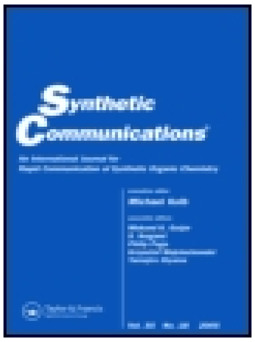

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PHASE-TRANSFER CATALYZED ADDITIONS. VII[1]. PREPARATION OF 3-ARYL-3-ARYLAMINO-2-(N-DIPHENYLMETHYLENEAMINO)-PROPANENITRILES

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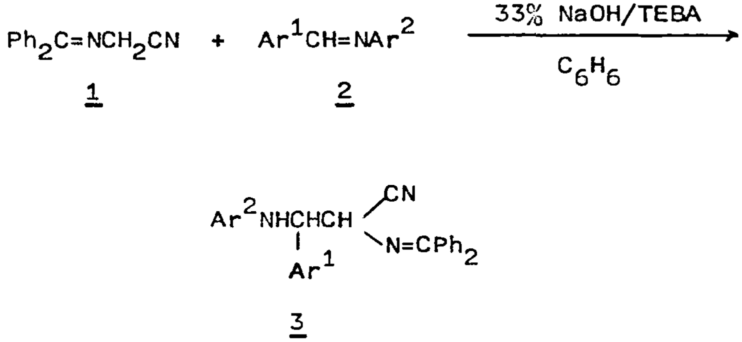
Abstract: The phase-transfer catalyzed reaction of N-diphenylmethyleneaminoacetonitrile 1 with arylideneanilines 2 gives the title compounds in good yields.

Schiff bases derived from glycine derivatives are versatile reagents in organic synthesis. They generate 2-azaallyl anions under phase-transfer catalysis conditions and their reactions with alkylating agents or Michael acceptors afford higher amino acids.[2-4] Compared to the broad application of the Schiff bases of glycine esters, the Schiff bases derived from aminoacetonitrile have received little attention[5-9] although N-diphenylmethyleneaminoacetonitrile, the Schiff base of aminoacetonitrile and benzophenone, is easily available[10] crystaline compound, stable under PTC conditions. Besides, its acidity is 1.1, and 1.7 units greater than that of the Schiff bases derived from ethyl glycinate and benzaldehyde, respectively benzophenone,[3] and only monoalkylation is observed under PTC conditions.[5] Recently, one of us reported on the phase-transfer catalyzed reaction of 1 with aromatic aldehydes resulting in substituted 2-aza-butadienes.[1] Now we report the preparation of 3-aryl-3-arylamino-2-(N-diphenylmethyleneamino)-propanenitriles (3a-g) by addition of N-diphenylmethyleneaminoacetonitrile (1) to the azomethine bond of the Schiff bases 2 (Scheme A).

The reactions were performed by stirring, for 10 minutes at room temperature, benzene solutions of 1 and 2 with the phase-transfer catalyst and excess of sodium hydroxide. As shown in Table 1, the previously unknown nitriles 3a-g were isolated as one diastereoisomer in moderate to good yields. It should be noted that better results were obtained in the cases when the products crystallized from the reaction mixture, nevertheless the nature of the substituent (3a,b,d,f) and, on the other hand, no reaction occured in the absence of the catalyst. The change of the solvent to acetonitrile or methylene chloride resulted in decreasing of the stereoselectivity. In addition, lower yields of 3 and more by-products were observed when the reaction time



$$\underset{\mathbf{1}}{Ph_2C{=}NCH_2CN} + \underset{\mathbf{2}}{Ar^1CH{=}NAr^2} \xrightarrow[C_6H_6]{33\%\ NaOH/TEBA} \underset{\mathbf{3}}{Ar^2NHCH(Ar^1)CH(CN)N{=}CPh_2}$$

2,3	Ar^1	Ar^2
a	C_6H_5	C_6H_5
b	$4\text{-}ClC_6H_4$	C_6H_5
c	C_6H_5	$4\text{-}ClC_6H_4$
d	$4\text{-}CH_3C_6H_4$	C_6H_5
e	C_6H_5	$4\text{-}CH_3C_6H_4$
f	$4\text{-}CH_3OC_6H_4$	C_6H_5
g	C_6H_5	$4\text{-}CH_3OC_6H_4$

Scheme A

was prolonged from 10 to 60 minutes. While for the compound 3a best results were obtained at reaction time one minute, it was not isolated any reaction product when 1 was reacted with Schiff bases 2a-g for one minute, and the yield of 3b was lower (36%).

Attempts to react 1 with N-diphenylmethyleneaniline under these conditions failed. On the other hand, the reaction of 1 with N-benzylideneethylamine (4) resulted

Table 1. Compounds 3a-g Prepared

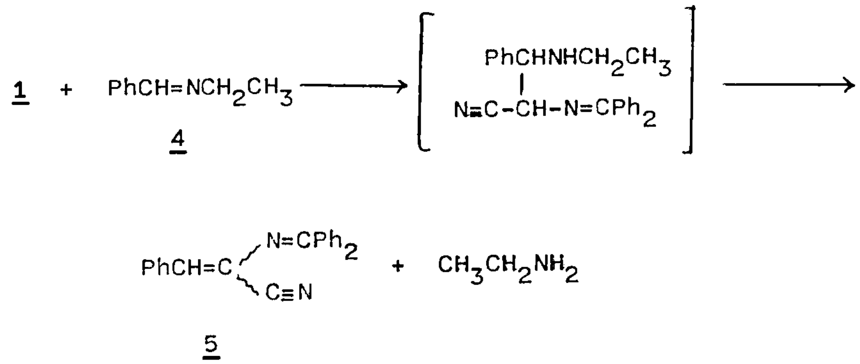
Compound	Yield[a] (%)	M.p.(°C)[b,c]	Molecular Formula
3a	62[d]	160-162	$C_{28}H_{23}N_3$ (401.5)
3b	67	149-151	$C_{28}H_{22}ClN_3$ (436.0)
3c	42	149-151	$C_{28}H_{22}ClN_3$ (436.0)
3d	80	166-168	$C_{29}H_{25}N_3$ (415.5)
3e	38	137-139	$C_{29}H_{25}N_3$ (415.5)
3f	63	148-150	$C_{29}H_{25}N_3O$ (431.5)
3g	20	114-116	$C_{29}H_{25}N_3O$ (431.5)

[a] Yield of isolated pure diastereoisomer; the yields of the crude products (diastereomeric mixtures) were 20-30% higher.

[b] Satisfactory microanalyses obtained.

[c] The products are 100% (3a, 3b, 3g) or more than 99% (3c-f) pure according to HPLC.

[d] Reaction time one minute.



Scheme B

in the formation of 3-cyano-1,1,4-triphenyl-2-aza-1,3-butadiene (5) both at reaction time one and ten minutes (Scheme B).

EXPERIMENTAL

Melting points were determined on a Boetius micro melting point apparatus and are uncorrected. The IR spectra were recorded on Specord 71 spectrometer. ^{1}H NMR spectra were obtained on a Brucker WM-250 spectrometer using TMS as internal standard. All solvents were commercially available and used without purification. N-Diphenylmethyleneaminoacetonitrile 1[10] and the Schiff bases 2[11] were prepared according to the published procedures.

Table 2. Spectral Data of the Compounds 3a-g

Compound	IR ($CHCl_3$) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
3a	2240, 3440	4.56 (d, 1H, J=3.0), 4.50 (d, 1H, J=3.1), 5.50 (bs, 1H), 6.52-7.61 (m, 20H)
3b	2240, 3440	4.54 (d, 1H, J=3.1), 4.88 (d, 1H, J=3.1), 5.50 (bs, 1H), 6.54-7.60 (m, 19H)
3c	2260, 3430	4.54 (d, 1H, J=2.8), 4.88 (bs, 1H, 5.61 (bs, 1H), 6.48-7.58 (m, 19H)
3d	2240, 3430	2.30 (s, 3H), 4.54 (d, 1H, J=3.05), 4.88 (bs, 1H), 5.42 (bs, 1H), 6.53-7.64 (m, 19H)
3e	2250, 3430	2.18 (s, 3H), 4.54 (d, 1H, J=3.0), 4.88 (bs, 1H), 5.35 (bs, 1H), 6.45-7.59 (m, 19H)
3f	2250, 3440	3.76 (s, 3H), 4.54 (d, 1H, J=3.3), 4.86 (d, 1H, J=3.2), 6.54-7.61 (m, 19H)
3g	2250, 3440	3.70 (s, 3H), 4.56 (d, 1H, J=3.4), 4.84 (d, 1H, J=3.5), 6.53-7.61 (m, 19H)

3-Aryl-3-arylamino-2-(N-diphenylmethyleneamino)-propanenitrile 3; General procedure:

Method A (for compounds 3a, 3c, 3e-g):

Aqueous sodium hydroxide (33%, 3 ml) is added all at once to the magnetically stirred solution of 1 (2.20 g, 10 mmol), 2 (10 mmol) and TEBA (0.12g, 0.5 mmol) in benzene (5 ml). The reaction mixture is stirred for 10 min at room temperature. Then water (100 ml) is added and the mixture is extracted with methylene chloride. The combined extracts are washed with water, dried (Na_2SO_4) and evaporated. The residue is taken up in ethanol to afford 3 as a white solid which is recrystallized from ethanol (Table 1 and 2).

Method B (for 3b and 3d):

Aqueous sodium hydroxide (33%, 3 ml) is added all at once to the magnetically stirred solution of 1 (2.20 g, 10 mmol), 2b or 2d (10 mmol) and TEBA (0.12 g, 0.5 mmol) in benzene (5 ml). After stirring for 5 min at room temperature, water (100 ml) is added and the resulting precipitate is collected by filtration, washed with water until neutral and dried. It is then suspended in ethanol (50 ml) for 30 min (in order to remove the unreacted 1 and 2), filtered, and finally recrystallized from ethanol.

3-Cyano-1,1,4-triphenyl-2-aza-1,3-butadiene (5):

This is prepared in 14% yield using the above procedure, Method A, from 1 (2.20 g, 10 mmol) and 4 (1.35 g, 10 mmol); m.p. 163-164°C (Lit.[1] 162-164°C); spectroscopic data are in agreement with those reported earlier; the yield of 5 obtained at reaction time one minute is 26%, m.p. 163-164°C.

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