anion reacts via S_N2 mechanisms with DMC (eq 8). Reaction 8 is decidedly selective since no trace of PhN(COOCH₃)₂ was detected. The observed selectivity then might arise from the exclusive carboxymethylation of the amine (eq 4) followed by the exclusive N-alkylation of the anion derivative of the urethane (eq 8). Finally, the reaction of CH₃OCOO⁻ with the protonated base allows the regeneration of the catalytic bed (eq 9).

For the overall reaction 3 to occur, PhNCH₃COOCH₃ is in equilibrium with PhNHCH₃ according eq 10. The correctness of this latest assumption was experimentally demonstrated^{8a} and also arises from thermodynamic cal-

culations. In fact in eq 10 the standard free energy, Δ*G*^o, computed in a gaseous state with the method of group contributions^{8b} is -1.1 kcal/mol at 298 K and of -3.0 kcal/mol at 453 K.

Also without ascribing high precision to these theoretically computed data, it is possible to assert that they, being small and negative, refer to a moderately favorable reaction.

However, other reaction pathways are possible; the mechanism here illustrated seems the more probable.

The differences observed between the reaction carried out in liquid phase and under GL-PTC conditions can be attributed to the low rate of reaction 8 under liquid-phase conditions. This result may be due to the fact that in batch conditions only low temperatures have been used with DMC,^{3d} owing to its low boiling point.

Reaction Environment. GL-PTC provides a peculiar reaction microenvironment not previously reported for continuous-flow syntheses:⁹ the reaction occurs in the liquid film of the molten catalyst, which, moreover, allows the activation of anions and bases present.

The gaseous reagents pass by a reversible exchange process in the liquid phase of the catalyst and thus increase their local concentration. The high reactivity observed¹⁰ then depends both on the reaction environment and the increased concentration of the reactive compounds. In this regard a comparison may be made with micellar catalysis¹¹ because both the catalyses depend on the same phenomena: however, no other common points exist between them. A better parallelism exists with gas-liquid chromatography: while here the presence of a liquid phase promotes the separation of the compounds, in GL-PTC the liquid phase allows the reaction.

The importance of reaction environment is emphasized by data reported in Table II, where different low-boiling compounds were used as gaseous carriers: both conversion and selectivity are affected.

Because the carrier is adsorbed on the liquid film, it may modify the properties of the catalyst; in particular the use of aprotic solvents allows high conversion and high selectivity. This behavior is in agreement with the solvent influence on the nucleophilic displacement rates.¹²

Methanol depressed the rate of eq 4 (lower conversion) and much more the rate of eq 6 (higher amount of PhNHCOOCH₃). Nevertheless, a strict comparison cannot be made between the type of solvent and the microenvironment because we do not know how much reagent and solvent are in the liquid film. To improve reaction con-

(8) (a) Feeding at 180 °C the solid bed (20 g of α-alumina pellets coated with 5% of PEG 6000 and 5% of K₂CO by weight) with a PhNCH₃COOCH₃-CH₃OH mixture (1:25 mol/mol) produces a moderate conversion (may be due to the unfavorable microenvironment) into PhNHCH₃ and DMC: these latter compounds are present in equal molar quantity. (b) Hougen, O. A.; Watson, K. M.; Ragatz, R. A. *Chemical Process Principles*; Wiley: New York, 1959; Part II, p 1004.

(9) Catalytic liquid films supported on solids and used in heterogeneous catalysis under continuous-flow conditions are largely applied in industry; they range from SO₂ → SO₃ oxidation to aromatic alkylation. For a review, see: Villadsen, J.; Livbjerg, H. *Catal. Rev.-Sci. Eng.* 1978, 17, 203-271.

(10) From the reaction reported in the Experimental Section, (aniline and DMC), one finds that about 9 g of PEG is able to convert 1 g of aniline per hour.

(11) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982.

(12) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; pp 316-322.

ditions, accurate determinations of such thermodynamically controlled and reversible exchanges will be necessary.

The formation of alkylated amines depends on the existence of PhN-COOCH_3 which comes from the reaction of PhNHCOOCH_3 with the base K_2CO_3 (eq 7). Here the nature of the liquid phase is important because the presence of a phase-transfer catalyst promotes the anionic activation of K_2CO_3 , increasing its basic properties.^{1e}

Finally, changing the nature of the liquid phase changes the reaction products: while the use of PEG leads to high selectivity, onium salts produce high amounts of ureas.

Conclusions

The synthesis of mono-*N*-alkylanilines shows some peculiarities of GL-PTC and its advantages. Compared with known methods that work under continuous-flow conditions, the GL-PTC synthesis operates at lower temperatures, at atmospheric pressure, and with a shorter contact time. This method is applicable to aromatic amines in general including more complex structures like α -naphthylamine.

Experimental Section

All the compounds employed were commercial samples (ACS grade) and used without further purification. α -Alumina pellets were acquired from "Industrie Bitossi", Vinci-Firenze. *n*-Tetrabutylphosphonium bromide¹³ and the reference compounds (urethanes and ureas) were synthesized according to the literature.¹⁴

Preparation of the Catalytic Beds. As report in Results, several beds were prepared, following similar procedures. Detailed explanation are here given for two of them.

Potassium Carbonate Coated with PEG 6000 (Table I, Entry 3, and Tables II and III). PEG 6000 (10.0 g) was dissolved in 300 mL of dichloromethane, and then 190 g of potassium carbonate was added. The solvent was removed under vacuum, and the solid obtained was put in an oven for 2 h at 120 °C.

α -Alumina Pellets Coated with 5% of K_2CO_3 and 5 wt % of PEG 6000 (Figure 1). K_2CO_3 (10.0 g) and 10.0 g of PEG 6000 were dissolved in 150 mL of water. Then 180 g of pellets was added and the water removed under vacuum; the coated spheres

were put in an oven at 110 °C for one night.

Execution of the Reactions. The columns used were of different types: the first one (48-cm length, 2-cm diameter) was filled with potassium carbonate supporting the catalyst and was employed for the results reported in Tables I-III. A second, smaller column (48-cm length, 1.4-cm diameter) was used for the experiences of Figures 1-4 and contained the coated α -alumina pellets.

The columns were packed with the required amount of catalytic bed (see all tables and figures) and thermostated at 180 °C with continuous circulation of oil (Ultrathermostat Lauda MGW). The mixture of aromatic amines and dialkyl carbonates was continuously sent in the reactor with a syringe pump (Sage Instruments 341A).

The reaction products were recovered at the outlet of the column by collecting the gas with a Liebig condenser. The mixtures of the products were analyzed by gas chromatography (Varian Vista 6000) by comparison with authentic samples.

Reaction of Aniline with DMC and Diethyl Carbonate in a Larger Reactor. In order to reach higher conversions, the reaction between aniline and DMC was carried out in a large column (60-cm length, 3.5-cm diameter) containing 175 g of catalytic bed composed by α -alumina coated with 5% of K_2CO_3 and 5 wt % of PEG 6000.

The mixture of aniline and DMC (1:10 mol/mol) was sent continuously through the column at a liquid flow of 10 mL/h. The temperature was 180 °C and the pressure atmospheric. After 6 h the composition of the affluent remains unchanged; it was as follows: $\text{PhNH}_2 = 8.6\%$; $\text{PhNHCH}_3 = 60.5\%$; $\text{PhNHCOOCH}_3 = 1.0\%$; $\text{PhNCH}_3\text{COOCH}_3 = 29.9\%$.

Under the same conditions the reaction between aniline and diethyl carbonate was performed. After the steady conditions were reached, the composition of reaction mixture was as follows: 24.4% of unreacted aniline, 56.5% of *N*-ethylaniline, and 19.7% of *N*-(ethoxycarbonyl)-*N*-ethylaniline.

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Registry No. PhNH_2 , 62-53-3; Ph, 103-69-5; $\text{PhNCH}_3\text{COOCH}_2\text{CH}_3$, 1013-75-8; PhNHCH_3 , 100-61-8; $\text{PhN}(\text{CH}_3)_2$, 121-69-7; $\text{PhNCH}_3\text{COOCH}_3$, 28685-60-1; *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$, 95-53-4; *o*- $\text{ClC}_6\text{H}_4\text{NH}_2$, 95-51-2; *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$, 106-47-8; *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{NHCH}_3$, 611-21-2; *o*- $\text{ClC}_6\text{H}_4\text{NHCH}_3$, 932-32-1; *p*- $\text{ClC}_6\text{H}_4\text{NHCH}_3$, 932-96-7; *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{NCH}_3\text{COOCH}_3$, 104189-18-6; *o*- $\text{ClC}_6\text{H}_4\text{NCH}_3\text{COOCH}_3$, 106712-21-4; *p*- $\text{ClC}_6\text{H}_4\text{NCH}_3\text{COOCH}_3$, 60561-39-9; DMC, 616-38-6; diethyl carbonate, 105-58-8.

(13) Fukui, K.; Kanai, K.; Takezono, T.; Kitano, H. *Kogyo Kagaku Zasshi* **1964**, *67*, 1131.

(14) Starting from the corresponding amine with phosgene or methyl chloroformate.