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Gas-phase pyrolytic reaction of 3-anilino-1-propanol derivatives: kinetic and mechanistic study

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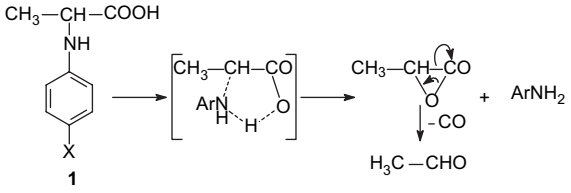
Abstract—3-Anilino-1-propanol derivatives **4a–c**, **5a–c**, **6a–c** containing primary, secondary, and tertiary alcohols and PhNH, PhNMe, and $(Ph)_2N$ were prepared and subjected to gas-phase pyrolysis in a static reaction system. The pyrolytic reactions were homogeneous and followed a first-order rate equation. Reactions took place by retro-ene process, with the exception of compounds **5a** and **5b**. Analysis of the pyrolysate showed the products to be *N*-substituted aniline and carbonyl compounds. The kinetic results and product analysis of each of the nine investigated 3-amino alcohols are rationalized in terms of a plausible transition state for the elimination pathway.

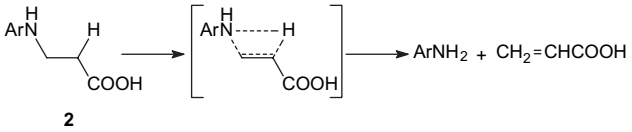
1. Introduction

We have recently shown that the thermal gas-phase elimination reaction of 2-*N*-arylaminopropanoic acid **1** and 3-*N*-arylaminopropanoic acid **2** are homogeneous and free from catalytic and radical pathways. The pyrolysate of **1** showed the elimination products to be CO, CH_3CHO, and aniline (Scheme 1), while the pyrolysate of **2** reveals the formation of acrylic acid in addition to aniline.[1]



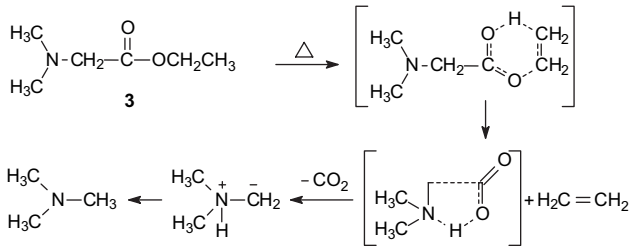
Scheme 1. Pyrolysis of 2-*N*-arylaminopropanoic acid.

This together with theoretical calculation on **2** suggest a reaction pathway involving σ four-membered transition state (Scheme 2).



Scheme 2. Pyrolysis of 3-*N*-arylaminopropanoic acid.

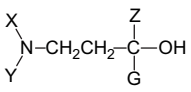
The gas-phase elimination reaction of ethyl *N*,*N*-dimethylglycinate **3** in a static reaction system leads to the formation of the corresponding α-amino acid and ethylene,[2] the amino acid intermediate then undergoes an extremely rapid decarboxylation process (Scheme 3).



Scheme 3. Pyrolysis of ethyl *N*,*N*-dimethylglycinate.

In this study, we look at the pyrolysis reaction of 3-amino primary, secondary, and tertiary propyl alcohols, the amino substituents are: PhNH- (**4a–c**), PhNMe- (**5a–c**), and $(Ph)_2N$- (**6a–c**) (Table 1).

Table 1. Substrates under study



Compound	X	Y	Z	G
4a	Ph	H	H	H
4b	Ph	H	H	Me
4c	Ph	H	Me	Me
5a	Ph	Me	H	H
5b	Ph	Me	H	Me
5c	Ph	Me	Me	Me
6a	Ph	Ph	H	H
6b	Ph	Ph	H	Me
6c	Ph	Ph	Me	Me

Keywords: 3-Anilino-1-propanol; Pyrolysis; Kinetics; Reaction mechanism.
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2. Results and discussion

2.1. Synthesis

Substrates **4a–c**, **5a–c**, and **6a–c** were prepared and fully characterized by NMR and MS as described in Section 3.

2.2. Pyrolysates

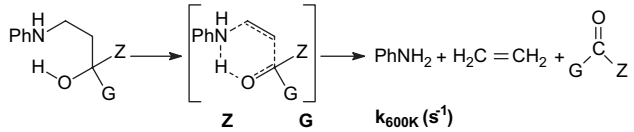
Reaction products for complete pyrolysis were qualitatively and quantitatively obtained for all the nine substrates in a sealed-tube pyrolyser (static method) at temperatures exceeding those used in the kinetic investigations (Table 2). The static-method reactions were used to allow ample residence time to ensure maximum pyrolysis. The constituents of the pyrolysates obtained by this method were isolated using preparative liquid chromatography and analyzed using GC–MS and ^{1}H NMR techniques.

Table 2. Pyrolysis products and % yield

No.	Compound	Product/% yield		
4a	$PhNH(CH_2)_3OH$	$PhNH_2$/85	CH_2O/28	$CH_2{=}CH_2$
4b	$PhNH(CH_2)_2CH(OH)CH_3$	$PhNH_2$/51	CH_3CHO/46	
4c	$PhNH(CH_2)_2CH(OH)(CH_3)_2$	$PhNH_2$/74	$(CH_3)_2CO$/20	
5a	$PhN(Me)(CH_2)_3OH$	$PhNMe_2$/76	CH_3CHO/42	
5b	$PhN(Me)(CH_2)_2CH(OH)CH_3$	$PhNMe_2$/82	$(CH_3)_2CO$/25	
5c	$PhN(Me)(CH_2)_2CH(OH)(CH_3)_2$	PhNHMe/68	$(CH_3)_2CO$/32	
6a	$(Ph)_2N(CH_2)_3OH$	Ph_2NH/88	CH_2O/8	$CH_2{=}CH_2$
6b	$(Ph)_2N(CH_2)_2CH(OH)CH_3$	Ph_2NH/64	CH_3CHO/26	
6c	$(Ph)_2N(CH_2)_2CH(OH)(CH_3)_2$	Ph_2NH/85	$(CH_3)_2CO$/30	

2.3. Reaction mechanism and molecular reactivities

2.3.1. 3-Anilino-1-propanol 4a, 3-anilino-2-butanol 4b, and 3-anilino-2-methyl-2-butanol 4c. Each of the 3-anilino alcohols eliminates aniline and ethylene together with a carbonyl compound CH_2O, CH_3CHO, and $(CH_3)_2CO$ from **4a**, **4b**, and **4c**, respectively. Identification of these pyrolysis products suggest the reaction pathway shown in Scheme 4.



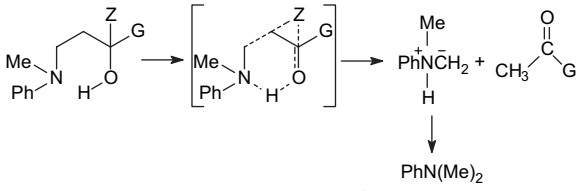
	Z	G	k_{600K} (s^{-1})
4a	H	H	5.95×10^{-5}
4b	H	Me	1.74×10^{-3}
4c	Me	Me	5.06×10^{-2}

Scheme 4. Reaction pathway and first-order rate constant at 600 K for the pyrolytic reaction of **4a–c**.

The pyrolysis of the 3-amino tertiary alcohol is faster than the secondary alcohol, which in turn is faster than the primary one. The rate enhancement of 850 produced by electron-donating groups (Z and G=Me) in **4c** over **4a** (Z and G=H) is consistent with polarization of the O–C bond creating $C^{\delta+}$–$O^{\delta-}$. The reactivity order of **4b** (Z=H, G=Me) over **4a** (Z and G=H) could be rationalized by the same effect of the methyl group as an electron-donating group.

The effect of methylation has been observed in the following series: ethyl, isopropyl, *tert*-butyl acetate pyrolysis and explained in terms of increasing stabilization of the incipient carbocation.[3]

2.3.2. 3-*N*-Methylanilino-1-propanol 5a, 3-*N*-methylanilino-2-butanol 5b, and 3-*N*-methylanilino-2-methyl-2-butanol 5c. The pyrolysates from the pyrolytic reaction of substrates **5a** and **5b** were ascertained to be dimethylaniline $PhN(Me)_2$, together with CH_3CHO and $(Me)_2CO$ from **5a** and **5b**, respectively. The reaction pathway shown in Scheme 5 is compatible with the products of pyrolysis.

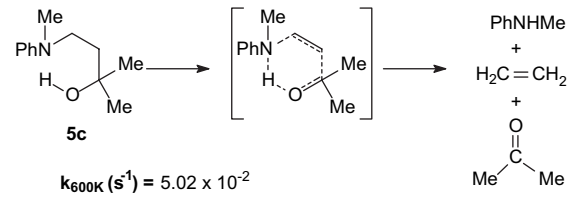


	Z	G	k_{600K} (s^{-1})
5a	H	H	5.22×10^{-4}
5b	H	Me	1.17×10^{-3}

Scheme 5.

Changing G from H in **5a** to Me in **5b** did not enhance the reaction rate considerably, which could be justified by the more important rate controlling factor of protophilic attack by the nitrogen atom on the hydrogen of the hydroxyl group. Comparable reactivity of **5a** and **5b** supports this suggestion, as the basicity of the nitrogen atom involved in the reaction is the same in both substrates **5a** and **5b**.

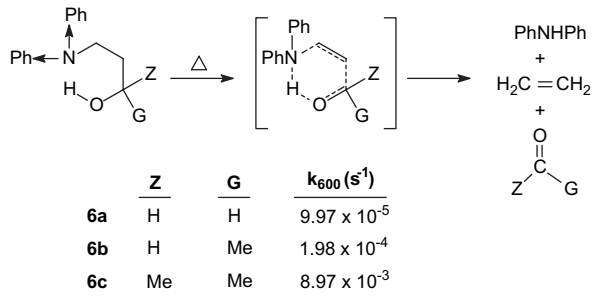
The pyrolysates from the pyrolytic reaction of the substrate **5c** were identified as *N*-methylaniline and acetone. Formation of these products can be explained in terms of a six-membered transition state (Scheme 6).



Scheme 6.

The only structural feature which distinguishes **5c** from **5a** and **5b** is the two electron-donating groups, Z=G=Me in **5c**, this has not only produced rate enhancement, but also changed the reaction pathway.

2.3.3. 3-*N*,*N*-Diphenylamino-1-propanol 6a, 3-*N*,*N*-diphenylamino-2-butanol 6b, and 3-*N*,*N*-diphenylamino-



	Z	G	k_{600} (s^{-1})
6a	H	H	9.97×10^{-5}
6b	H	Me	1.98×10^{-4}
6c	Me	Me	8.97×10^{-3}

Scheme 7.

2-methyl-2-butanol 6c. Each of the 3-*N*,*N*-diphenylamino alcohols **6a–c** eliminates diphenylamine (Ph_2NH together with CH_2O, CH_3CHO, and acetone from **6a**, **6b**, and **6c**, respectively) suggesting a reaction pathway shown in Scheme 7.

The two phenyl groups at the nitrogen in the substrates **6a–c** will reduce the basicity of the nitrogen atom by effective delocalization of nitrogen lone pair, this will increase the polarization of the N–C bond and hence increase the rate of its cleavage. The extent of this polarization of the N–C bond should be similar in each substrate **6a–c**. The reactivity order of 90 and 45 of **6c** over **6a** and **6b**, respectively, could be explained in terms of the stabilization caused by the two methyl groups in **6c** on the six-membered transition state proposed in the mechanistic pathway for these substrates. Kinetic results and Arrhenius parameters are shown in Table 3.

Table 3. Rate coefficient (k, s^{-1}) and Arrhenius parameters of compounds (**4–6**)

Compound	T (K)	10^4 k (s^{-1})	log A (s^{-1})	E_a (kJ mol^{-1})	K_{600K} (s^{-1})
4a	615.05	0.960	4.690±0.18	102.45±2.37	5.95×10^{-5}
	634.05	1.956			
	653.05	3.681			
	671.65	4.534			
	691.45	8.900			
	749.55	35.71			
4b	528.65	2.270	3.818±0.25	75.556±2.74	1.74×10^{-3}
	543.95	3.838			
	558.15	5.714			
	586.75	10.63			
	615.35	25.50			
	629.55	38.30			
4c	456.55	0.853	7.552±0.43	101.65±3.93	5.06×10^{-2}
	473.45	2.650			
	482.05	3.801			
	409.55	4.969			
	507.85	13.33			
5a	609.25	6.560	3.884±0.13	82.333±1.63	5.22×10^{-4}
	637.75	14.19			
	652.05	19.96			
	666.35	26.78			
	680.75	36.53			
5b	519.65	2.710	1.267±0.071	48.232±0.80	1.17×10^{-3}
	544.25	4.335			
	570.15	6.814			
	595.95	10.76			
	621.65	16.28			
	647.35	24.58			
5c	456.55	0.787	7.589±0.44	102.11±0.98	5.02×10^{-2}
	473.45	2.065			
	482.05	3.801			
	499.05	4.906			
	507.85	12.44			
6a	611.95	1.572	7.797±0.34	135.55±4.25	9.97×10^{-5}
	624.75	3.183			
	650.55	7.945			
	663.45	14.81			
	676.35	20.78			
	689.15	32.20			
6b	608.25	2.465	5.167±0.23	101.91±2.92	1.98×10^{-4}
	622.65	4.531			
	651.65	9.930			
	680.05	20.87			
	708.75	46.54			
6c	472.05	4.555	2.830±0.34	56.035±0.32	8.97×10^{-3}
	484.75	5.853			
	489.15	8.570			
	510.15	12.56			
	522.45	17.54			

3. Experimental

3.1. General

All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz super-conducting NMR spectrometer. Mass spectra were measured on VG Autospec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalysis was performed on a LECO CHNS-932 Elemental Analyzer. The starting compounds **4a–c**, **5a**,**b**, and **6a** were prepared by modifications of reported procedures.

3.1.1. 3-Anilino-1-propanol 4a.[6,7] A mixture of aniline (5.4 mL, 5.5 mmol) and 3-chloro-1-propanol (1.74 mL, 1.8 mmol) was heated at 95–105 °C for 5 h. After cooling, the product was extracted with ether (50 mL), washed with aqueous sodium hydroxide (20 mL, 1 N), and dried over anhydrous sodium sulfate. After removal of the solvent, the product was obtained by vacuum distillation under reduced pressure, bp 128–132 °C, 0.5 mm (lit.[7] bp 140 °C, 0.5 mm) as greenish yellow oil, yield 1.9 g (72%). MS: *m*/*z*=151 (M^+, 80%). ^{1}H NMR ($CDCl_3$): δ 1.86 (quint, 2H, *J* 6.1, CH_2), 3.26 (t, 2H, *J* 6.1, CH_2N), 3.53 (br, 2H, NH, OH), 3.76 (t, 2H, *J* 6.1, CH_2O), 6.69 (d, 2H, *J* 8.0), 6.75 (t, 1H, *J* 8.1), 7.24 (t, 2H, *J* 7.6). Anal. Calcd for $C_9H_{13}NO$ (151.2): C 71.49; H 8.67; N 9.26. Found: C 71.24; H 8.72; N 9.44.

3.1.2. 3-*N*-Methylanilino-1-propanol 5a. A mixture of 3-chloro-1-propanol (6.8 g, 77 mmol), freshly distilled *N*-methylaniline (7.7 g, 77 mmol), KI (0.35 g, 2.15 mmol), K_2CO_3 (10 g, 77 mmol), and butanol (40 mL) was heated under reflux for 4 days under nitrogen. After cooling and filtration of the suspended salts, the solvent was removed in vacuo. The remaining yellow oil was purified by vacuum distillation, bp 170–175 °C, 0.5 mm (lit.[7] 160 °C, 0.5 mm), yield 7 g (53%). MS: *m*/*z*=165 (M^+, 80%). ^{1}H NMR ($CDCl_3$): δ 1.86 (quint, 2H, *J* 6.2), 1.90 (br, 1H, OH), 2.96 (s, 3H, NCH_3), 3.49 (t, 2H, *J* 6.2), 3.77 (t, 2H, *J* 6.2), 6.76 (t, 1H, *J* 7.2), 6.81 (d, 2H, *J* 7.9), 7.27 (t, 2H, *J* 6.9).[10,11] ^{13}C NMR ($CDCl_3$): δ 29.6 (CH_3), 38.5 (CH_2), 50.0 (CH_2), 60.7 (CH_2), 112.9 (2CH), 116.9 (CH), 129.3 (2CH), 149.7 (C).

3.1.3. 3-*N*,*N*-Diphenylamino-1-propanol 6a. A mixture of diphenylamine (1.69 g, 1.0 mmol), 3-iodo-1-propanol (1.86 g, 1.0 mmol), anhydrous K_2CO_3 (0.2 gm), and tetrabutylammonium bromide (0.2 g) was placed in the microwave oven (Panasonic, Model Dimension, 4, NN-C 200S), and irradiated with power at high temperature for 3 min. The product was then extracted with ethyl acetate (10 mL) and purified with silica gel column chromatography using ethyl acetate–hexane solvent mixture, R_f=0.73 (EtOAc–hexane, 1:9), dark yellow oil, yield 0.6 g (26%).[13,14] MS: *m*/*z*=227 (M^+, 20%). ^{1}H NMR ($CDCl_3$): δ 1.5 (br, 1H, OH), 1.94 (quint, 2H, *J* 6.3), 3.46 (t, 2H, *J* 6.3), 3.86 (t, 2H, *J* 6.2), 6.95 (t, 2H, *J* 7.8), 7.04 (d, 4H, *J* 8.0), 7.27 (t, 4H, *J* 8.0).

3.2. Synthesis of 4-anilino-2-butanols 4b, 5b, and 6b: general procedure

To a solution of the appropriate 4-anilino-2-butanone (10 mmol) in methanol (50 mL) was added $NaBH_4$ at room temperature portionwise with stirring (0.5 g, 15 mmol). The reaction mixture was then stirred at room temperature for 1 h and the solvent was removed in vacuo. The product was extracted with ether (3×50 mL), washed with water, and dried over anhydrous sodium sulfate. The solvent was then removed in vacuo and the remaining product was purified by silica gel column chromatography.

3.2.1. 4-Anilino-2-butanol 4b. Prepared from 4-anilino-2-butanone,[8] colorless oil, yield 1.4 g (85%), purified using ethyl acetate–hexane as an eluent [R_f=0.4, EtOAc–hexane (1:4)] and recrystallized from hexane as colorless crystals, mp 62–63 °C (lit.[9a] 60–62 °C). MS: *m*/*z*=165 (M^+, 90%), 93 (30%); ^{1}H NMR ($CDCl_3$): δ 1.26 (d, 3H, *J* 6.2, CH_3), 1.78 (m, 2H, CH_2COH), 2.19 (br, 2H, NH, OH), 3.29 (m, 2H, N–CH_2), 4.00 (m, 1H, CH–O), 6.70 (d, 2H, *J* 7.9), 6.79 (t, 1H, *J* 7.8), 7.24 (t, 2H, *J* 7.8). ^{13}C NMR ($CDCl_3$): δ 24.0 (CH_3), 38.1 (CH_2), 39.9 (CH_2), 67.3 (CH–OH), 113.5 (2CH), 119.8 (CH), 129.4 (2CH), 148.5 (C).

3.2.2. 4-*N*-Methylanilino-2-butanol 5b.[9b,12] Prepared from 4-*N*-methylanilino-2-butanone,[12] colorless oil, yield 1.4 g (77%), purified using $CHCl_3$–pet. ether 60–80 as an eluent [R_f=0.74, $CHCl_3$–pet. ether 60–80 (1:2)]. ^{1}H NMR ($CDCl_3$): δ 1.27 (d, 3H, *J* 6.2, CH_3), 1.73 (m, 2H, CH_2), 2.36 (br, 1H, OH), 2.95 (s, 3H, NCH_3), 3.47 (m, 2H, CH_2), 3.94 (m, 1H), 6.78 (t, 1H, *J* 7.2), 6.83 (d, 2H, *J* 8.0), 7.28 (t, 2H, *J* 8.0). ^{13}C NMR ($CDCl_3$): δ 24.3 (CH_3), 35.9 (CH_3), 38.9 (CH_2), 51.1 (CH_2), 67.2 (COH), 113.6 (2CH), 117.4 (CH), 129.5 (2CH), 150.1 (C).

3.2.3. 4-*N*,*N*-Diphenylamino-2-butanol 6b. Prepared from 4-*N*,*N*-diphenylamino-2-butanone,[15] dark yellow oil, yield 1.0 g (71%), purified using ethyl acetate–hexane as an eluent [R_f=0.44, EtOAc–hexane (1:4)]. MS: *m*/*z*=241 (M^+, 30%), 182 (100%), 168 (15%). ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 3H, *J* 6.2, CH_3), 1.79 (m, 3H, CH_2–, OH), 3.89 (m, 3H, NCH_2, CHO), 6.99 (t, 2H, *J* 7.6), 7.06 (d, 4H, *J* 7.6), 7.31 (t, 4H, *J* 7.6). ^{13}C NMR ($CDCl_3$): δ 24.3 (CH_3), 36.6 (CH_2), 49.4 (CH_2), 66.5 (C), 121.2 (4CH), 121.5 (2CH), 129.5 (4CH), 148.2 (2C). Anal. Calcd for $C_{16}H_{19}NO$ (241.3): C 79.63; H 7.94; N 5.80. Found: C 79.54; H 7.72; N 5.64.

3.3. Synthesis of 4-anilino-2-butanols 4c, 5c, and 6c: general procedure

To a solution of MeMgI (freshly prepared from 1.0 g Mg and 2.5 mL MeI in 40 mL dry ether) was added the appropriate 4-anilino-2-butanone (10 mmol) at room temperature portionwise with stirring under a nitrogen atmosphere. The reaction mixture was heated under reflux for 24 h. After cooling to room temperature, the mixture was quenched with saturated aqueous ammonium chloride solution, the ethereal layer was separated, and the aqueous layer was further extracted with ether (3×50 mL). The combined ethereal extract was dried over anhydrous sodium sulfate. The solvent was then removed in vacuo and the remaining product was purified by silica gel column chromatography.

3.3.1. 4-Anilino-2-methyl-2-butanol 4c. Prepared from 4-anilino-2-butanone,[8] colorless oil, yield 1.0 g (60%), purified using ethyl acetate–pet. ether 60–80 as an eluent [R_f=0.4, EtOAc–pet. ether 60–80 (1:9)] and recrystallized from hexane

to give colorless crystals, mp 58–60 °C (lit.[10] 58–60 °C). MS: *m*/*z*=179 (M^+, 20%), 106 (100%), 77 (20%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 6H, $2CH_3$), 1.84 (t, 2H, *J* 6.8), 2.68–2.92 (br, 2H, NH, OH), 3.32 (t, 2H, *J* 6.8), 6.68 (d, 2H, *J* 8.0), 6.76 (t, 1H, *J* 7.2), 7.21 (t, 2H, *J* 7.2).[9a,10] ^{13}C NMR ($CDCl_3$): δ 30.0 ($2CH_3$), 39.9 (CH_2), 42.2 (CH_2), 71.3 (COH), 113.6 (2CH), 118.2 (CH), 129.6 (2CH), 148.5 (C).

3.3.2. 4-*N*-Methylanilino-2-methyl-2-butanol 5c. Prepared from 4-*N*-methylanilino-2-butanone,[12] brown oil, yield 1.5 g (77%),[13] purified using $CHCl_3$–pet. ether 60–80 as an eluent [R_f=0.44, $CHCl_3$–pet. ether 60–80 (3:7)]. MS: *m*/*z*=193 (M^+, 90%). ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 6H, $2CH_3$), 1.77 (t, 2H, *J* 7.7, CH_2), 2.16 (br, 1H, OH), 2.94 (s, 3H, NCH_3), 3.49 (t, 2H, *J* 7.7, CH_2), 6.77 (t, 1H, *J* 7.2), 6.82 (d, 2H, *J* 8.0), 7.28 (t, 2H, *J* 8.0). ^{13}C NMR ($CDCl_3$): δ 29.9 ($2CH_3$), 38.8 (CH_2), 38.9 (CH_2), 49.3 (NCH_3), 70.8 (C–OH), 113.7 (2CH), 117.4 (CH), 129.5 (2CH), 149.9 (C). Anal. Calcd for $C_{12}H_{19}NO$ (193.3): C 74.57; H 9.91; N 7.25. Found: C 74.44; H 9.72; N 7.14.

3.3.3. 4-*N*,*N*-Diphenylamino-2-methyl-2-butanol 6c. Prepared from 4-*N*,*N*-diphenylamino-2-butanone,[15] brown oil, yield 1.5 g (58%), purified using ethyl acetate–pet. ether 60–80 as an eluent [R_f=0.4, EtOAc–pet. ether 60–80 (1:4)]. MS: *m*/*z*=255 (M^+, 60%), 182 (100%), 168 (20%). ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 6H, $2CH_3$), 1.56 (br, 1H, OH), 1.89 (t, 2H, *J* 7.2, CH_2), 3.91 (t, 2H, *J* 7.2, CH_2), 6.98 (t, 2H, *J* 7.2), 7.05 (d, 4H, *J* 7.2), 7.30 (t, 4H, *J* 7.2). ^{13}C NMR ($CDCl_3$): δ 29.7 ($2CH_3$), 40.1 (CH_2), 48.1 (CH_2), 70.5 (C–OH), 121.1 (4CH), 121.4 (2CH), 129.5 (4CH), 148.0 (2C). Anal. Calcd for $C_{17}H_{21}NO$ (255.3): C 79.96; H 8.29; N 5.49. Found: C 79.84; H 8.12; N 5.44.

3.4. Kinetic runs and data analysis

Procedures for the kinetic measurements have been detailed in our earlier paper.[1–4]

3.5. General procedure for product analysis

The sample was volatilized from a tube in a Büchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 600 °C, the temperature being monitored by a Pt/Pt-13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be $\cong$10 ms. The different zones of the products collected in the U-shaped trap were analyzed by ^{1}H NMR, LCMS, and GC–MS. Relative and percent yields were determined from ^{1}H NMR.[4,5]

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