Tetrahedron Vol. 49, No. 35, pp. 7761-7768, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Naphthalene-Catalysed Lithiation of Phenone Imines in the Presence of Carbonyl Compounds: Preparation of 1,2-Aminoalcohols

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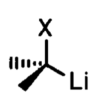
(*Received in UK* 21 *June* 1993)

Abstract: The lithiation of different phenone imines **1** with an excess of lithium powder and a catalytic amount (8 mol %) of naphthalene in the presence of several carbonyl compounds **2** in tetrahydrofuran at temperatures ranging between -78 and 20°C leads, after hydrolysis with water, to the corresponding 1,2-aminoalcohols **3** in moderate yields.

Introduction

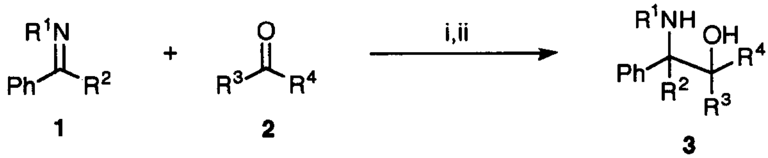
Reagents of the type **I**[1], which should be consider as d^1 reagents following Seebach's nomenclature[2], are interesting functionalised organolithium compounds[3] in organic synthesis. Their umpolung reactivity[2] permits the preparation of 1,2-difunctionalised compounds, which are of difficult access by other conventional routes. We have recently described[4] the preparation of dianionic intermediates of the type **I** with X=OLi by direct lithiation of diaryl ketones catalyzed by naphthalene[5,6], and studied their application to the synthesis of functionalised diaryl methanols. In the present paper we describe the preparation of intermediates of the type **I** with X=RNLi by naphthalene catalyzed lithiation of phenone imines and their *in situ* reaction with carbonyl compounds in a Barbier-type process.



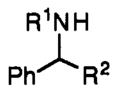
I

Results and Discussion

The reaction of different phenone imines **1**[7] with an excess of lithium powder[8] (1:14 molar ratio) and a catalytic amount of naphthalene [1:0.16 molar ratio (8 mol %)] in the presence of several carbonyl compounds **2** (1:1.2 molar ratio) in tetrahydrofuran at temperatures ranging between -78 and 20°C led, after hydrolysis with water, to the corresponding 1,2-aminoalcohols **3** in moderate yields (Scheme 1 and Table 1). Together with the products **3** we always obtained variable amounts of the corresponding amine **4**, resulting from the reduction of the starting imine by means of the metal[9]. In the case of starting from diphenylmethyleneaniline only the corresponding amine **4e** was isolated in good yields (Table 1, entries 12 and 13). When aldehydes were used as carbonyl compounds the corresponding mixture of diastereoisomers was isolated (Table 1, entries 1 and 2 and footnotes b and d). It is noteworthy that only conjugate addition was observed in the case of using 2-cyclohexenone as carbonylic component, the corresponding diastereoisomer mixture being isolated (Table 1, entry 7 and footnotes e and f). Concerning other possible reaction products, such as pinacoline coupling compounds derived from the imines **1** or the carbonyl compounds **2**, we found in all cases less than 13% and 17% yield in both by-products, respectively, being in most cases around 5% in each case (exception: 23% of 2,3-dimethylbutane-2,3-diol in the reaction with acetone; see Table 1, entry 3). The separation of the pinacoline-type by-products and, consequently, the purification of aminoalcohols **3** was carried out easily in all cases by routine flash chromatography[10].



Scheme 1. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ cat. (8 mol %), THF, -78 to 20°C; ii, H_2O.



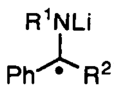
4a : R^1=Ph, R^2=H
4b : R^1=Cy, R^2=H
4c : R^1=Me, R^2=H
4d : R^1=Ph, R^2=Me
4e : R^1=R^2=Ph

The formation of byproducts **4** could take place in the last hydrolysis with water since at this point an excess of lithium is still present. However, when the reaction of benzylidenecyclohexylamine with acetone under the reaction conditions indicated above (Table 1, entry 8) was filtered off before the hydrolysis with water in order to eliminate the excess of lithium powder, the same result was practicaly obtained. It would mean that the probable mechanism involves an electron transfer from the small amount of lithium naphthalenide present in the solution to the imine giving successively the species **II** and **III**; this last intermediate either reacts with the carbonyl compound **2** giving the 1,2-aminoalcohol **3** or takes a proton fron the reaction media (probably from the alfa position of the carbonyl group in compound **2**) to yield the amine **4**.

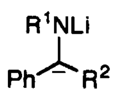
Table 1. Preparation of 1,2-aminoalcohols **3**

	Imine **1**		Carbonyl compound **2**		Aminoalcohol **3**
Entry	R^1	R^2	R^3	R^4	no. [yield (%)[a]]
1	Ph	H	Pr^i	H	**3a**[b] [22 (18)[c]]
2	Ph	H	Ph	H	**3b** [32 (40)[c]]
3	Ph	H	Me	Me	**3c** [33 (17)[c]]
4	Ph	H	Et	Et	**3d** [75 (3)[c]]
5	Ph	H	$-[CH_2]_4-$		**3e** [41 (6)[c]]
6	Ph	H	$-[CH_2]_5-$		**3f** [51 (8)[c]]
7	Ph	H	-[e]		**3g**[f] [25 (17)[c]]
8	Cy[g]	H	Me	Me	**3h** [20 (51)[c]]
9	Cy[g]	H	Et	Et	**3i** [32 (53)[c]]
10	Me	H	$-[CH_2]_5-$		**3j** [21 (20)[c]]
11	Ph	Me	Et	Et	**3k** [31 (46)[c]]
12	Ph	Ph	Pr^i	H	**3l** [- (85)[c]]
13	Ph	Ph	$-[CH_2]_5-$		**3m** [- (91)[c]]

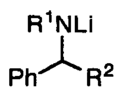
[a] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting imine **1**; all isolated products were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Diastereoisomers ratio: 2.7/1 (GLC). [c] In parenthesis isolated yield of the corresponding amines **4** based on the starting imine **1**. [d] Diastereoisomers ratio: 7.3/1 (300 MHz ^{1}H NMR). [e] 2-Cyclohexenone was used as electrophile. [f] 3-[1-(Phenylamino)-phenylmethyl]cyclohexanone; diastereoisomers ratio: 1.3/1 (75 MHz ^{13}C NMR). [g] Cy=cyclohexyl.



II



III



IV

From the results described in this paper we conclude that in spite of the generally modest yields in the preparation of 1,2-aminoalcohols **3** the method here reported can be useful because (a) compounds **3** are easily separated from the amines **4** and other pinacoline-type by-products by flash chromatography, and (b) they are important structural moiety in both organic and medicinal chemistry[11].

Experimental Part

General.- For general information see reference 6c. Retention times (t_r) are given under the conditions described in reference 6d. Microanalyses were performed by the Microanalyses Service of the University of Alicante. High resolution mass spectra (HRMS) were measured at the University of Zaragoza. The starting imines **1** were prepared according to the literature procedures[7].

Catalytic Lithiation of Phenone Imines 1 in the Presence of Carbonyl Compounds 2. Isolation of 1,2-Aminoalcohols 3 and Amines 4. General Procedure.- To a stirred green suspension of lithium powder (100 mg, 14 mmol) and naphthalene (20 mg, 0.16 mmol) in dry tetrahydrofuran (5 ml) was added a solution of the corresponding imine **1** (1 mmol) and the carbonyl compound **2** (1.2 mmol) in tetrahydrofuran (2 ml) at -78°C under an argon atmosphere. Stirring was continued for 5 additional h allowing the temperature to rise to 20°C. The resulting mixture was then hydrolyzed with water (5 ml) and extracted with diethyl ether (3x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was chromatographed (silica gel, hexane/ethyl acetate) yielding the products **3** and **4**. Yields are included in Table 1; analytical, physical and spectral data, as well as literature references for known compounds, follow.

(1R, 2S*)-3-Methyl-1-phenyl-1-phenylamino-2-butanol* (**3a**)[12]: R_f 0.23 (hexane/ethyl acetate: 6/1), t_r 15.32 min; ν_{max} (film) 3390 (OH), 3040, 3010, 1595 and 1500 cm^{-1} (HC=C); δ_H 0.99, 1.04 (3 H each, 2 d, J=6.8, 2xMe), 1.26 (1 H, br s, OH), 1.88 (1 H, octet, J=6.8, C*H*Me), 3.50 (1 H, dd, J=6.8, 4.0, CHO), 4.49 (1 H, d, J=4.0, C*H*Ph), 6.54 (2 H, d, J=7.8, *o*-PhN), 6.63 (1 H, t, J=7.3, *p*-PhN), 7.05-7.10 (2 H, def. t, *m*-PhN) and 7.23-7.34 (5 H, m, *Ph*CH); δ_C 18.2, 19.65 (2xMe), 30.05 (*C*HMe), 59.4 (CHN), 81.25 (CO), 113.45, 117.35, 126.85, 127.35, 128.8, 129.15, 141.6 and 147.2 (ArC); *m/z* 256 (M^++1, <1%), 255 (M^+, <1), 183 (14), 182 (100), 104 (11) and 77 (15).

(1R, 2R*)-3-Methyl-1-phenyl-1-phenylamino-2-butanol* (**3a**)[12]: R_f 0.18 (hexane/ethyl acetate: 6/1), t_r 15.48 min; ν_{max} (film) 3340 (OH), 3050, 3020, 1595 and 1490 cm^{-1} (HC=C); δ_H 0.95, 1.07 (3 H each, 2 d, J=6.6, 2xMe), 1.42 (1 H, d, J=7.3, OH), 1.48-1.60 (1 H, m, C*H*Me), 3.58 (1 H, td, J=7.3, 4.1, CHO), 4.54 (1 H, d, J=4.1, CHN), 4.61 (1 H, br s, NH), 6.54 (2 H, dd, J=7.8, 0.7, *o*-PhN), 6.62 (1 H, td, J=7.4, 0.7, *p*-PhN), 7.04-7.10 (2 H, m, *m*-PhN) and 7.23-7.41 (5 H, m, *Ph*CH); δ_C 18.15, 19.8 (2xMe), 30.55 (*C*HMe), 59.3 (CHN), 79.85 (CO), 113.4, 117.4, 127.6, 128.0, 128.6, 129.1, 139.15 and 146.8 (ArC); *m/z* 256 (M^++1, <1%), 255 (M^+, <1), 183 (13), 182 (100) and 77 (12).

1,2-Diphenyl-2-phenylaminoethanol (**3b**)[13,14]: R_f 0.48 (hexane/ethyl acetate: 1/1), t_r 18.13 min; ν_{max} (film) 3400 (OH), 3050, 3010, 1595 and 1495 cm^{-1} (HC=C); δ_H 2.43 (1 H, br s, OH), 4.45 (1 H, br s, NH), 4.65 (1 H, d, J=4.7, CHN), 5.04 (1 H, d, J=4.7, CHO), 6.50 (2 H, dd, J=8.5, 0.8, *o*-PhN), 6.63 (1 H, t, J=7.3, *p*-PhN), 7.02-7.13 and 7.18-7.33 (6 H each, 2 m, ArH); δ_C 63.65 (CHN), 77.1 (CO), 113.9, 117.85, 126.5, 127.5, 127.85, 127.9, 128.15, 128.2, 129.05, 138.45, 140.0 and 146.75 (ArC); *m/z* 289 (M^+, 1%), 183 (13), 182 (100), 104 (15) and 77 (33).

2-Methyl-1-phenyl-1-phenylamino-2-propanol (**3c**): R_f 0.33 (hexane/ethyl acetate: 2/1), t_r 14.53 min; ν_{max} (film) 3520 (NH), 3390 (OH), 3040, 3020, 1600 and 1500 cm^{-1} (HC=C); δ_H 1.13, 1.38 (3 H each, 2 s, 2xMe), 1.69 (1 H, s, OH), 4.21 (1 H, s, CHN), 4.74 (1 H, br s, NH), 6.53 (2 H, dd, J=8.5, 0.9, *o*-PhN), 6.61 (1 H, td, J=7.4, 0.9, *p*-PhN), 7.05 (2 H, dd, J=8.5, 7.4, *m*-PhN) and 7.21-7.36 (5 H, m, *Ph*C); δ_C 27.0, 27.65 (2xMe), 66.5 (CHN), 72.85 (CO), 113.65, 117.35, 127.45, 128.1, 128.3, 129.05, 140.05 and 147.4 (ArC); *m/z* 242 (M^++1, <1%), 241 (M^+, 4), 183 (24), 182 (100), 104 (16), 77 (23) (Found: M^+, 241.146664. $C_{16}H_{19}NO$ requires M, 241.146934).

3-[Phenyl(phenylamino)methyl]-3-pentanol (**3d**): R_f 0.24 (hexane/ethyl acetate: 6/1), t_r 15.94 min; ν_{max} (film) 3550 (NH), 3410 (OH), 3050, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 0.84 (3 H, t, J=7.4, 1xMe), 0.91 (3 H, t, J=7.5, 1xMe), 1.10-1.22 (1 H, m, 1xCH_2), 1.31-1.43 (2 H, m, 1xCH_2 and OH), 1.65-1.87 (1 H each, 2 m, 2xCH_2), 4.32 (1 H, s, CHN), 4.80 (1 H, br s, NH), 6.52 (2 H, d, J=8.4, *o*-PhN), 6.57 (1 H, t, J=7.4, *p*-PhN), 7.04 (2 H, dd, J=8.4, 7.4, *m*-PhN) and 7.08-7.36 (5 H, m, ArH); δ_C 7.45, 8.25 (2xMe), 27.0, 28.75 (2xCH_2), 61.75 (CHN), 77.15 (CO), 113.1, 116.85, 127.25, 128.25, 128.35, 129.05, 140.1 and 147.2 (ArC); *m/z* 270 (M^++1, <1%), 269 (M^+, 3), 183 (31), 182 (100), 104 (14) and 77 (19).

1-[Phenyl(phenylamino)methyl]cyclopentanol (**3e**): R_f 0.44 (hexane/ethyl acetate: 2/1), t_r 16.54 min, m. p. 106°C (hexane/ethyl acetate); ν_{max} (CH_2Cl_2) 3520 (NH), 3400 (OH), 3040, 3010, 1595 and 1495 cm^{-1} (HC=C); δ_H 1.10-1.25, 1.55-2.00 (1 H and 7 H respectively, 2 m, 4xCH_2 ring), 1.40 (1 H, s, OH), 4.27 (1 H, s, C*H*Ph), 4.86 (1 H, br s, NH), 6.49 (2 H, dd, J=7.8, 0.9, *o*-PhN), 6.57 (1 H, td, J=7.3, 0.9, *p*-PhN), 6.55-6.60 (2 H, m, *m*-PhN) and 7.19-7.37 (5 H, m, PhC); δ_C 23.4, 23.6, 37.75, 38.9 (4xCH_2 ring), 65.2 (CHN), 84.55 (CO), 113.15, 116.85, 127.35, 127.75, 128.35, 129.0, 140.45 and 147.05 (ArC); *m/z* 267 (M^+, 2%), 183 (29), 182 (100), 104 (17) and 77 (30)(Found: C, 81.1; H, 7.9; N, 5.1. $C_{18}H_{21}NO$ requires C, 80.86; H, 7.92; N, 5.24).

1-[Phenyl(phenylamino)methyl]cyclohexanol (**3f**)[15]: R_f 0.26 (hexane/ethyl acetate: 6/1), t_r 17.36 min; ν_{max} (film) 3400 (OH), 3050, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 1.21-1.60 (10 H, m, 5xCH_2 ring), 2.00 (1 H, d, J=11.0, OH), 4.23 (1 H, s, C*H*Ph), 4.80 (1 H, br s, NH), 6.52 (2 H, d, J=7.7, *o*-PhN), 6.58 (1 H, t, J=7.7, *p*-PhN), 7.05 (2 H, t, J=7.7, *m*-PhN) and 7.23-7.35 (5 H, m, *Ph*CH); δ_C 21.65, 22.0, 25.65, 35.2, 35.35 (5xCH_2 ring), 65.55 (CHN), 73.45 (CO), 113.3, 116.95, 127.3, 128.25, 129.05, 139.9 and 147.45 (ArC); *m/z* 281 (M^+, 3%), 183 (41), 182 (100), 180 (10), 106 (10), 104 (22), 81 (14), 77 (40), 55 (13) and 41 (10).

3-[1-(Phenylamino)benzyl]cyclohexanone (**3g**)[16]: R_f 0.34[17] (hexane/ethyl acetate: 2/1), t_r 18.19, 18.22 min, m. p. 151-161°C (hexane/ethyl acetate); ν_{max} (CH_2Cl_2) 3340 (NH), 3040, 3010, 1595, 1495 (HC=C) and 1695 cm^{-1} (C=O); δ_H 1.36-1.75, 1.98-2.37 (6 H and 10 H respectively, 7xCH_2 ring and 2xCH ring), 2.63 (2 H, d, J=10.0, 1xCHCH_2CO), 4.15 (2 H, br s, 2xNH), 4.21 (1 H, d, J=5.4, 1xC*H*Ph), 4.27 (1 H, d, J=4.8, 1xC*H*Ph), 6.51 (4 H, d, J=8.1, 2x*o*-PhN), 6.62 (2 H, t, J=7.3, 2x*p*-PhN), 7.03-7.09 (4 H, m, 2x*m*-PhN) and 7.19-7.32 (10 H, m, 2x*Ph*CH); δ_C 24.85, 24.9, 27.6, 28.15, 45.0, 45.05, 45.3 (2C)(8xCH_2 ring), 41.15, 41.2 (2xCH ring), 62.0, 62.5 (2x*C*HPh), 113.35, 117.45, 117.5, 127.0, 127.05, 127.3, 128.45, 129.0, 129.05, 140.75, 141.05, 147.05 (ArC), 210.85 and 211.0 (2xC=O); *m/z* 280 (M^++1, 1%), 279 (M^+, 4), 183 (13), 182 (100) and 77 (10)(Found: C, 81.3; H, 7.5; N, 4.8. $C_{19}H_{21}NO$ requires C, 81.68; H, 7.58; N, 5.01).

1-Cyclohexylamino-2-methyl-1-phenyl-2-propanol (**3h**): R_f 0.27 (hexane/ethyl acetate: 2/1), t_r 14.15 min; ν_{max} (film) 3400 (OH), 3050, 3010, 1595 and 1485 cm^{-1} (HC=C); δ_H 1.00, 1.13 (3 H each, 2 s, 2xMe), 1.05-1.15, 1.52-1.69 (5 H each, 2 m, 5xCH_2 ring), 1.90 (1 H, br s, OH), 1.95 (1 H, br s, NH), 3.59 (1 H, s, C*H*Ph) and 7.21-7.34 (5 H, m, ArH); δ_C 23.95, 27.3 (2xMe), 24.45, 24.9, 26.05, 32.9, 34.95 (5xCH_2 ring), 54.0 (CH_2*C*H), 68.75 (*C*HPh), 71.45 (CO), 127.1, 128.0 (2 C) and 140.8 (ArC); *m/z* 232 (M^+-15, <1%), 189 (14), 188 (100), 106 (78) (Found: M^+-CH_3, 232.170140. $C_{15}H_{22}NO$ requires M, 232.170101).

3-[(Cyclohexylamino)phenylmethyl]-3-pentanol (**3i**): R_f 0.35 (hexane/ethyl acetate: 6/1), t_r 15.20 min; ν_{max} (film) 3420 (OH), 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.80 (3 H, t, J=7.4, 1xMe), 0.93 (3 H, t, J=7.5, 1xMe), 1.00-1.20 (6 H, m, 5xC*H* ring and OH), 1.21-1.46 (2 H and 1 H respectively, 2 m, 3xCH_2Me), 1.52-1.75 (6 H, m, 1xCH_2Me, 4xCH ring and NH), 1.87-1.95, 2.20-2.25 (1 H each, 2 m, 2xCH ring) and 7.22-7.34 (5 H, m, ArH); δ_C 7.55, 7.9 (2xMe), 24.5, 24.95, 26.05, 33.0, 34.9 (5xCH_2 ring), 27.35, 27.55 (2x*C*H_2Me), 54.05 (CH_2*C*HN), 64.35 (Ph*C*HN), 75.15 (CO), 126.9, 128.0, 128.15 and 141.2 (ArC); *m/z* 246 (M^+-29, 3%), 189 (14), 188 (100), (39) (Found: M^+-C_2H_5, 246.185790. $C_{16}H_{24}NO$ requires M, 246.186233).

1-[(Methylamino)phenylmethyl]cyclohexanol (**3j**): R_f 0.28 (hexane/ethyl acetate: 1/4), t_r 13.22 min; ν_{max} (film) 3360 (OH), 3050, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.85-1.69 (10 H, m, 5xCH_2 ring), 2.26 (3 H, s, Me), 2.28 (1 H, s, OH), 3.33 (1 H, s, C*H*Ph) and 7.22-7.36 (5 H, m, ArH); δ_C 21.5, 21.85, 25.75, 34.95, 35.6 (5xCH_2 ring), 32.3 (Me), 72.7 (CHN), 74.4 (CO), 127.15, 127.95, 128.6 and 139.6 (ArC); *m/z* 121 (M^+-98, 15%), 120 (100) and 42 (11).

3-Ethyl-2-phenyl-2-phenylamino-3-pentanol (**3k**): R_f 0.42 (hexane/ethyl acetate: 6/1), t_r 17.02 min; ν_{max} (film) 3550 (NH), 3370 (OH), 3070, 3040, 1590 and 1495 cm^{-1} (HC=C); δ_H 0.75, 0.95 (3 H each, 2 t, J=7.5, 2x*Me*CH_2), 1.38 (1 H, s, OH), 1.55, 1.72 (2 H each, 2 q, J=7.5, 2xCH_2), 1.78 (3 H, s, *Me*CN), 4.94 (1 H, br s, NH), 6.28 (2 H, d, J=8.5, *o*-PhN), 6.56 (1 H, t, J=7.4, *p*-PhN), 6.97 (2 H, dd, J=8.5, 7.4, *m*-PhN), 7.23-7.34 (3 H, m, *m* and *p*-PhC) and 7.47 (2 H, dd, J=7.0, 1.6, *o*-PhC); δ_C 9.0, 9.1 (*Me*CH_2), 19.95 (*Me*CN), 26.85, 27.25 (2xCH_2), 65.5 (CN), 78.35 (CO), 115.65, 116.65, 126.75, 128.05, 128.5, 142.45 and

145.95 (ArC); *m/z* 283 (M^+, 1%), 197 (14) and 196 (100).

N-Phenylbenzylamine (**4a**)[7a]: R_f 0.68 (Et_2O), t_r 12.91 min; ν_{max} (film) 3410 (NH), 3050, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 3.90 (1 H, br s, NH), 4.30 (2 H, s, CH_2), 6.62 (2 H, d, J=8.5, *o*-PhN), 6.70 (1 H, t, J=7.4, *p*-PhN), 7.16 (2 H, dd, J=8.5, 7.4, *m*-PhN) and 7.21-7.37 (5 H, m, PhC); δ_C 65.8 (CH_2), 112.8, 117.5, 127.15, 127.45, 128.55, 129.2, 139.4 and 148.1 (ArC); *m/z* 183 (M^+, 1%), 182 (10), 181 (65), 180 (100), 77 (47) and 51 (22).

N-Cyclohexylbenzylamine (**4b**)[18]: R_f 0.32 (Et_2O), t_r 12.30 min; ν_{max} (film) 3290 (NH), 3050, 3010, 1595 and 1485 cm^{-1} (HC=C); δ_H 1.05-1.33, 1.59-1.63, 1.70-1.76, 1.89-1.93 (5 H, 1 H, 2 H and 2 H respectively, 4 m, 5xCH_2 ring), 1.35 (1 H, br s, NH), 2.44-2.51 (1 H, m, CHN), 3.80 (2 H, s, CH_2N) and 7.21-7.31 (5 H, m, ArH); δ_C 24.95 (2 C), 26.1, 33.5 (2 C)(5xCH_2 ring), 50.95 (CHN), 56.1 (CH_2N), 126.65, 128.0, 128.3 and 140.9 (ArC); *m/z* 191 (M^++2, <1%), 190 (M^++1, 4), 189 (M^+, 25), 147 (10), 146 (99), 91 (100), 65 (17) and 41 (11).

N-Methylbenzylamine (**4c**)[7a]: R_f 0.27 (Et_2O), t_r 6.59 min; ν_{max} (film) 3300 (NH), 3050, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 1.99 (1 H, s, NH), 2.42 (3 H, s, Me), 3.72 (2 H, s, CH_2) and 7.20-7.35 (5 H, m, ArH); δ_C 35.8 (Me), 55.85 (CH_2), 126.85, 128.05, 128.25 and 139.9 (ArC); *m/z* 122 (M^++1, 4%), 121 (M^+, 48), 120 (100), 92 (11), 91 (66), 77 (14), 65 (23), 63 (13), 51 (20), 50 (11), 44 (78) and 42 (43).

α-Methyl-N-phenylbenzylamine (**4d**)[19]: R_f 0.70 (Et_2O), t_r 12.83 min; ν_{max} (film) 3400 (NH), 3050, 3020, 1595 and 1500 cm^{-1} (HC=C); δ_H 1.42 (3 H, d, J=6.7, Me), 3.95 (1 H, br s, NH), 4.39 (1 H, q, J=6.7, C*H*Me), 6.43 (2 H, d, J=8.5, *o*-PhN), 6.56 (1 H, t, J=7.3, *p*-PhN), 7.00 (2 H, t, J=7.5, *m*-PhN) and 7.10-7.37 (5 H, m, PhC); δ_C 24.9 (Me), 53.5 (CHMe), 113.35, 117.3, 125.8, 126.85, 128.6, 129.05, 145.1 and 147.1 (ArC); *m/z* 199 (M^++2, <1%), 198 (M^++1, 7), 197 (M^+, 41), 183 (13), 182 (100), 105 (70), 104 (14), 103 (11), 93 (47), 79 (13), 77 (42) and 51 (14).

α,N-Diphenylbenzylamine (**4e**)[20]: R_f 0.62 (Et_2O), t_r 16.96 min; ν_{max} (film) 3400 (NH), 3050, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 4.20 (1 H, br s, NH), 5.48 (1 H, s, C*H*Ph), 6.52 (2 H, d, J=8.5, *o*-PhN), 6.69 (1 H, t, J=7.3, *p*-PhN), 7.24-7.35 (5 H, m, *m*-PhN, *m* and *p*-PhC) and 7.78 (2 H, d, J=8.4, *o*-PhC); δ_C 62.95 (CHN), 113.4, 117.6, 127.3, 127.4, 128.15, 128.4, 129.05, 130.0, 132.35, 142.8, 142.85 and 147.3 (ArC); 261 (M^++2, 4%), 260 (M^++1, 25), 259 (M^+, 18), 169 (12), 168 (96), 167 (100), 166 (32), 165 (26), 153 (13), 152 (17), 77 (27), 65 (10) and 51 (13).

Acknowledgements

This work was financially supported by the Dirección General de Investigación Científica y Técnica (DGICYT, no. PB91-0751) from the Ministerio de Educación y Ciencia of Spain. D. G. thanks the Conselleria de Cultura, Educació i Ciencia de la Generalitat Valenciana for a fellowship.

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