0.71073 Å), μ(Mo Kα) = 12.8 cm^{-1}.

Crystals of **8** were grown from benzene. A colorless block-shaped crystal (0.14 × 0.26 × 0.53 mm), mounted in a Lindemann glass capillary, was used for data collection on an Enraf-Nonius CAD-4F diffractometer. Unit cell dimensions were calculated from the SET4 setting angles of 25 carefully centered reflections in the range 25° < 2θ < 38°.[25] The intensity data of 4604 reflections were collected within one quadrant of the reflection sphere (−13 ≤ h ≤ 13, −15 ≤ k ≤ 0, 0 ≤ l ≤ 19; 1.27 ≤ θ ≤ 25.0°). Scan mode $\omega/2\theta$ with $\Delta\omega$ = (0.60 + 0.35 tan θ)°. The reflections were corrected for Lorentz and polarization effects. Averaging of equivalent reflections resulted in 2905 independent reflections (R_{int} = 0.017) with $I \geq 2.5\sigma(I)$. Three reference reflections (−1 −8 0, 4 3 7, and −3 0 9) were measured every hour and showed a small linear decay of 2% during 67 h of X-ray exposure time.

The structure was solved by Patterson (SHELXS-86)[26b] and Fourier methods and refined on F by full-matrix least-squares techniques (SHELX-76).[26a] All hydrogen atoms were located in a difference Fourier map and except for H(1), H(11), H(21), and H(31) refined riding on their carrier atoms with C–H = 0.98 Å. In the final cycles of the refinement 254 parameters (including an extinction parameter) were varied, which resulted in the R value of 0.038, wR = 0.042, $w^{-1} = (\sigma^2(F) + 0.00028F^2)$ and S = 1.09. Six common isotropic thermal parameters for the hydrogen atoms were used because of the large difference in the anisotropic parameters of the non-hydrogen atoms in different parts of the molecule. Especially atoms C(81), C(82), and C(83) have a large thermal motion, indicating a slightly disordered *tert*-butyl group. The average and maximum shift error ratios were 0.045 and 0.047 (for H(11) y/b), respectively. Final residual electron density: −0.25 ≤ $\Delta\rho$ ≤ 0.55 eÅ^{-3}, the highest densities lying near C(81), C(82), and C(83). Scattering factors were taken from Cromer and Mann and corrected for anomalous dispersion.[27] The structure determination and refinement were carried out on an in-house microvax-II cluster. All derived geometry calculations were performed with the programs of the EUCLID package.[26c]

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Registry No. **1a**, 78605-23-9; **1b**, 2644-21-5; **4a**, 30834-74-3; **4b**, 21478-42-2; **4c**, 135639-14-4; **4d**, 63503-18-4; **4e**, 107768-97-8; **4f**, 83948-29-2; **4g**, 67122-50-3; **4h**, 111601-45-7; *trans*-**5a**, 135682-67-6; *cis*-**5a**, 135682-68-7; *trans*-**5b**, 129276-50-2; *trans*-**5c**, 133693-68-2; *cis*-**5c**, 135613-77-3; *trans*-**5e**, 135613-78-4; *cis*-**5e**, 135613-79-5; *trans*-**5f**, 135613-80-8; *cis*-**5f**, 135613-81-9; *trans*-**6a**, 135613-82-0; *cis*-**6a**, 135613-83-1; *trans*-**6b**, 133693-65-9; *trans*-**6e**, 133693-66-0; *cis*-**6e**, 135613-84-2; *trans*-**6f**, 133693-67-1; *cis*-**6f**, 135613-85-3; *erythro*-**8**, 135613-86-4; *threo*-**8**, 135682-69-8; *N*-(trimethylsilyl)thiophene-2-carbaldimine–zinc chloride complex, 135639-15-5; *N,N'*-di-*tert*-butyl-1,4-diaza-1,3-butadiene–zinc chloride complex, 79949-45-4.

Supplementary Material Available: Tables of final coordinates, bond distances, angles, anisotropic thermal parameters for non-hydrogen atoms, and fractional coordinates and isotropic thermal parameters for hydrogen atoms and ^{1}H NMR spectra of some of the new compounds (16 pages); tables with observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

(25) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *B40*, 159.

(26) (a) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, 1976. (b) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, 1986. (c) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

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Novel Synthesis of *N,N*-Diarylarylmethanamines from *N*-(Arylmethylene)arenamines and (Arylmethoxy)arenes

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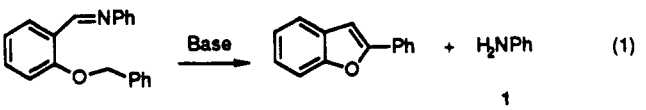
Various *N,N*-diarylarylmethanamines were synthesized by the reaction of *N*-(arylmethylene)arenamines with (arylmethoxy)arenes in dimethylformamide solution in the presence of a strong base as a catalyst which is obtained *in situ* by reacting metallic sodium with this solvent. In general, the reaction may be depicted as the reduction of the imine and addition, on the original imino nitrogen atom, of the aryl group (of the aryloxy moiety) of the ether and presumably oxidation of the arylmethoxy group of the ether to its corresponding aldehyde. Side reactions and a proposed reaction mechanism are discussed.

Introduction

The anil reaction discovered by Siegrist[1,2] has been used to synthesize a large number of substituted stilbenes by the reaction of Schiff's bases with methyl-substituted aromatic compounds. The preparation of 2-phenylbenzofuran[3] (eq 1) by a base-catalyzed intramolecular



(1)

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condensation reaction of 2-(phenylmethoxy)-*N*-phenylbenzenemethylenamine has been described. It was expected that the acyclic analogue of this reaction might result in a new preparation of aromatic enol ethers that could then be hydrolyzed readily to the corresponding deoxybenzoins and thus provide the intermediates for the

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(2) (a) Siegrist, A. E.; Liechti, P.; Meyer, H. R.; Weber, K. U.S. Patent 4,158,099, 1979. This patent is not abstracted in Chemical Abstracts. Similar is: *Ibid.* South African Patent 6,804,421, 1967; *Chem. Abstr.* **1969**, *71*, 71927. (b) Siegrist, A. E.; Liechti, P.; Meyer, H. R.; Weber, K. *Helv. Chim. Acta* **1969**, *52*, 2521.

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Table I. Tertiary Amines Prepared from *N*-Arylbenzaldimines and (Phenylmethoxy)benzenes in Na/DMF[a]

ether Ar	ether Ar^1	product[b]	time[c] (h)	yield[d] (%)	mp (°C) (solvent)
$PhCH{=}NPh + ArOCH_2Ar^1 \rightarrow PhCH_2N(Ph)Ar$					
Ph	Ph	4[e]	0.5	73	88–90[f] (MeOH)
1-$C_{10}H_7$	1-$C_{10}H_7$	6	0.7	68	133–134 (EtOAc)
4-MePh	Ph	7	0.5	36[g,h]	85–86 (MeOH)
2-MePh	Ph	8	0.5	36[g]	101–102 (MeOH)
4-BrPh	Ph	9	24[i]	22[g,j]	97–98 (PE[k]/MeOH)
4-ClPh	Ph	10	7[l]	17[g,m]	94–95[n] (MeOH)
4-Ph_2CNPh	Ph	11	1[o]	31	120–122 (MeOH)
1-$C_{10}H_7CH{=}NPh + ArOCH_2Ar^1 \rightarrow$ 1-$C_{10}H_7CH_2N(Ph)Ar$					
Ph	Ph	12	0.5	74	170–172 (EtOH)
1-$C_{10}H_7$	1-$C_{10}H_7$	13	0.5	65[p]	179–180 (EtOAc)
1-$C_{10}H_7$	Ph	13	0.5	58	
4-MeOPh	Ph	14	0.5[q]	15	157–159 (hexane)
4-*t*-BuPh	Ph	15	0.5[q]	29	135–137 (MeOH)

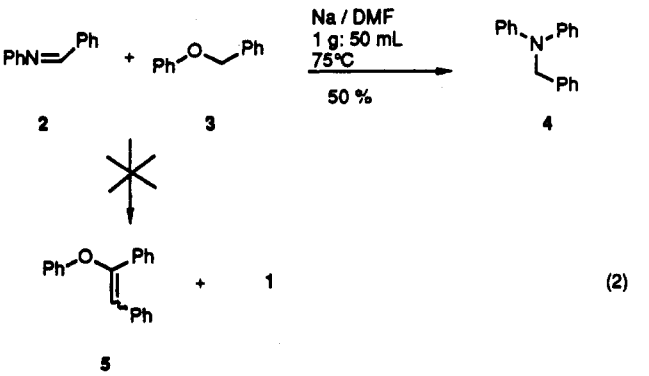
[a] 1 g of Na, total volume of DMF 50 mL unless specified otherwise.[4] [b] 10 mmol of each reactant unless specified differently. [c] 75 °C unless otherwise state. [d] Yield of product after recrystallization unless stated otherwise. [e] See Experimental Section for the different conditions used in this synthesis. [f] Lit.[13,45] mp 88–89 °C. [g] After chromatography and recrystallization. [h] 98.1% pure by HPLC. [i] At 30 °C (see Experimental Section). [j] 98% pure by HPLC. [k] PE = petroleum ether, 35–60 °C. [l] At 50 °C. [m] 99% pure by HPLC. The other contaminant was 4. [n] Lit.[46] mp 97–97.5 °C. [o] At 100 °C. [p] Based on a calibration curve after 15 min. The recovered yield after chromatography is ~35%. [q] 20 mmol of each reactant was used.

Table II. Bis-tertiary Amines Prepared from Bis-Imines or Bis-Ethers in (Na/DMF)[a] (Eqs 4–7)

reactants: imine	reactants: ether	product	time[b] (h)	yield[c] (%)	mp (°C) (solvent)
16[d]	3[e]	17	1	16	156–159 (EtOAc)
2[e]	20[e]	17	1	10[f,g]	
18[d]	3[e]	19	1	14	99–100 (hexane)
2[h]	21a[e]	22a	5[i]	60[f]	115–116 (EtOH)
2[h]	21b[e]	22b	1	20	136–137 (EtOAc/MeOH)

[a] Same as footnote a of Table I. [b] 100 °C unless stated otherwise. [c] After chromatography and recrystallization unless stated otherwise. [d] 5 mmol. [e] 10 mmol. [f] Based on a calibration curve and HPLC aliquot of the reaction mixture. [g] Not isolated. [h] 20 mmol. [i] 75 °C.

facile preparation of substituted benzils which, in turn, are useful monomers for a number of high-temperature polymers. Equimolar amounts of *N*-phenylbenzaldimine (**2**) and (phenylmethoxy)benzene (**3**) were allowed to react in *N*,*N*-dimethylformamide (DMF) solution in the presence of a catalyst that is principally sodium dimethylamide, generated *in situ* from sodium metal and DMF,[4,5] which had been used as a effective catalyst in earlier experiments.[6] This medium will be referred to as Na/DMF below. The resulting product was not the expected enol ether **5** (eq 2), but instead a 50% yield of *N*,*N*-diphenylbenzenemethanamine (**4**) was obtained.

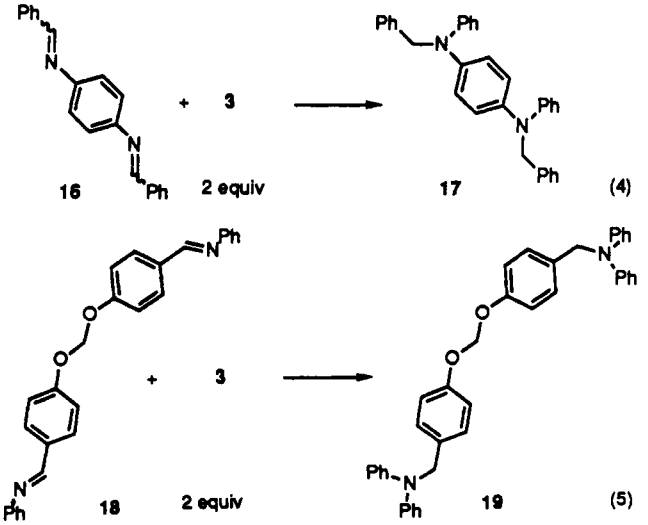


This unexpected reaction was used to prepare various N,N-diaromatic benzenemethanamines (examples in Tables I and II). Amines of this type have been used extensively to produce charge-transport layers in xerography.[7] This paper is concerned with the reaction of (arylmethoxy)arenes with aromatic Schiff's bases including a discussion of the scope of the reaction and some preliminary observations on the mechanism of the reaction.

Results and Discussion

1. General Reaction. The general reaction under discussion is depicted in eq 3. In the presence of a strong base (Na/DMF) the aromatic imines react with aromatic ethers at temperatures of 30–100 °C to give tertiary amines. The results listed for the compounds in Tables

I and II (see also eqs 2, 4–7) lead to eq 3 as a general

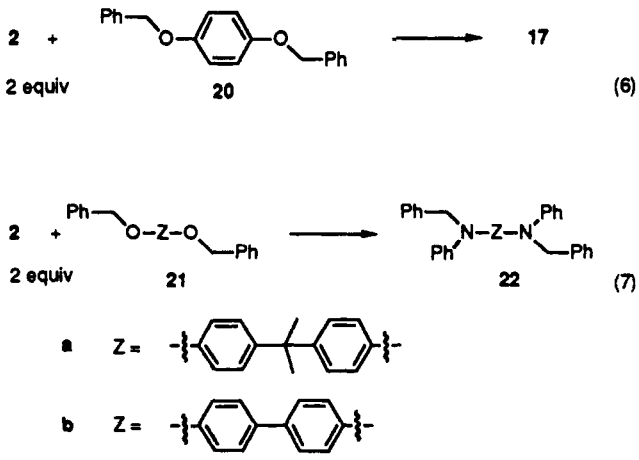


(4) For its preparation see ref 6.

(5) Bredereck, H.; Effenberger, F.; Gleiter, R. *Angew. Chem.* **1965**, *77*, 964; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 951.

(6) Paventi, M.; Hay, A. S. *Synthesis* **1990**, 878.

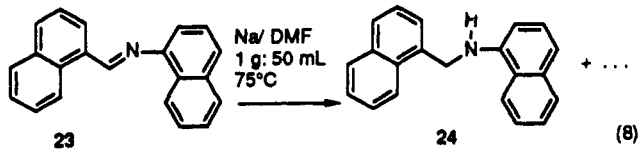
(7) For instance, see the patents issued to Xerox Corp.: (a) Limbug, W. W.; Pai, D. M. U.S. Patent 4,232,103, 1980; *Chem. Abstr.* **1981**, *94*, 93635q. (b) Stolka, M.; Yanus, J. F.; Pai, D. M. Ger. Offen. 2,712,557, 1977; *Chem. Abstr.* **1978**, *88*, 113328y. (c) Hogan, A. M. U.S. Patent 4,081,274 (Cl. 96-1PC; G03G5/04), 1978; *Chem. Abstr.* **1978**, *89*, 120873w; (d) *Ibid.* U.S. Patent 4,047,949, 1977; *Chem. Abstr.* **1978**, *88*, 81833r; (e) *Ibid.* 4,047,948, 1977; *Chem. Abstr.* **1978**, *88*, 43748j.



description of the reaction. Thus, the aryl moieties originally derived from a phenol (AOH) and an aniline (ENH_2) end up as the aryl substituents of the tertiary nitrogen atom while the arylmethyl group (DCH_2) of this tertiary amine (eq 3) derives from the aldehyde (DCHO) used to prepare the Schiff's base. The fate of the arylmethoxy group (BCH_2O) to the aldehyde (BCHO) was deduced from indirect observations (see below).

2. Stability of Reactants. Several of the reactants were submitted to the conditions of the reaction (75 °C; Na/DMF, 1 g/50 mL; 2 h) in the absence of the counter reactant. The stability was determined by reversed-phase high-pressure liquid chromatography (HPLC) analysis of aliquots of the individual compounds in solution. If no change in retention time or less than 20% change in area of the signal was observed after 2 h the compound is referred to as stable. The compounds studied are listed in Table III. The simple Schiff's bases are stable; however, those with extended conjugation such as those obtained from cinnamaldehyde, *N*-(3-phenyl-2-propenylidine)-benzenamine, or the diimine obtained from terephthaldehyde and aniline are unstable in this basic medium even at ambient temperature. *N*-(9-anthracenenylmethylene)benzenamine and *N*-(diphenylmethylene)-benzenamine are unreactive in this reaction. If the diaryl ethers are 2,6-disubstituted on the aryloxy moiety they likewise show exceptional stability and no reactivity. Steric hindrance in either the imine or the ether also makes them unreactive.

The base *N*-(1-naphthalenylmethylene)-1-naphthalenamine (23) is unstable in the presence of (Na/DMF) (eq 8). The decay curve of area, obtained from the HPLC



chromatogram, versus time of 23 is first order, but the infinity value is not zero: $A_\infty/A_0 = 0.25$ (A_∞ = area after an infinite time, A_0 = area at zero time). The half-life for the decomposition of 23 is about 5 min at 75 °C. This indicates a partial conversion and a farraginous mixture. The reaction was worked up as described in the experimental to recover 24 which is the equivalent of the alcohol in the Cannizzaro reaction.

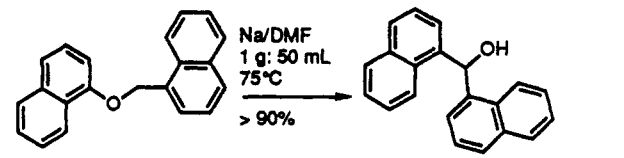
For (1-naphthalenylmethoxy)-1-naphthalene (25), although there is formation of the expected tertiary amine 13 when *N*-(1-naphthalenylmethylene)benzenamine and 25 react, a second pathway for the decomposition of 25 is preponderant. This route is illustrated in eq 9,[8-10] where

Table III. Stability[a] of Some Imines and Ethers in Na/DMF (1 g/50 mL) at 75 °C for 2 h

Stable	
PhCH=NPh	$PHCH_2OPH$
9-$C_{14}H_8CH$=NPh[b]	1-$C_{10}H_7CH_2$-OPh
$(Ph)_2$-CH=NPh[b]	$PhCH_2O$-1-$C_{10}H_7$
	2,6-$Ph_2(Ph)OCH_2Ph$[b]
	2,6-$Me_2(Ph)OCH_2PH$[b]
Unstable	
PhCH=CHCH=NPh[b]	1-$C_{10}H_7CH_2O$-1-$C_{10}H_7$
1,4-PhCH=N-(C_6H_4)-N=CHPh	
1,4-PhN=CH-(C_6H_4)-CH=NPh	
1-$C_{10}H_7CH$=N-1-$C_{10}H_7$[b]	

[a] See text for explanation. [b] Does not participate in the formation of the tertiary amine.

25 in the absence of *N*-(1-naphthalenylmethylene)-benzenamine undergoes the well-known Wittig rearrangement.[11,12]



Under the identical conditions outlined in eq 9, (phenoxymethyl)-1-naphthalene (28) and (phenylmethoxy)-1-naphthalene are stable. The color of their solutions, as for all the other benzyl ethers, is reddish brown indicating the presence of anions. The color can be discharged temporarily upon addition of more dimethylformamide, which contains traces of water. Reaction of the stable (phenylmethoxy)-1-naphthalene and *N*-(1-naphthalenylmethylene)benzenamine yields 60% of the tertiary amine 13.

3. Reactions in the Presence of Aniline. In some cases we have identified minor amounts of tertiary amines that have to be formed from imines different from the reactant added, which indicates that aniline and an aldehyde are generated in the reaction. On the assumption that the benzyl moiety can end up as a benzaldehyde we performed a series of experiments in which the concentrations of 1–3 were varied and the formation of 4 was monitored. These results are listed in Table IV. Runs 1 and 2 demonstrate that the Schiff's base 2 and the ether 3 are essential reagents for the reaction. Runs 3–6 show that aniline is not required for the reaction; an excess of 2 gives a yield close to theory based on benzylphenyl ether, whereas an excess of 3 has almost no effect on the yield. When an equivalent amount of 2 and 3 is employed for the synthesis of 4, the isolated yield is ~70% (see Table I).

Increasing the amount of the ether increases the yield in the presence of aniline by up to 30%, based on 2 which is the limiting reagent. We suggest that the reaction evolves benzaldehyde, which condenses with the added aniline to give more of 2, which in turn reacts with an excess of 3 to give the increased amount of 4.

When aniline is added to the reaction mixture and the amount of 3 is progressively increased, the yield of 4 based

(8) Product 26 identification was rendered difficult because the obtained mp of 126–7 °C was much lower than the reported 144 °C[9,10] and because the derivatives prepared[9] have been assigned the wrong structural formula (cf. Experimental Section and supplementary material).

(9) Schmidlin, J.; Massini, P. *Chem. Ber.* **1909**, *42*, 2377.
(10) Blicke, F. F. *J. Am. Chem. Soc.* **1927**, *49*, 2843.
(11) Eisch, J. J.; Kovacs, C. A.; Rhee, S.-G. *J. Organomet. Chem.* **1974**, *65*, 289.
(12) Schöllkopf, U.; Eisert, M. *Liebigs Ann. Chem.* **1963**, *664*, 76.

Table IV. Effect of Concentrations of Species 1–3 on the Yield of the Tertiary Amine 4[a]

run no.	1 (mmol)	2 (mmol)	3 (mmol)	yield of 4[b] (%)
1	3.3	0	10	0
2	3.3	10	0	0
3	0	2.5	10	73
4	0	10	2.5	97
5	0	10	10	65[c]
6	0	2.5	5.0	69
7	3.3	2.5	2.5	82
8	3.3	2.5	5.0	95
9	3.3	2.5	7.5	108
10	3.3	2.5	10	126
11	3.3	2.5	12.5	130[d]
12	3.3	3.3	10	100
13	3.3	10	2.5	69

[a] Na/DMF (1 g/50 mL) at 75 °C under N_2 atmosphere. [b] Calculated, based on the smaller concentration of **2** or **3**, from area of the HPLC peak at λ 254 nm, unless otherwise stated, and a calibration curve for **4**. Plateau value of concentration reached after ca. 30 min. Not isolated except where otherwise stated. [c] Monitored at λ 292 nm; λ_{max} for **4**. Aliquots 10 times greater than for the other runs. Isolated yield after recrystallization. [d] Isolated 96% after recrystallization (see Experimental Section).

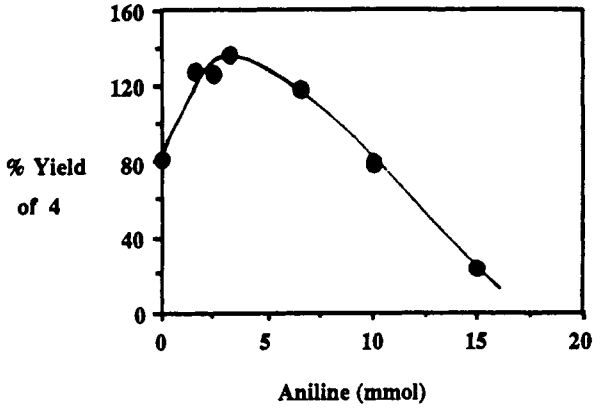


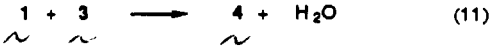
Figure 1. Variation of percent yield of **4** vs concentration of aniline. The conditions were Na/DMF (1 g/50 mL) at 75 °C for an average of 80 min. Concentrations of **2** and **3** are the same as for run 11 in Table IV and constant throughout.

on the limiting reagent **2** increases to 130% (runs 7–11), which indicated that additional **2** is generated in the reaction. If additional aniline is now added to the reaction mixture (see Figure 1), the yield gradually decreases to zero. At the higher concentrations of aniline the catalyst, sodium dimethylamide, is probably converted to sodium anilide which is not a catalyst for the reaction. When the latter is prepared as a catalyst *in situ* from sodium naphthalene and aniline no reaction occurs.

4. Byproducts and Stoichiometry. A product study was attempted for the reaction (eq 2). A major product of the reaction is *N*,*N*-dimethylbenzamide, which could be obtained by reaction of benzaldehyde (from the arylmethoxy group) with sodium dimethylamide. *N*,*N*-Dimethyl-α-(phenylamino)benzeneacetamide, which could be obtained by direct addition of sodium *N*,*N*-dimethylformamide to **2**,[6] is also isolated. Small amounts of *N*,*N*-dimethyl-*N*-phenylurea, which could result from oxidation of the addition product of aniline and dimethylformamide, are also detected.

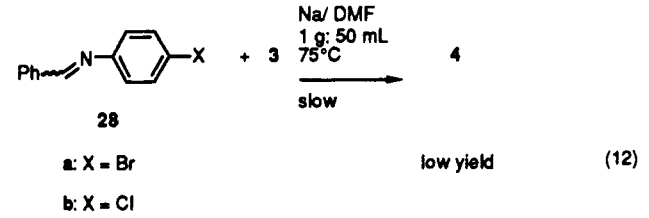
In several cases in addition to the expected tertiary amine **4** (eq 10; the numbers in brackets below the respective products are the HPLC areas × 10^{-4} of the peaks immediately prior to quenching the reaction) a second amine is formed as a byproduct in which the arylmethylene moiety is derived from the arylmethylene moiety of the starting ether. This provides further evidence of an aldehyde intermediate that is converted to an imine in the reaction.

From the available information the reaction may be formulated as shown in eq 3 (**A** = **B** = **C** = **D** = Ph). Conceptually, the reaction can be written as shown in eq 11 in which **2** is present in catalytic amounts. However,



because of other reactions involving the presumed benzaldehyde intermediate larger quantities of (phenylmethoxy)benzene are required in eq 11 (cf. runs 7–11 with runs 3–5 in Table IV).

5. Substituents. When the substitution on the aniline moiety is 4-chloro, 4-bromo, or 4-methoxy none of the expected tertiary amine is obtained. Reaction of the halo imines with **3** removes the halogen to produce a low yield of **4** (eq 12). Replacing the phenyl group on the nitrogen

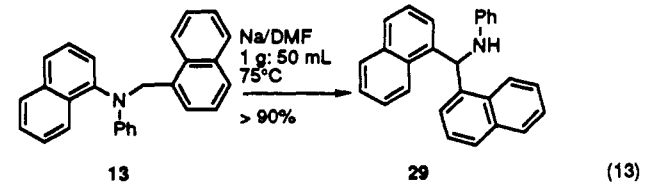


atom by 1-naphthalenyl gives an unstable imine. As in the Siegrist reaction,[1,2] substituents on the aldehyde and even substituted dialdehydes have been employed and are stable (Tables I and II, **12–15**, **19**). The ring of the arylmethoxy moiety of the ether may also be substituted by a variety of groups. A 4-*tert*-butyl group slows down the formation of **4** in the reaction of 1-(1,1-dimethylethyl)-4-(phenoxymethyl)benzene with *N*-(1-naphthalenylmethylene)benzenamine.

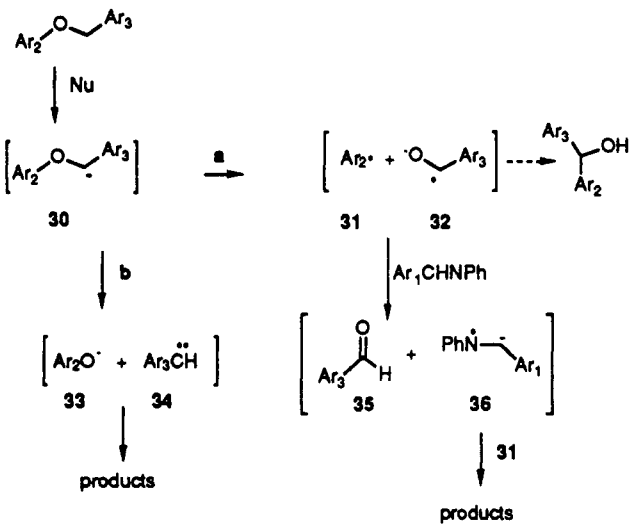
Substituents on the phenolic moiety of the benzyl ether are also stable. Examples include methyl, chloro, bromo, and methoxy substituents (see Table I). When there is 2,6-disubstitution as discussed above (Table III) reaction does not occur.

N-(Diphenylmethylene)benzenamine (Table III) is stable and unreactive and the diphenylmethylene moiety can be used to protect the amino group in the reaction and subsequently removed.

Tertiary amines listed in Tables I and II show good stability in Na/DMF medium. The one exception, *N*-1-naphthalenyl-*N*-phenyl-1-naphthalenemethanamine (**13**), was studied in more detail. By monitoring the reaction of (1-naphthalenylmethylene)benzenamine and (1-naphthalenylmethoxy)-1-naphthalene (**25**) to give **13**, it was observed that the concentration of **13** reached a maximum and then slowly decreased. We have found that tertiary amine **13** undergoes a smooth exponential decay to α-1-naphthalenyl-*N*-phenyl-1-naphthalenemethanamine (**29**) as outlined in eq 13 when allowed to stand in Na/DMF



Scheme I



at 75 °C. This rearrangement of tertiary amines has been studied by Eisch and probably proceeds by an anionic pathway.[13,14]

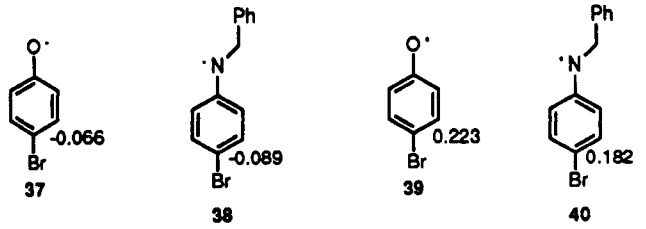
The reaction of (1-naphthalenylmethylene)benzenamine and the ether **25** involves a trifurcate path. The production of **26** from the rearrangement of **25** (eq 9), formation of **13**, and formation of **29** from **13** (eq 13). The yield of **13** was increased by interchanging the ether **25** for (phenylmethoxy)-1-naphthalene and reacting with the same Schiff's base *N*-(1-naphthalenylmethylene)benzenamine and by quenching the reaction when **13** reaches a maximum concentration (see Experimental Section).

In the reaction of **2** and **27** (eq 10) a small amount of 1-naphthalenyl-2-phenylethylene was also isolated.[2]

6. Mechanism. Eisch[11] has studied the reaction of benzylphenyl ether in THF solution in the presence of butyllithium. The product of the reaction is benzhydrol, and he proposes a Wittig rearrangement involving an initial abstraction of a proton from benzylphenyl ether followed by dissociation to a radical ion cage intermediate which collapses to give benzhydrol (see Scheme I).

It was noted previously that halogen substituents are readily lost only when they are substituents on the aniline. It is known that the 4-bromophenoxide ion is relatively stable but that rapid polymerization occurs at room temperature when the phenoxy radical is formed, via a single-electron-transfer mechanism in which bromide ion is eliminated.[15] This is in line with the calculated net charge densities at the 4-positions of the radical **37** and anion **39**. The calculated net charge densities[16] for the corresponding anion **38** and radical **40** obtained from *N*-(4-bromophenyl)benzenemethanamine are similar, which infers that since halogen is lost only when it is present on the aniline that an intermediate radical such as **40** is present in the reaction.

We therefore propose that an electron-transfer reaction occurs between the ion radical **32** and the imine to give a new radical anion **36**, which then collapses to give the tertiary amine product. The intermediate **36** would be expected to be unstable when the substituents are halogen. The aldehyde produced as a coproduct could then participate in the reaction as discussed previously.



As an alternative route the anion **30** could cleave to give the carbene **34** as occurs with butyllithium[12] (path b of Scheme I). Carbenes should react with imines to produce aziridines with a C–C bond formation. It is difficult to see how the tertiary amines could be generated from these intermediates. However, it may be possible that aziridines are intermediates in the formation of the ethylene compounds.

Other experimental observations[17] do not corroborate any of the two paths proposed above, but good kinetic data is lacking to piece together a third possibility.

Conclusion

The investigations carried out have shown that tertiary amines may be obtained in moderate to high yields with aromatic Schiff's bases and (arylmethoxy)arenes in the presence of strong base. *N,N*-diphenylbenzenemethanamine can be obtained in yields over 100% by addition of aniline and keeping the amount of imine low compared to the ether. The syntheses of other tertiary amines have not been optimized. This novel route makes possible the preparation of unsymmetrical tertiary amines from readily available starting materials. Their utility in xerography and photoimage enhancers[18] makes this synthesis very attractive. The preparation of the tertiary amines was due to a fortuitous choice of base because other strong bases lead, as will be published subsequently, to different products.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra ($CDCl_3$) were recorded (200 or 300 MHz) using Me_4Si as internal standard; ^{13}C NMR (250 MHz) were run in $CDCl_3$.[19] Ratios, purity, and reaction conversion given below are all taken from the peak area of the HPLC runs. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Petroleum ether (bp 35–60 °C) is abbreviated below as PE. The reactions in DMF containing 0.15% H_2O and sodium metal were carried out under N_2 atmosphere. The Na/DMF mixture was prepared as reported previously.[6] Reactions were monitored quantitatively by taking 10-μL aliquots of the Na/DMF mixture and diluting with MeOH to 10 mL.

Imines: General Procedure. Stoichiometric amounts of the aromatic amine (or diamine) (0.30 equiv) and the aromatic aldehyde (or dialdehyde) (0.30 equiv) were heated under reflux in 200 mL of benzene with azeotropic removal of 5.4 mL of H_2O.

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(14) Eisch, J. J.; Kovacs, C. A.; Chobe, P. *J. Org. Chem.* **1989**, *54*, 1275.
(15) Koch, W.; Risse, W.; Heitz, W. *Makromol. Chem., Suppl.* **1985**, *12*, 105.
(16) Huckel MO calculations using HMO software from Trinity Software, P.O. Box 960, Campton, NH 03233.
(17) One is compound **11**: an imine chromophore should trap any radical formed. A second is that the reaction of **2** and **3** appears to be first order although stoichiometric amounts react. These first-order rate constants at four temperatures give a straight Arrhenius plot with an evaluated activation energy of 20 kcal/mol, which is not consistent with a radical-anionic or carbenic mechanism. A third is that no isomeric materials were detected for compounds **6–10** and **13–15**, and thus a benzyne mechanism, which forms **10**,[46] is not possible. A fourth is that (arylmethoxy)arenes in the presence of metallic sodium in toluene[47] or generated anion radicals give methylarenes and arenols.[28] Methylarenes in turn react with the available Schiff's base, in the Siegrist reaction,[1,2] to give diarylethylenes, which were isolated in some reactions.
(18) Vagapov, M.; Kartuzhanskii, A.; Larinov, Yu.; Vannikov, A.; Chernov, G. *Poligrafiya* **1984**, *1*, 23; *Chem. Abstr.* **1984**, *100*, 112135n.
(19) Results and interpretation were obtained from Gennaro Barbiero at the University of Sherbrooke, Sherbrooke, Quebec, Canada. The COLOC technique was used.

Concentration of benzene left a solid residue which was recrystallized. Yields were between 85 and 100%.

Thus, the following imines were prepared: **2**, mp 49–51 °C (hexanes) (lit.[20] mp 51 °C, lit.[21] mp 56 °C, lit.[22] mp 52 °C); *N*-(1-naphthalenylmethylene)benzenamine, yellow needles, mp 68–70 °C (EtOH) (lit.[20] mp 71 °C); **16**, beige plates, mp 143–144 °C (MeOH) (lit.[23] mp 139–140 °C); **23**, yellow crystals, mp 116–118 °C (benzene/MeOH 1:2) (lit.[21] mp 113–115 °C); **28a**, mp 61–63 °C (PE) (lit.[22] mp 66 °C); **28b**, mp 53–56 °C (PE) (lit.[22] mp 62–63 °C); 4-methoxy-*N*-(phenylmethylene)benzenamine, mp 73–75 °C (PE) (lit.[22] mp 70–71 °C); *N*-(9-anthracenylmethylene)-benzenamine, yellow needles, mp 115–117 °C (MeOH) (lit.[20] mp 112 °C, lit.[24] mp 112.5–113 °C); *N,N*-[(1,4-phenylene)dimethylene]bis(benzenamine), green-yellow plates, mp 162–163 °C (benzene) (lit.[25] mp 164–165 °C); *N*-(1-phenylprop-1-en-3-ylidene)benzenamine, mp 112–114 °C (EtOH) (lit.[26] mp 108 °C).

Prepared as outlined in the literature were **18** (mp 84–85 °C)[6] and *N*-(diphenylmethylene)benzenamine (mp 113–115 °C).[27]

***N*-(1-Naphthalenyl)-1-naphthalenemethanamine (24).** The imine **23** (2.81 g, 0.01 mol) was heated at 75 °C in Na/DMF (1 g/50 mL) for 2 h. The DMF mixture was poured into H_2O (150 mL) and extracted with $CHCl_3$ (3 × 75 mL). The organic phase was washed with H_2O (2 × 50 mL), dried, and concentrated. Chromatography of the residue (PE/$CHCl_3$ 4:1) gave **24** recrystallized (MeOH) to give (0.5 g, 18%) white prisms which partially melt from 128–129 °C, resolidifying with further heating and melting from 135–137 °C; ^1H NMR δ 4.69 (br s, 1 H, NH), 4.90 (s, 2 H, CH_2N), 6.76 (dd, $J_{2,3}$ = 7.1, $J_{2,4}$ = 1.0 Hz, 2 H, C2H), 7.26–7.95 (m, 12 H), 8.11–8.16 (m, 1 H). Anal. Calcd for $C_{21}H_{17}N$ (283.38): C, 89.01; H, 6.05; N, 4.94. Found: C, 88.47; H, 6.08; N, 4.97.

Ethers: General Procedure. The potassium aryl oxide (or dipotassium aryl dioxide) (0.30 equiv), prepared from methanolic KOH (0.30 equiv of OH^-) and evaporation of solvent, and arylmethyl chloride (or bromide) (0.30 equiv) were heated at 80 °C for 2 h in DMF (100 mL). The ether was precipitated by pouring into H_2O (300 mL), filtered, dried, and recrystallized.

In this manner were prepared: **3** (95%), mp 38–39 °C (lit.[11] 37–38 °C); **27** (~100%), mp 72–74 °C after three recrystallizations (EtOH) (lit.[28] mp 76–77 °C); (phenylmethoxy)-1-naphthalene (80%), mp 78–79% °C (MeOH) (lit.[28] mp 75–77 °C, lit.[29] mp 77.0–77.5 °C, lit.[30] mp 75 °C[30]); 1-methyl-4-(phenylmethoxy)-benzene (~100%), 34–35 °C (EtOH) (lit.[30,31] mp 40 °C); 1-bromo-4-(phenylmethoxy)benzene (90%), mp 61–62 °C (MeOH) (lit.[32] 64 °C, bp 226 °C/(50 mmHg)); 1-chloro-4-(phenylmethoxy)benzene (90%), needles, mp 72–73 °C (MeOH) (lit.[30] mp 71 °C, lit.[31] mp 71–72 °C); 1-methoxy-4-(phenylmethoxy)benzene (~100%), large leafs, mp 69–70 °C (EtOH) (lit.[33] mp 74 °C); 1-(1,1-dimethylethyl)-4-(phenylmethoxy)benzene (90%), mp 63–64 °C (MeOH) (lit.[11] 59–60 °C).

This procedure was used to prepare the following:

1-Methyl-2-(phenylmethoxy)benzene. Potassium 2-methylphenoxide and (chloromethyl)benzene precipitated an oil which was decanted from the aqueous DMF. It was dissolved in PE (200 mL) washed with 2 N NaOH (2 × 50 mL) and H_2O (3 × 100 mL), dried, and concentrated. The residual reddish oil (95% pure) was used without further purification in the preparation of **8** (lit.[30] bp 284 °C, lit.[31] bp 158 °C (14 mm Hg), lit.[34] bp 183 °C (24 mm Hg)).

1,3-Dimethyl-2-(phenylmethoxy)benzene. Potassium 2,6-dimethylphenoxide and (chloromethyl)benzene gave the title compound, after an identical workup as for 1-methyl-2-(phenylmethoxy)benzene, as an oil (90% yield, 95% pure) used without further purification (lit.[31] bp 162 °C (14 mm Hg), lit.[35] bp 115–116 °C (0.3 mm Hg)).

1,3-Diphenyl-2-(phenylmethoxy)benzene. Potassium 2,6-diphenylphenoxide and (chloromethyl)benzene gave (90% yield) needles: mp 88–89 °C (MeOH); ^1H NMR δ 4.14 (s, 2 H, OCH_2), 6.60–6.65 (m, 2 H), 7.05–7.16 (m, 3 H), 7.23–7.47 (m, 9 H), 7.60–7.66 (m, 4 H). Anal. Calcd for $C_{25}H_{20}O$ (336.44): C, 89.25; H, 5.99. Found: C, 89.20; H, 6.19.

***N*-(Diphenylmethylene)-4-(phenylmethoxy)benzenamine.** Potassium 4-(*N*-acetylamino)phenoxide[36] (0.20 mol) and (chloromethyl)benzene (22.5 g, 0.217 mol) reacted in DMF (100 mL) at 80 °C for 2 h. This mixture was poured into H_2O (200 mL). The precipitate was filtered and dried. The acetyl group was hydrolyzed with H_2O/HCl (3:1; 200 mL) and MeOH (100 mL) by heating at reflux until the solution was clear (~3 h), then cooled and made alkaline (NaOH, 2 N, pH paper). The solvent was decanted from the oily 4-(phenylmethoxy)benzenamine, which slowly hardened to a brown solid (~13 g). To this solid (13 g, 0.0652 mol) was added benzophenone (12 g, 0.0658 mol), 22 g of 5 Å molecular sieves (cf. other examples[27]), and 200 mL of benzene heated under reflux, and the mixture was stirred (5 days). The solid, obtained from filtration and evaporation of benzene, was washed with PE (10 mL), and treated with activated charcoal (~3 g) in boiling MeOH (50 mL), and the solution was filtered. The filtrate upon cooling crystallized the title imine as pale green-yellow needles (~5 g): mp 87–88 °C (MeOH); ^1H NMR δ 4.97 (s, 2 H, OCH_2Ph), 6.65–6.81 (m, 5 H, $CH_2C_6H_5$), 7.10–7.17 (m, 2 H), 7.26–7.51 (m, 10 H), 7.70–7.77 (m, 2 H). Anal. Calcd for $C_{26}H_{21}NO$ (363.46): C, 85.92; H, 5.82; N, 3.85. Found: C, 86.26; H, 5.76; N, 3.98.

1,4-Bis(phenylmethoxy)benzene (20). The dipotassium salt of hydroquinone (0.10 mol) and (chloromethyl)benzene (0.20 mol) gave (90% yield) needles: mp 130 °C (EtOH); ^1H NMR δ 5.01 (s, 4 H, OCH_2), 6.91 (s, 4 H, C_6H_4), 7.28–7.46 (m, 10 H, C_6H_5). Anal. Calcd for $C_{20}H_{18}O_2$ (290.37): C, 82.73; H, 6.25. Found: C, 82.50; H, 6.19.

1,1′-(Methylethylidene)-bis(4-phenylmethoxybenzene) (21a). Dipotassium 4,4′-(methylethylidine)bis(phenoxide) and (chloromethyl)benzene gave (90% yield) long needles: mp 125–127 °C (acetone); ^1H NMR δ 1.63 (s, 6 H, CH_3), 5.02 (s, 4 H, OCH_2), 6.84–6.91 (m, 4 H), 7.11–7.18 (m, 4 H), 7.26–7.46 (m, 10 H, $C_6H_5CH_2O$). Anal. Calcd for $C_{29}H_{28}O_2$ (408.54): C, 85.26; H, 6.91. Found: C, 85.15; H, 6.84.

4,4′-Bis(phenylmethoxy)-1,1′-biphenyl (21b). Dipotassium 4,4′-(1,1′-biphenyl) dioxide (0.050 mol) and (chloromethyl)benzene (0.10 mol) reacted to give (>90% yield) the title compound: mp 224–226 °C (benzene); ^1H NMR δ 5.10 (s, 4 H, OCH_2), 6.99–7.07 (m, 4 H), 7.33–7.51 (m, 14 H). Anal. Calcd for $C_{26}H_{22}O_2$ (366.46): C, 85.22; H, 6.05. Found: C, 85.32; H, 5.93.

1-(1-Naphthalenylmethoxy)naphthalene (25). (Chloromethyl)-1-naphthalene and potassium 1-naphthoxide gave (80% yield) colorless plates; mp 115–117 °C (PE); ^1H NMR δ 5.68 (s, 2 H, OCH_2), 7.48 (q, J = 1.6, 7.2 Hz, 1 H, C2*H*), 7.36–7.58 (m, 7 H, $C_{10}H_7CH_2O$), 7.69–7.97 (m, 4 H, C5*H*-C8*H*), 8.08–8.15 (m, 1 H, C3*H*), 8.24–8.28 (m, 1 H, C4*H*). Anal. Calcd for $C_{21}H_{16}O$ (284.36): C, 89.02; H, 5.34. Found: C, 88.99; H, 5.19.

Product of Wittig Rearrangement of 25. Di-1-naphthalenylmethanol (26). The ether **25**[37] was heated in Na/DMF (1 g/50 mL) at 75 °C for 20 min resulting in total

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(35) Curtin, D. Y.; Crawford, R. J.; Wilhem, M. *J. Am. Chem. Soc.* **1958**, *80*, 1391.
(36) The phenol was prepared as per: Ferniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry, Including Qualitative Organic Analysis*, 4th ed.; Wiley: New York, 1978; Chapter IV, p 753. The oxide was prepared as per the general procedure.
(37) Used for heat-sensitive recording sheets: Oji Paper Co. Ltd. Jpn. Kokai Tokkyo Koho JP 60, 109895 [85, 109, 895], 1985; *Chem. Abstr.* **1985**, *103*, 224473q.

conversion >90% yield of **26** and some 5–10% of other products. The title compound was precipitated after pouring the mixture into H_2O (100 mL) and filtering. Three recrystallizations (cyclohexane) gave small needles which incorporated cyclohexane:[38] mp 125–127 °C (lit.[9,10] mp 144 °C); ^1H NMR δ 2.40 (d, J = 4.7 Hz, 1 H, O*H*), 7.31 (d, J = 4.7 Hz, 1 H collapses to singlet when exchanged with D_2O, C*H*OH), 7.36–7.53 (m, 8 H), 7.81–7.93 (m, 4 H), 8.03–8.08 (m 2 H); ^{13}C NMR δ 69.1 (*C*HOH), 123.1 (*C*8), 124.4 (*C*7), 124.9 (*C*6), 125.1 (*C*3), 125.9 (*C*2), 128.0 (*C*4), 128.3 (*C*5), 130.5 (C8a), 133.4 (*C*4a), 137.9 (*C*1). Anal. Calcd for $C_{21}H_{16}O$ (284.36): C, 88.70; H, 5.67. Found: C, 88.92; H, 6.23.

Tertiary Amines. N,N-Diphenylbenzenemethanamine (4). Method a. The imine **2** (2.35 g, 0.013 mol) and **3** (1.84 g, 0.010 mol) were heated at 75 °C in Na/DMF (2.0 g/50 mL) for 30 min. The solution was then poured in 200 mL of H_2O, and the precipitate was filtered, washed with H_2O (3 × 30 mL), dried, and recrystallized as needles. No depression in mp occurred when this material was admixed with an authentic sample:[39] UV–vis (MeOH) λ_{max} (ϵ_{max}) 292 (11953), 242 (9416), 212 (10616) nm. Anal. Calcd for $C_{19}H_{17}N$ (259.35): C, 87.99; H, 6.61. Found: C, 88.15; H, 6.44.

Method b. The reaction of **28** (2.34 g, 0.010 mol) and **2** (1.81 g, 0.010 mol) under the same conditions as above gave after 30 min **4** (42%), **12** (see below), and 1-naphthalenyl-2-phenylethylene (combined peak area of 23% and of similar retention time) and the more polar *N,N*-dimethyl-α-(phenylamino)benzeneacetamide.[6]

Chromatography (PE/$CHCl_3$ (4:1)) separated three compounds. The amine **4** was extracted at room temperature (MeOH) and recrystallized (mp 88–90 °C (MeOH)). The rest of the mass fractionally recrystallized (MeOH) **12**, which was recrystallized to a constant mp of 171–173 °C. Evaporation of the mother liquors from the first crystallization of **12** and then two recrystallizations (MeOH) of the residue gave the ethylene compound (mp 58–60 °C) with identical mp, IR, and mass spectra as an authentic sample.[2b,40]

The amide was eluted with PE/EtOH (9:1) and identified by mp and mixed mp with an authentic sample.[6]

Method c. In run 11 (Table II) **1** (0.31 g, 0.033 mol), **2** (0.45 g, 0.0025 mol), and **3** (2.30 g, 0.0125 mol) reacted 30 min in Na/DMF (1 g/50 mL). Aqueous workup as in method a precipitated **4**, which after one crystallization (MeOH) weighed 0.62 g (96% yield), mp 83–87 °C. Recrystallization (MeOH) gave long needles (mp 88–90 °C). In another experiment a mixture of **3** and **4** was crystallized from the aqueous workup, filtered, and dried (1.28 g of which 0.65 g was **4** (100%)). After the aqueous solution was extracted with $CHCl_3$ (3 × 30 mL) and evaporation of the solvent the oily residue contained an additional 0.20 g of **4** for a total 103% isolated material.

Isolated Materials from the Preparation of 4. Reaction at 100 °C. The mother liquors from the recrystallization of **4** (method a for **4**, a different reaction carried out for 2 h) were combined with the PE extracts 3 × 150 mL of the aqueous DMF filtrate. The organics were evaporated, and the residual oil was chromatographed first with PE, giving more **4**. Another fraction gave after evaporation of solvent some material (mp 203–4 °C; m/e = 181) which was not characterized further. Evaporation of solvent from the later fractions gave a material (mp 168–70 °C (MeOH); m/e = 197) consistent with *N*-phenylbenzamide.

Further elution with PE/EtOAc (9:1) gave *N,N*-dimethyl-α-(phenylamino)benzeneacetamide, whose properties are described elsewhere.[6]

The aqueous DMF was extracted with $CHCl_3$ (3 × 150 mL). The solvent was evaporated, and the residual oil was chromatographed (EtOAc/PE (1:1)). The later fractions upon concentration and cooling slowly crystallized some material which was washed (Et_2O) and recrystallized (mp 134–7 °C (Et_2O)) as colorless needles. The spectra are consistent with the literature[41] for *N,N*-dimethyl-*N'*-phenylurea (mp 132–3 °C[42] and 131–2 °C[43]). The earlier fractions gave a small amount of *N,N*-dimethyl-α-(phenylamino)benzeneacetamide.[6] Both fractions contained the most abundant *N,N*-dimethylbenzamide: impure oil characterized by comparing IR and MS of an authentic sample. The IR spectrum indicated at least another product (NH stretch) contaminating this *N,N*-dimethylbenzamide.

The following tertiary amines were prepared as per Table I. The workup follows the procedure utilized for **4** (method a).

***N*-(1-Naphthalenyl)-*N*-phenylbenzenemethanamine (6):** ^1H NMR δ 5.03 (s, 2 H, NC*H*$_2$), 6.56–6.74 (m, 3 H), 7.05–7.52 (m, 11 H), 7.75–7.93 (m, 3 H). Anal. Calcd for $C_{23}H_{19}N$ (309.41): C, 89.28; H, 6.19; N, 4.53. Found: C, 88.96; H, 6.20; N, 4.56.

***N*-(4-Methylphenyl)-*N*-phenylbenzenemethanamine (7).** The aqueous mixture was extracted with PE (3 × 100 mL) and chromatographed (PE/EtOAc (95:5)). The purer fractions containing **4** and **7** (6:94) were combined, and the solvent was removed. The residual oil (1 g) was dissolved in MeOH (some PE added), and on cooling **7** crystallized. Two recrystallizations gave pure **7**: ^1H NMR δ 2.29 (s, 3 H, methyl), 4.97 (s, 2 H, -NC*H*$_2$Ph), 6.80–6.97 (m, 3 H), 7.06–7.27 (d, J = 1.37 Hz, 4 H, -NC$_6$*H*$_4$CH$_3$), 7.14–7.36 (m, 7 H). Anal. Calcd for $C_{20}H_{19}N$ (273.38): C, 87.87; H, 7.00; N, 5.12. Found: C, 88.21; H, 7.02; N, 5.01.

***N*-(2-Methylphenyl)-*N*-phenylbenzenemethanamine (8).** Workup as for **7** and evaporation of the PE gave a solid residue. This material was washed with a little Et_2O and recrystallized: ^1H NMR δ 2.15 (s, 3 H, Me), 4.84 (s, 2 H, PhC*H*$_2$N), 6.50–6.56 (m, 2 H), 6.66–6.77 (m, 1 H), 7.07–7.42 (m, 11 H). Anal. (average of two runs). Calcd for $C_{20}H_{19}N$ (273.38): C, 87.87; H, 7.00; N, 5.12. Found: C, 87.85; H, 7.23; N, 5.05.

***N*-(4-Bromophenyl)-*N*-phenylbenzenemethanamine (9).** The ether 1-bromo-4-(phenylmethoxy)benzene (2.63 g, 0.010 mol) and **2** (1.81 g, 0.010 mol) were dissolved in Na/DMF (1 g/50 mL) and heated at 50 °C for 145 min. Two other reactions were run at the same molar ratios at 100 °C for 15 min and at 30 °C for 24 h. After the stated periods **9** and **4** were produced in the following ratios: at 100 °C 31:69, at 50 °C 77:33, and at 30 °C 94:6. The conversion decreased with temperature: at 100 °C ~100%, at 50 °C ~95%, and at 30 °C ~50%. The reaction run at 30 °C was poured into H_2O (150 mL) and chromatographed (PE/$CHCl_3$ (9:1)) obtaining **9**: ^1H NMR δ 4.96 (s, 2 H, -NC*H*$_2$Ph), 6.83–6.88 (m, 2 H), 7.01–7.32 (m, 12 H). Anal. Calcd for $C_{19}H_{16}BrN$ (338.25): C, 67.47; H, 4.77; Br, 23.62; N, 4.14. Found: C, 67.92; H, 4.97; Br, 23.54; N, 4.10.

The attempted reaction of 1-bromo-4-(phenylmethoxy)benzene and **27a** in the same solvent mixture at 50 °C for 7 h gave, among other things, **9** and **4** in a ratio of 9:1 with no detection of the *N,N*-bis-(4-bromophenyl)benzenemethanamine (for its preparation see supplementary material).

***N*-(4-Chlorophenyl)-*N*-phenylbenzenemethanamine (10).** At 90% conversion, **10**, **4**, and some unknown material were in a ratio of 65:18:17. Similar aqueous workup as for the preparation of **9** and chromatography (PE/$CHCl_3$ (9:1)) gave 0.50 g of **10**, contaminated (<1%) with **4**: ^1H NMR[44] δ 5.03 (s, 2 H, Ph_2NCH_2Ph), 6.96–7.38 (m, 14 H). Anal. Calcd for $C_{19}H_{26}ClN$ (293.80): C, 77.68; H, 5.49; N, 4.77; Cl, 12.07. Found: C, 77.77; H, 5.61; N, 4.59; Cl, 12.00.

***N*-(Diphenylmethylene)-*N'*-phenyl-*N'*-(phenylmethyl)-1,4-benzenediamine (11).** Chromatography (PE/EtOAc (98:2)) of the oily precipitate from the reaction separated the less polar contaminants. Changing the eluant to PE/EtOAc (45:5) separated **11**, which recrystallized to a yellow solid (1.36 g): ^1H NMR δ 4.90 (s, 2 H, C*H*$_2$N), 6.63–6.70 (m, 2 H), 6.78–6.98 (m, 5 H), 7.12–7.51 (m, 15 H), 7.71–7.76 (m, 2 H). Anal. (average of two runs). Calcd for $C_{32}H_{26}N_2$ (438.58): C, 87.64; H, 5.98; N, 6.39. Found: C, 87.86; H, 6.27; N, 6.26.

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***N,N*-Diphenyl-1-naphthalenemethanamine (12):** ^{1}H NMR δ 5.52 (s, 2 H, CH_2N), 7.00–8.10 (m, 17 H). Anal. Calcd for $C_{23}H_{19}N$ (309.41): C, 89.28; H, 6.19; N, 4.53. Found: C, 89.11; H, 6.26; N, 4.44.

***N*-(1-Naphthalenyl)-*N*-phenyl-1-naphthalenemethanamine (13). From 25 + (1-Naphthalenyl)methylenebenzenamine.** Chromatography (PE/EtOAc (98:2) separated **13**: ^{1}H NMR δ 5.47 (s, 2 H, CH_2N), 6.56–6.63 (m, 3 H), 7.06–7.14 (m, 2 H), 7.40–7.57 (m, 7 H), 7.73–7.97 (m, 7 H). Anal. Calcd for $C_{27}H_{21}N$ (359.47): C, 90.22; H, 5.89; N, 3.90. Found: C, 90.14; H, 6.02; N, 4.27.

From (Phenylmethoxy)-1-naphthalene and (1-Naphthalenyl)methylenebenzenamine. The precipitate obtained from the aqueous workup was recrystallized (58% yield of **13**). The solid residue, by evaporation of the mother liquors from the recrystallization of **13**, gave, after three recrystallizations, yellowish crystals of 1,2-di(1-naphthalenyl)ethylene; mp 148–155 °C (MeOH); MS identical with an authentic sample[2] (mp 161–163 °C (lit.[2] mp 163–163.5 °C)).

***N*-(4-Methoxyphenyl)-*N*-phenyl-1-naphthalenemethanamine (14):** ^{1}H NMR δ 3.78 (s, 3 H, OCH_3), 5.38 (s, 2 H, CH_2), 6.73–6.89 (m, 5 H, NC_6H_5), 7.10–7.25 (m, 4 H, $NC_6H_4OCH_3$), 7.34–7.59 (m, 4 H), 7.72–7.76 (d, 1 H), 7.87–7.91 (m, 1 H), 7.97–8.02 (m, 1 H). Anal. (average of two runs). Calcd for $C_{24}H_{21}NO$ (339.44): C, 84.92; H, 6.24; N, 4.13. Found: C, 85.06; H, 6.61; N, 3.99.

***N*-[4-(1,1-Dimethylethyl)phenyl]-*N*-phenyl-1-naphthalenemethanamine (15).** Chromatography (PE/chloroform (4:1)) gave **15** (1.06 g): ^{1}H NMR δ 1.30 (s, 9 H, $C(CH_3)_3$), 5.45 (s, 2 H, NCH_2), 6.84–8.02 (m, 16 H). Anal. Calcd for $C_{27}H_{27}N$ (365.52): C, 88.72; H, 7.44; N, 3.83. Found: C, 88.50; H, 7.49; N, 3.76.

The following were prepared under conditions described in Table II and isolated as for **4** in method a.

***N,N'*-Diphenyl-*N,N'*-bis(phenylmethyl)benzene-1,4-diamine (17). From 16 + 3.** Chromatography (PE/$CHCl_3$ (4:1)) of the precipitate from the aqueous workup gave **17** (0.35 g): ^{1}H NMR δ 4.96 (s, 4 H, $PhCH_2N$), 6.80–6.97 (6), 7.05 (s, 4 H, phenylene), 7.16–7.33 (m, 14 H). Anal. Calcd for $C_{32}H_{28}N_2$ (440.23): C, 87.24; H, 6.40; N, 6.36. Found: C, 87.44; H, 6.50; N, 6.39.

From 2 + 20. Reaction of **2** and **13** in the same relative proportions as for **16** + **3** produced **17** identified (HPLC) by spiking with some pure material above.

***N,N,N',N'*-Tetraphenyl-4-(methylenedioxy)bis(benzenemethanamine) (19).** Double chromatography (CCl_4) of the crude product gave **19** (0.40 g): ^{1}H NMR δ 4.96 (s, 4 H, CH_2N), 5.67 (s, 2 H, OCH_2O), 6.90–7.09 (m, 16 H), 7.20–7.30 (m, 12 H). Anal. Calcd for $C_{39}H_{34}N_2O_2$ (562.72): C, 83.25; H, 6.09; N, 4.98. Found: C, 83.44; H, 6.14; N, 4.96.

***N,N'*-Diphenyl-*N,N'*-[4,4'-(methylethylidine)diphenyl]bis(benzenemethanamine) (22a).** Prior to workup the proportion of **4**, a first unknown, **22a**, and a second unknown was estimated to be 30, 5, 60, and 6%, respectively. The crude product was washed with H_2O and MeOH (10 mL each) successively. Chromatography (PE/CCl_4/$CHCl_3$ (30:16:4)) eluted **4**, **22a**, and the first unknown in this order. The fractions containing **22a** were combined. The solvent was evaporated and the residue dissolved in a minimum of EtOAc to which was added MeOH until turbid crystallizing the diamine **22a**. Recrystallization gave needles mp 114–116 °C; ^{1}H NMR δ 1.62 (s, 6 H, $C(CH_3)_2$), 4.97 (s, 4 H, NCH_2Ph), 6.83–7.37 (m, 28 H). Anal. Calcd for $C_{41}H_{38}N_2$ (558.77): C, 88.12; H, 6.86; N, 5.02. Found: C, 87.81; H, 7.04; N, 5.01.

***N,N'*-Diphenyl-*N,N'*-bis(phenylmethyl)-1,1'-biphenyl-4,4'-diamine (22b).** Before workup, a complex mixture from which three products, **4** (14%), **22b** (10%), and I (see supplementary material; 8%), were isolated and identified as follows. The Na/DMF mixture was poured into H_2O (100 mL) and extracted with $CHCl_3$ (3 × 100 mL). The organic layer was dried and concentrated. The resulting oil was chromatographed (PE/$CHCl_3$ (4:1)) separating pure **4** and a mixture of **22b** and I. This mixture was again chromatographed (same eluent) to give the separated materials. **22b** (less polar): ^{1}H NMR δ 5.03 (s, 4 H, CH_2N), 6.92–7.44 (m, 28 H). Anal. (average of two runs) Calcd for $C_{38}H_{32}N_2$ (516.69): C, 88.33; H, 6.24; N, 5.42. Found: C, 88.30; H, 6.61; N, 5.40.

The rearrangement of **13**.

α-1-Naphthalenyl-*N*-phenyl-1-naphthalenemethanamine (29). The amine **13** (1 g, 0.002 78 mol) was heated in Na/DMF (1 g/50 mL) at 75 °C for 2.5 h with total conversion to **29**. This mixture was poured into H_2O (150 mL). The precipitate was filtered, dried, and recrystallized giving (90% yield) yellowish prisms: mp 230–233 °C (lit.[9] 233–238 °C) (EtOAc/MeOH); ^{1}H NMR δ 4.37 (d, J = 3.8 Hz, 1 H, NH), 6.52–6.75 (m, 5 H, phenyl), 6.92 (d, J = 3.8 Hz, 1 H, CHNHPh collapses to a singlet when shaken with D_2O), 7.08–7.95 (m, 14 H). Anal. Calcd for $C_{27}H_{21}N$ (359.48): C, 90.21; H, 5.89; N, 3.90. Found: C, 90.18; H, 5.89; N, 3.87.

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Registry No. **2**, 538-51-2; **3**, 946-80-5; **4**, 606-87-1; **6**, 135505-47-4; **7**, 135505-48-5; **8**, 135505-49-6; **9**, 135505-50-9; **10**, 57003-80-2; **11**, 135523-27-2; **12**, 135505-51-0; **13**, 135505-52-1; **14**, 135505-53-2; **15**, 135505-54-3; **16**, 797-20-6; **17**, 135505-55-4; **18**, 131189-16-7; **19**, 135505-56-5; **20**, 621-91-0; **21a**, 88216-41-5; **21b**, 72633-22-8; **22a**, 135505-57-6; **22b**, 65181-77-3; **23**, 20459-86-3; **24**, 14790-44-4; **25**, 135505-58-7; **26**, 62784-66-1; **26** acetate, 135505-62-3; **28a**, 780-20-1; **28b**, 780-21-2; **29**, 135505-59-8; 1-(phenylmethoxy)-naphthalene, 607-58-9; *p*-(phenylmethoxy)toluene, 834-25-3; 1-bromo-4-(phenylmethoxy)benzene, 6793-92-6; 1-chloro-4-(phenylmethoxy)benzene, 7700-27-8; *p*-(phenylmethoxy)anisole, 6630-18-8; 1-*tert*-butyl-4-(phenylmethoxy)benzene, 52458-10-3; *N*-(diphenylmethylene)-4-(phenylmethoxy)benzenamine, 135505-60-1; *o*-(phenylmethoxy)toluene, 19578-70-2; *N*-(1-naphthalenylmethylene)benzenamine, 890-50-6; 1,3-diphenyl-2-(phenylmethoxy)benzene, 135505-61-2; α-(1-naphthyl)-4-(1-napthylmethyl)phenol, 135505-63-4; *N,N*-bis(4-bromophenyl)-benzenemethanamine, 135505-64-5; 2,4-dibromo-*N*-(2,4-dibromophenyl)benzenamine, 38573-62-5.

Supplementary Material Available: Experimental details for **4**, **6–15**, **17**, **19**, **20**, **21a,b**, **22a,b**, and **24–26**, as well as other experimental products (5 pages). Ordering information is given on any current masthead page.