Synthesis of *N*- and *p*-(Diphenylmethyl)anilines. ESR Study of their Photofragmentation[1] ☆

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The reaction of *N*-substituted anilines **2** with diphenylmethyl halides **1** at room temperature in the presence of $AlCl_3$ affords *p*-substituted derivatives **3** in good yields according to an electrophilic aromatic substitution. In contrast, aniline itself is only converted to the *N*-substituted compounds **4**. A novel rearrangement from $Ph_3C-NHPh$ (**4c**) to *p*-(triphenylmethyl)-aniline (**5**) is described. Unexpected photofragmentations of **4a, b** are studied by using ESR and ENDOR spectroscopy; e.g., irradiation of **4b** with quartz- or pyrex-filtered light leads to the formation of the radicals $Ph_2\dot{C}-SiMe_3$ (**7b**) and $Ph_2\dot{C}-NHPh$ (**6**) respectively, following selective cleavage of the C–N and C–Si bond.

The main synthetic possibilities of the Friedel-Crafts alkylation are limited by frequently occuring rearrangement and formation of polyalkyl derivatives[3]. Furthermore, benzene alkylation with triphenylmethyl chloride yielding tetraphenylmethane suffers from an unfavorable dealkylation[4] of the latter due to the catalyst used.

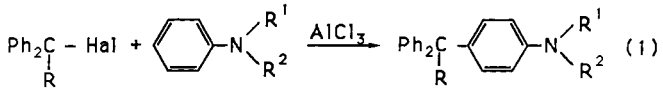
The introduction of the triphenylmethyl group into aromatic systems by electrophilic aromatic substitution is succesful only with activated substrates like phenol[5] and aniline[6–10] and under highly acidic conditions. In general, arylamines are alkylated by using drastic catalytic conditions, i.e. high pressure and temperature and special catalysts[11].

Alkylating agents like **4a, b** bearing easily isomerizable groups or/and sensitive metal-carbon bonds need extremely mild conditions regarding the temperature and the catalyst to be used. We present here an easy method to alkylate *N*-substituted anilines to yield exclusively *p*-substituted derivatives. Aniline itself is only converted into the *N*-substituted compounds which undergo very interesting photochemical fragmentations.

Results and Discussion

Alkyl halides **1** easily react with the anilines **2** at room temperature to afford the *p*-substituted compounds **3** in good yields and after short reaction times, see eq. (1). The presence of $AlCl_3$ as Lewis-acid catalyst is crucial here. The optimal molar ratio of **1** to aniline and $AlCl_3$ has been found to be 1:4:2.

No reaction takes place at room temperature without a catalyst, whereas heating at 110°C yields just 7% of **3a**. Similarly, no product is obtained when equimolar amounts of $AlCl_3$ and aniline (1:4:4) are used, a fact which should be attributed to the known ability of amines to complex with Lewis acids[12]. Fortunately, it is just this complexation which probably prevents the hard Lewis acid $AlCl_3$ from causing dealkylation[4,13] of **3**, rearrangement of the *tert*-butyldiphenylmethyl[14] and diphenyl(trimethylsilyl)methyl[15] group, and cleavage of the Si–C bond[16] as well as complications due to the Scholl reaction[17].



1a : R = *t* Bu, Cl
1b : R = $SiMe_3$, Br

2 3

	1		2		3			Yield
	R	Hal	R1	R2	R	R1	R2	(%)
a	*t*Bu	Cl	H	Me	*t*Bu	H	Me	54
b	*t*Bu	Cl	Me	Me	*t*Bu	Me	Me	71
c	*t*Bu	Cl	H	Et	*t*Bu	H	Et	36
d	*t*Bu	Cl	Et	Et	*t*Bu	Et	Et	66
e	$SiMe_3$	Br	H	Me	$SiMe_3$	H	Me	45
f	$SiMe_3$	Br	Me	Me	$SiMe_3$	Me	Me	76
g	$SiMe_3$	Br	H	Et	$SiMe_3$	H	Et	68
h	$SiMe_3$	Br	Et	Et	$SiMe_3$	Et	Et	82

Aniline itself reacts with **1** in a different way giving at room temperature clean *N*-substituted derivatives **4**, see eq. (2). The reaction is retarded by the addition of $AlCl_3$ due to the above mentioned complexation and ceases completely if the molar ratio of aniline to $AlCl_3$ becomes 1:1. Apparently, a nucleophilic substitution takes place here.

In the light of these results it was first surprising to find claims in the literature[7,10] that the reaction between Ph_3CCl and aniline at 184°C (b.p. of aniline) leads only to the

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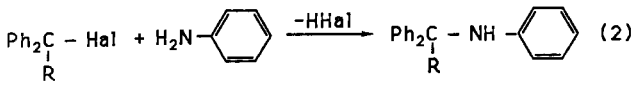


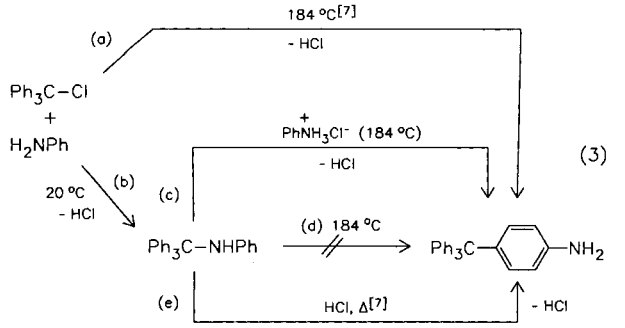
(2)

1 4

1	R	Hal
a	*t*Bu	Cl
b	$SiMe_3$	Br
c	Ph	Cl
d	H	Br

4	R	Yield (%)
a	*t*Bu	58
b	$SiMe_3$	62
c	Ph	63
d	H	77

p-substituted compound **5**, eq. (3a). Repeating this experiment[7], we really found only **5**. This discrepancy prompted us to conduct the reaction at room temperature to get **4c** and subsequently to boil the mixture (184 °C) for 2.5 hours. We obtained only **5**. On the other hand, while **4c** itself does not rearrange to **5** (eq. (3d)), a rearrangement occurs if an equimolar amount of aniline hydrochloride is present, eq. (3c). Furthermore, **4c** rearranges in conc. HCl to **5**, eq. (3e)[7].



(3)

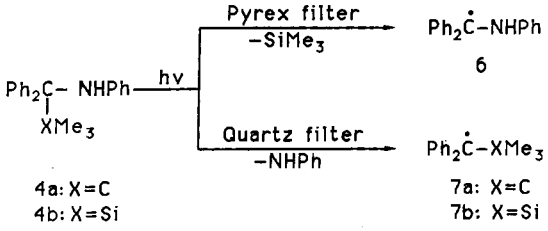
To explain the above findings we suggest that the reactions (3a, c, e) proceed via the anilinium salt $Ph_3C-\overset{+}{N}H_2PhCl^-$, which probably decomposes at 184 °C to yield Ph_3C^+, the latter in an electrophilic aromatic substitution being converted into **5**. The salt instability at high temperatures seems to be responsible for the formation of **5**. The reaction resembles the Hofmann-Martius rearrangement[18,19]. Similar rearrangements are known to proceed with zinc chloride as the catalyst[20].

Photochemical Fragmentations of 4. An ESR Study

The color change of the crystalline compound **4b** from white to red in the sunlight gave rise to a search for possible fragmentations.

It is known for example from the pioneer work of Lewis[21] and Norrish[22] as well as from contemporary studies[23,24], that irradiation of *N*-alkylamines with UV light yields products the formation of which is explicable by the cleavage of the C–N and C–H bonds and in the case of primary and secondary amines by scission of the N–H bond. In general[21], photodissociation (homolysis), photoionization (heterolysis), and photooxidation may take place.

Irradiation of degassed benzene or toluene solutions of **4b** at room temperature with Pyrex-filtered light of various sources (Philips HPL-N 125 W or CS 150 W, Hanau TQ 150 W, or Hanovia 1 kW Xe-Hg) results in red coloring and formation of the α-aminodiphenylmethyl radical **6** (eq. (4)), as we conclude from the analysis (see below) of its ESR and ENDOR spectrum.



(4)

Apparently, desilylation takes place here leading to the stabilized[25] radical **6** and $Me_3Si^\cdot$ radicals, a fact which is supported by the identification of $PhSiMe_3$ and Me_6Si_2 (GC) in the reaction mixture. Furthermore, using *n*-hexane or tBu_2O_2 as solvent, we recorded the same ESR spectrum and identified Me_6Si_2 and *t*BuOSiMe$_3$, respectively. If we conduct the photolysis in an oxygen-saturated toluene solution we obtain at −32 °C a broad unresolved ESR spectrum with $g = 2.0148$, a characteristic value for peroxy radicals $ROO^\cdot$[26]. $ROO^\cdot$ is presumably generated by the reaction of radical **6** with oxygen. Involvement of exited oxygen molecules is here unlikely because of the wavelengths ($\lambda > 290$ nm) used[27].

On the other hand, irradiation of **4b** in degassed toluene in a quartz tube affords – indeed only when the strong light source Hanovia Xe-Hg 1 kW is used – a completely different ESR spectrum which we assign to **7b**, formed by C–N bond cleavage. The ESR parameters [$g = 2.0027$, $a_o^H(4H) = 0.276$, $a_m^H(4H) = 0.115$, $a_p^H(2H) = 0.293$, and $a^H(9H, SiMe_3) = 0.016$ mT at 40 °C][28] are almost identical with the literature data for the radical **7b**[29]. The second possible fragment, the radical PhNH, is known to be ESR "silent"[30]. This finding implies that the photochemistry is dependent on the wavelength and intensity of the applied irradiation.

Likewise, photolysis of **4a** under the same conditions (quartz) gives rise to the spectrum of **7a** [$g = 2.0024$, $a_o^H(4H) = 0.268$, $a_m^H(4H) = 0.111$, $a_p^H(2H) = 0.285$, and $a^H(9H, CMe_3) = 0.024$ mT at 45 °C][28]. The parameters are in excellent agreement with literature data for the radical **7a**[31]; its occurrence indicates C–N bond cleavage. With a pyrex filter, however, we have not obtained any signal, thus providing evidence that in this case not any $C-CMe_3$ bond cleavage – in contrast to $C-SiMe_3$ – occurs.

Moreover, taking into account the similarity of the dissociation energies of the C–C and C–Si bonds[32] and the fact that only **4b** fragmentates to **6** (ESR) when **4a, b** is heated in tetralin at 190–210 °C, we are forced to assume that by the desilylation process a stabilizing interaction between the vacant silicon d orbitals and the nitrogen lone pair in the transition state takes place, thus facilitating C–Si cleavage.

Regarding the other compounds **4c, d** as well as Ph_3C-NH_2, only **4c** yields thermally (tetralin, 205 °C) triphenylmethyl radicals (ESR).

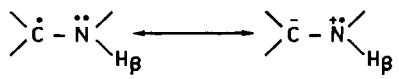
Whereas the C–N bond scission is a common dissociative pathway for alkylamines[21–24], the desilylation process represents, so far as we know, the first example of a C–Si bond cleavage and should be taken into account in photochemical studies of silylamines. Of course, there are a few reports in the literature on the direct benzylic carbon–silicon bond cleavage[29,33,34a] concerning, however, different chromophore systems.

In contrast, desilylation is observed in electron transfer-sensitized reactions[35] along with debenzylation[36] or deprotonation[37]. An amine cation radical is formed in this case which undergoes fragmentation. Whether the above described fragmentations or some of them follow the formation of such a cationic radical species, remains unclear[21]. In our study only radical fragments have been detected (ESR/ENDOR). Nevertheless, the mass spectrum of **4b** shows two main fragments [M^+ – NHPh] (100%) and [M^+ – $SiMe_3$] (65%), representing equivalents of the detected radicals **7b** and **6**.

Continuing efforts are devoted to the generation of the radical cations of **4** and the study of their fragmentation pattern.

Analysis of the ENDOR[38] spectrum of the radical **6** (toluene solution at –53 °C) gave the following coupling constants: $a_o^H(2H)$ = 0.314, $a_{o'}^H(2H)$ = 0.321, $a_m^H(4H)$ = 0.126, $a_p^H(2H)$ = 0.375, $a_{NH}^H(1H)$ = 0.022 mT.

We have used the ENDOR data as starting point to analyze the poorly resolved ESR spectrum (Figure 1a), thus producing an excellent simulation (Figure 1b). The relatively low g value of 2.0026 for an α-aminoalkyl radical[39] is attributed to a small nitrogen contribution, reflected by the low a^N = 0.125 mT. It is not surprising to find low values for a^N and $a_{NH}^{H_\beta}$(0.021 mT) if we consider that they are markedly dependent on the preferred conformation[40]. We suggest that the contributions due to the spin polarization to N and the hyperconjugation to H_β (form **Ia**) are partly compensated from contributions due to spin polarization to N and H_β (form **Ib**), respectively.



Ia **Ib**

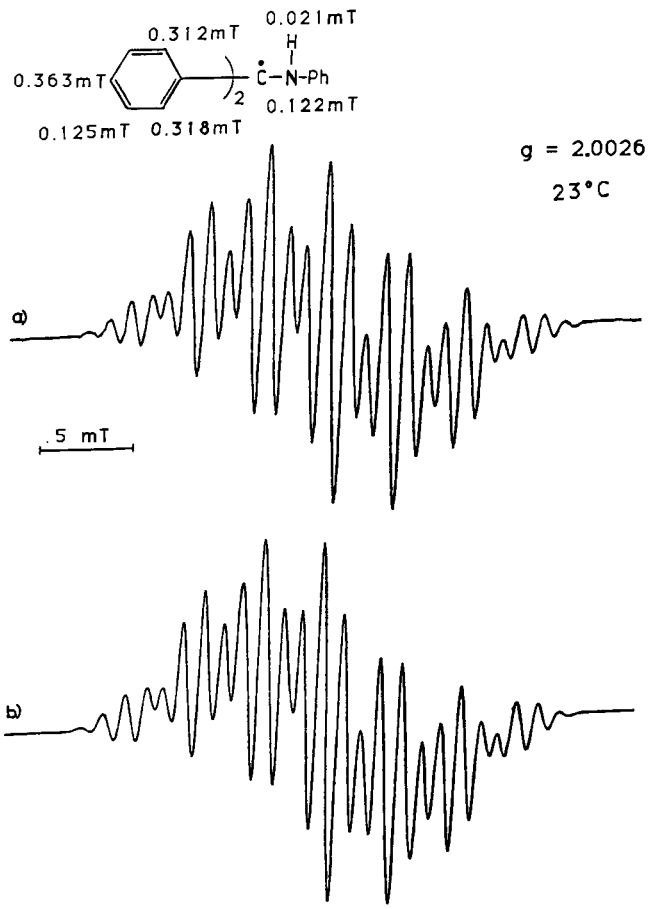


Figure 1. (a) ESR spectrum of the radical **6** in toluene at 23 °C. – (b) Computer simulation using the coupling constants shown in the formula [$a_o^H(2H)$ = 0.312 mT, $a_{o'}^H(2H)$ = 0.318, $a_m^H(4H)$ = 0.125, $a_p^H(2H)$ = 0.363, $a_{NH}^H(1H)$ = 0.021, and $a^N(1N)$ = 0.122]

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Experimental

$AlCl_3$, **1c**, **d**, **2a–d**, and aniline were purchased from Fluka and Ph_3CNH_2 from Aldrich. Compounds **1a**[31] and **1b**[41] were prepared according to literature procedures. All the materials were purified before use by distillation or recrystallization, and the reactions were performed under argon.

Melting points (uncorrected): Büchi 510. – IR: Perkin-Elmer 783 B. – NMR: ^1H Varian EM 390 A and ^{13}C Bruker AM 300. – MS: Finnigan Mat 8230, 70 eV. – Elemental analyses: Carlo Erba 1106. – UV/Vis: Perkin Elmer Lambda 15. – ESR: Varian E-109. – ENDOR: Bruker ER 220 D with resonator EN 801. – GC: Perkin Elmer 8310 B.

General Procedures

4-(Diphenylmethyl)benzenamines **3a–h**: A mixture of 8 mmol of **2a–d**, 4 mmol of $AlCl_3$ (sublimated grade), and 2 mmol of **1a, b** was stirred at room temp. for ca. 1 h and then diluted with 10 ml of dichloromethane. The brown solution was poured into ice/water (50 ml) and separated. The aqueous solution was extracted with CH_2Cl_2 (2 × 15 ml). The combined CH_2Cl_2 extracts were washed twice with satd. aq. $NaHCO_3$ and water (3 × 20 ml) and dried with magnesium sulfate. The solvent was evaporated and the viscous residue crystallized by the addition of 30 ml of methanol. Recrystallization from methanol.

N-Substituted Benzenamines **4a–d**: A solution of 5 mmol of **1a–d** in aniline (7.5 ml) was stirred at room temp. for ca. 1 h. The mixture was poured into ice/water (40 ml) and extracted with ether (3 × 20 ml). The combined ether extracts were washed twice with satd. aq. $NaHCO_3$ and water (3 × 20 ml) and dried with $MgSO_4$. The solvent was evaporated and the excess aniline distilled off in

vacuo (0.1 Torr). The crude product was recrystallized from methanol.

4-(tert-Butyldiphenylmethyl)-N-methylbenzenamine (**3a**): From 0.65 g (2.5 mmol) of **1a**, 1.1 ml (10 mmol) of **2a**, and 0.66 g (5 mmol) of $AlCl_3$ 0.44 g (54%) of **3a** was obtained after 1 h, m.p. 124–125°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3418 cm^{-1} (NH), 818 (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 253 nm (4.257), 301 (3.551). – ^1H NMR (CCl_4): δ = 1.27 [s, 9H, $C(CH_3)_3$], 2.78 (s, 3H, NCH_3), 3.23 (s, 1H, NH), 6.35, 6.94 (AB, $^3J_{AB}$ = 8.9 Hz, 4 aromatic H), 7.03–7.23 (m, 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 30.66 [$C(CH_3)_3$], 35.51 (NCH_3), 39.75 [$C(CH_3)_3$], 64.45 (CPh_2), 110.83, 125.52, 126.78, 131.41, 132.23 ($C_{ar}H$), 135.76, 146.84, 147.69 (C_{ar}).

$C_{24}H_{27}N$ (329.5) Calcd. C 87.48 H 8.26 N 4.25
Found C 87.31 H 8.12 N 4.34

4-(tert-Butyldiphenylmethyl)-N,N-dimethylbenzenamine (**3b**): From 1.29 g (5 mmol) of **1a**, 1.3 ml (10 mmol) of **2b**, and 0.66 g (5 mmol) of $AlCl_3$ 1.22 g (71%) of **3b** was obtained after 20 min; m.p. 137–138°C (methanol). – IR (KBr): $\tilde{\nu}$ = 820 cm^{-1} (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 247 nm (4.336), 290 (3.543). – ^1H NMR (CCl_4): δ = 1.28 [s, 9H, $C(CH_3)_3$], 2.88 [s, 6H, $N(CH_3)_2$], 6.48, 6.97 (AB, $^3J_{AB}$ = 8.9 Hz, 4 aromatic H), 6.99–7.30 (m, 10H, aromatic H). – MS (70 eV), *m/z* (%): 343 [M^+] (100), 286 [$M^+ - CMe_3$] (95), 194 [$PhCC_6H_4NMe^+$] (3).

$C_{25}H_{29}N$ (343.5) Calcd. C 87.41 H 8.51 N 4.08
Found C 87.02 H 8.34 N 4.12

4-(tert-Butyldiphenylmethyl)-N-ethylbenzenamine (**3c**): According to the general procedure from 0.65 g (2.5 mmol) of **1a**, 2.0 ml (16 mmol) of **2c**, and 0.66 g (5 mmol) of $AlCl_3$ 0.31 g (36%) of **3c** was obtained after 20 min; m.p. 116–117°C (petroleum ether). – IR (KBr): $\tilde{\nu}$ = 3398 cm^{-1} (NH), 814 (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 254 nm (4.272), 301 (3.485). – ^1H NMR (CCl_4): δ = 1.22 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.27 [s, 9H, $C(CH_3)_3$], 3.10 (q, ^3J = 6.9 Hz, 2H, CH_2), 3.23 (s, 1H, NH), 6.30, 6.88 (AB, $^3J_{AB}$ = 8.6 Hz, 4 aromatic H), 7.01–7.56 (m, 10H, aromatic H).

$C_{25}H_{29}N$ (343.5) Calcd. C 87.41 H 8.51 N 4.08
Found C 87.31 H 8.65 N 3.91

4-(tert-Butyldiphenylmethyl)-N,N-diethylbenzenamine (**3d**): From 0.65 g (2.5 mmol) of **1a**, 2.0 ml (12 mmol) of **2d**, and 0.66 g (5 mmol) of $AlCl_3$ 0.61 g (66%) of **3d** was obtained after 10 min; m.p. 172–173°C (petroleum ether). – IR (KBr): $\tilde{\nu}$ = 819 (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 270 nm (4.388), 309 (3.582). – ^1H NMR (CCl_4): δ = 1.17 [t, ^3J = 6.6 Hz, 6H, $N(CH_2CH_3)_2$], 1.27 [s, 9H, $C(CH_3)_3$], 3.32 [q, ^3J = 6.9 Hz, 4H, $N(CH_2CH_3)_2$], 6.43, 6.92 (AB, $^3J_{AB}$ = 9.0 Hz, 4 aromatic H), 7.00–7.30 (m, 10H, aromatic H).

$C_{27}H_{33}N$ (371.5) Calcd. C 87.29 H 8.95 N 3.77
Found C 86.89 H 8.85 N 3.61

4-[Diphenyl(trimethylsilyl)methyl]-N-methylbenzenamine (**3e**): From 0.79 g (2.5 mmol) of **1b**, 1.1 ml (10 mmol) of **2a**, and 0.66 g (5 mmol) of $AlCl_3$ 0.39 g (45%) of **3e** was obtained after 1 h, m.p. 119–121°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3406 cm^{-1} (NH), 811 (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 256 nm (4.352), 305 (3.506). – ^1H NMR (CCl_4): δ = 0.00 [s, 9H, $Si(CH_3)_3$], 2.57 (s, 3H, NCH_3), 3.07 (s, 1H, NH), 6.25, 6.63 (AB, $^3J_{AB}$ = 8.8 Hz, 4 aromatic H), 6.21–7.14 (m, 10H, aromatic H).

$C_{23}H_{27}NSi$ (345.5) Calcd. C 79.95 H 7.88 N 4.05
Found C 79.63 H 7.82 N 4.39

4-[Diphenyl(trimethylsilyl)methyl]-N,N-dimethylbenzenamine (**3f**): According to the general procedure from 1.20 g (3.8 mmol) of **1b**, 1.1 ml (8.7 mmol) of **2b**, and 0.66 g (5 mmol) of $AlCl_3$ 1.04 g (76%) of **3f** was obtained after 1 h; m.p. 122–123°C (methanol). – IR (KBr): $\tilde{\nu}$ = 812 cm^{-1} (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 250 nm (4.385), 295 (3.505). – ^1H NMR (CCl_4): δ = 0.12 [s, 9H, $Si(CH_3)_3$], 2.92 [s, 6H, $N(CH_3)_2$], 6.44, 6.70 (AB, $^3J_{AB}$ = 9.0 Hz, 4 aromatic H), 6.83–7.23 (m, 10 aromatic H).

$C_{24}H_{29}NSi$ (359.6) Calcd. C 80.16 H 8.13 N 3.89
Found C 79.86 H 7.91 N 3.79

4-[Diphenyl(trimethylsilyl)methyl]-N-ethylbenzenamine (**3g**): From 0.89 g (2.8 mmol) of **1b**, 1.4 ml (11.1 mmol) of **2c**, and 0.75 g (5.6 mmol) of $AlCl_3$ 0.68 g (68%) of **3g** was obtained after 1 h; m.p. 128–129°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3406 cm^{-1} (NH), 811 (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 258 nm (4.358), 306 (3.473). – ^1H NMR (CCl_4): δ = 0.12 [s, 9H, $Si(CH_3)_3$], 1.23 (t, ^3J = 6.9 Hz, 3H, CH_3), 3.08 (q, ^3J = 7.2 Hz, 2H, CH_2), 3.25 (s, 1H, NH, H/D exchange with D_2O), 6.35, 6.71 (AB, $^3J_{AB}$ = 8.7 Hz, 4 aromatic H), 6.87–7.25 (m, 10H, aromatic H).

$C_{24}H_{29}NSi$ (359.6) Calcd. C 80.16 H 8.13 N 3.89
Found C 80.24 H 8.32 N 3.75

4-[Diphenyl(trimethylsilyl)methyl]-N,N-diethylbenzenamine (**3h**): From 0.96 g (3 mmol) of **1b**, 2.0 ml (12.5 mmol) of **2d** and 0.81 g (6 mmol) of $AlCl_3$ 0.95 g (82%) of **3h** was obtained after 1 h; m.p. 143–144°C (petroleum ether). – IR (KBr): $\tilde{\nu}$ = 813 cm^{-1} (1,4-disubst. benzene). – UV (hexane): λ (lg ε) = 270 nm (4.423), 313 (3.567). – ^1H NMR (CCl_4): δ = 0.15 [s, 9H, $Si(CH_3)_3$], 1.17 [t, ^3J = 6.9 Hz, 6H, $N(CH_2CH_3)_2$], 3.31 [q, ^3J = 7.2 Hz, 4H, $N(CH_2CH_3)_2$], 6.49, 6.76 (AB, $^3J_{AB}$ = 8.7 Hz, 4 aromatic H), 6.93–7.23 (m, 10H, aromatic H).

$C_{26}H_{33}N$ (387.6) Calcd. C 80.56 H 8.58 N 3.61
Found C 80.25 H 8.64 N 3.38

N-(tert-Butyldiphenylmethyl)benzenamine (**4a**): According to the general procedure from 0.79 g (3.1 mmol) of **1a** and 7.5 ml (82 mmol) of aniline 0.57 g (58%) of **4a** was obtained after 1 h; m.p. 115–116°C (methanol) (ref.[43] 117.5–118.5°C). – IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1} (NH). – UV (hexane): λ (lg ε) = 231 nm (4.258), 282 (3.455). – ^1H NMR (CCl_4): δ = 1.03 [s, 9H, $C(CH_3)_3$], 4.65 (s, 1H, NH), 5.90–7.85 (m, 15H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.24 [$C(CH_3)_3$], 42.13 [$C(CH_3)_3$], 71.61 (CPh_2), 116.39, 117.17, 127.33, 129.00, 131.50 ($C_{ar}H$), 140.98, 146.91 (C_{ar}). – MS (70 eV); *m/z* (%): 300 [$M^+ - Me$] (2), 258 [$M^+ - CMe_3$] (100), 180 [$PhCNPh^+$] (21).

N-[Diphenyl(trimethylsilyl)methyl]benzenamine (**4b**): From 1.5 g (4.7 mmol) of **1b** and 7.5 ml (82 mmol) of aniline 0.97 g (62%) of **4b** was obtained after 1 h; m.p. 99–101°C (methanol) (ref.[42] 102–103°C). – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (w) and 3395 (s) (NH). – UV (hexane): λ (lg ε) = 233 nm (4.155), 294 (3.552). – ^1H NMR (CCl_4): δ = 0.00 [s, 9H, $SiCH_3$], 4.53 (s, 1H, NH), 6.20–7.53 (m, 15H, aromatic H). – MS (70 eV), *m/z* (%): 331 [M^+] (2), 258 [$M^+ - SiMe_3$] (65), 239 [$M^+ - NHPh$] (100), 180 [$PhCNPh^+$] (12).

4-(Triphenylmethyl)benzenamine (**4c**): According to the general procedure from 10.0 g (36 mmol) of **1c** and 50 ml (550 mmol) of aniline 7.6 g (63%) of **4c** was obtained after 1.5 h at 50°C; m.p. 148–149°C (hexane) (ref.[44] 148–149°C). – IR (KBr): $\tilde{\nu}$ = 3408 cm^{-1} (NH). – UV (hexane): λ (lg ε) = 233 nm (4.265). – ^1H NMR (CCl_4): δ = 4.78 (s, 1H, NH), 6.10–7.42 (m, 20H, aromatic H).

N-(Diphenylmethyl)benzenamine (**4d**): From 0.50 g (2 mmol) of **1d** and 0.85 ml (9 mmol) of aniline at room temp. after 1.5 h 0.40 g (77%) of **4d** was obtained after purification by column chromatography (3 × 12 cm, silica gel; eluent hexane/ethyl acetate, 18:2). The light yellow viscous oil was distilled (0.002 Torr/156–160°C) and solidified to an amorphous light yellow product of m.p. 53–55°C

(ref.[45] 53–54.5°C). – IR (KBr): $\tilde{\nu}$ = 3412 cm^{-1} (NH). – UV (hexane): λ (lg ε) = 246 nm (4.169), 292 (3.492). – ^1H NMR (CCl_4): δ = 3.95 (s, 1H, NH), 5.42 (s, 1H, Ph_2CH), 6.21–7.26 (m, 15H, aromatic H).

Rearrangement of **4c** *to* **5**

a) A solution of 1.4 g (5 mmol) of **1c** in 6.9 ml of aniline was stirred at room temp. for 1.5 h to give **4c** (see above). The reaction mixture was subsequently refluxed for 2.5 h (development of a violet color) and poured into ice/water (60 ml). Treatment as in the general procedure gave a slightly rose-colored crude product, which was recrystallized from toluene: 0.90 g (54%), m.p. 250°C (ref.[6b] 256°C). – ^1H NMR ($CDCl_3$): δ = 3.37 (s, 2H, NH_2), 6.48, 7.00 (AB, ^3J = 8.6 Hz, 4H, aromatic H), 7.26 (s, 15H, aromatic H).

b) A solution of 0.82 g (2.4 mmol) of **4c** and 0.62 g (4.8 mmol) of $PhNH_3^+Cl^-$ in 3.2 ml of aniline was refluxed for 2 h. The violet reaction mixture was poured into ice/water and treated as described before: 0.53 g (64%) of **5**; m.p. 250°C.

☆ Dedicated to Professor *W. P. Neumann*.

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1a: 1657-59-6 / **1b**: 17922-21-3 / **1c**: 76-83-5 / **1d**: 776-74-9 / **2a**: 100-61-8 / **2b**: 121-69-7 / **2c**: 103-69-5 / **2d**: 91-66-7 / **3a**: 143143-24-2 / **3b**: 143143-25-3 / **3c**: 143143-26-4 / **3d**: 143143-27-5 / **3e**: 143143-28-6 / **3f**: 143143-29-7 / **3g**: 143143-30-0 / **3h**: 143143-31-1 / **4a**: 7714-61-6 / **4b**: 64434-62-4 / **4c**: 4471-22-1 / **4d**: 1865-12-9 / **5**: 22948-06-7 / **6**: 143143-32-2 / **7a**: 51974-45-9 / **7b**: 76241-07-1 / aniline: 62-53-3