Reactions of Trimethylsilyl Cyanide and *N*-(Trimethylsilyl)diphenylmethyleneamine with Nitrones and Thermal Decompositions of Their Adducts

Otohiko Tsuge,* Satoshi Urano, and Takahiko Iwasaki

Research Institute of Industrial Science, Kyushu University 86, Hakozaki, Higashi-ku, Fukuoka 812

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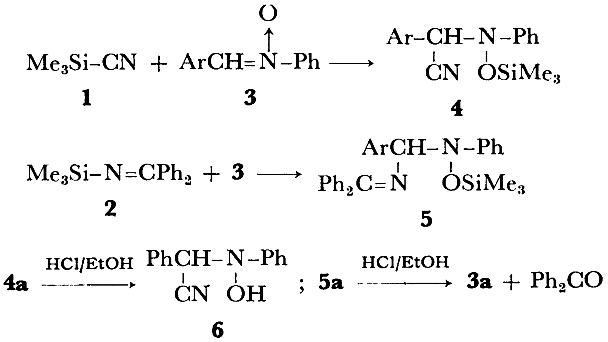
Trimethylsilyl cyanide (**1**) and *N*-(trimethylsilyl)diphenylmethyleneamine (**2**) reacted with α-aryl-*N*-phenylnitrones to afford the corresponding 1 : 1 adducts **4** and **5** respectively. Thermal decomposition of **4** in refluxing xylene gave azoxybenzene, stereoisomers of 2,3-diarylsuccinonitriles, α-iminonitriles and/or benzanilides, whose yields depended on the nature of substituents on phenyl group of **4**. On heating in benzene **5** afforded a mixture of azoxybenzene and *meso*-*N*,*N'*-bis(diphenylmethylene)-1,2-diarylethylenediamines. On the other hand, reactions of **1** and **2** with *N*-(diphenylmethylene)aniline *N*-oxide or *N*-(9-fluorenylidene)aniline *N*-oxide did not give the corresponding 1 : 1 adducts, but instead compounds arising from thermal decomposition of initial 1 : 1 adducts were directly obtained. The reaction of **1** with *N*-(*p*-diethylaminophenyl)-α-phenylnitrone leading to the corresponding α-imino nitrile is also described.

It is known that trimethylsilyl cyanide (**1**) is a good reagent for introducing cyano group, acylation, protecting and activating carbonyl groups in organic syntheses.[1] Recently, Ojima and his coworkers have developed versatility of **1** for syntheses of heterocyclic compounds by the reaction with isocyanates[2] or isothiocyanate,[3] and of α-amino nitriles by the reaction with Schiff bases.[4,5] It has also been reported that *N*-(trimethylsilyl)diphenylmethyleneamine (**2**) reacted with isocyanates, isothiocyanates, and benzimidoyl chlorides to give useful products for syntheses of heterocyclic compounds.[6]

However, little attention has been drawn to the reactions of **1** and **2** with nitrones. In this paper we wish to report on the reactions of **1** and **2** with α-aryl-*N*-phenylnitrones (**3**) and thermal decomposition of the adducts. In this context, the reactions of **1** and **2** with aromatic nitrones other than **3** are also described.

Results and Discussion

Reactions of Trimethylsilyl Cyanide (1) and N-*(Trimethylsilyl)diphenylmethyleneamine (2) with α-Aryl-*N-*phenylnitrones (3).* Treatment of **1** with nitrones, **3a**—**3d**, afforded the corresponding 1 : 1 adducts, α-[*N*-(trimethylsilyloxy)phenylamino]arylacetonitriles, **4a**—**4d**, in excellent yields respectively. Also, **2** reacted with nitrones, **3a**—**3d**, to give the corresponding 1 : 1 adducts, α-[*N*-(trimethylsilyloxy)phenylamino]-*N*-(diphenylmethylene)benzylamines, **5a**—**5d**, in good yields (Scheme 1).



a: Ar=Ph, **b**: Ar=p-MeOC$_6$H$_4$, **c**: Ar=p-ClC$_6$H$_4$, **d**: Ar=p-NO$_2$C$_6$H$_4$

Scheme 1.

Structural elucidation of these adducts **4** and **5** was accomplished on the basis of elemental analysis and spectral data. Detrimethylsilylation of **4a** with hydrochloric acid in ethanol afforded α-(*N*-hydroxyphenylamino)phenylacetonitrile (**6**) in good yield, whereas **5a** was readily converted into nitrone **3a** and benzophenone under similar conditions.

The reaction conditions, yields, physical and analytical data for **4** and **5** are summarized in Tables 1 and 2.

Although **1** did not react with *N*-(diphenylmethylene)aniline *N*-oxide (**7**) or *N*-(9-fluorenylidene)aniline *N*-oxide (**8**) in refluxing benzene, on heating with **7** or **8** at 120 °C without solvent **1** afforded a mixture of tetraphenylsuccinonitrile (**9**) or 9,9'-dicyano-9,9'-bifluorenyl (**10**) and azoxybenzene (**11**) respectively.

Table 1. Reaction conditions, yields, melting points, and appearance for 4 and 5

Compound	Reaction conditions	Yield/%	Mp/°C	Appearance
4a	C$_6$H$_6$, reflux, 4 h	95[a)]	88—89	colorless prisms
4b	C$_6$H$_6$, reflux, 2.5 h	97	102—102.5	colorless prisms
4c	C$_6$H$_6$, reflux, 3 h	95	94—96	colorless needles
4d	C$_6$H$_6$, reflux, 5.5 h	97	118—119.5	colorless needles
5a	CH$_2$Cl$_2$, r.t., 12 h	84	105—106	colorless needles
5b	CH$_2$Cl$_2$, r.t., 14 h	73	102—104	colorless prisms
5c	CH$_2$Cl$_2$, r.t., 16 h	83	93—95	colorless prisms
5d	CH$_2$Cl$_2$, r.t., 13 h	74	125.5—127	colorless prisms

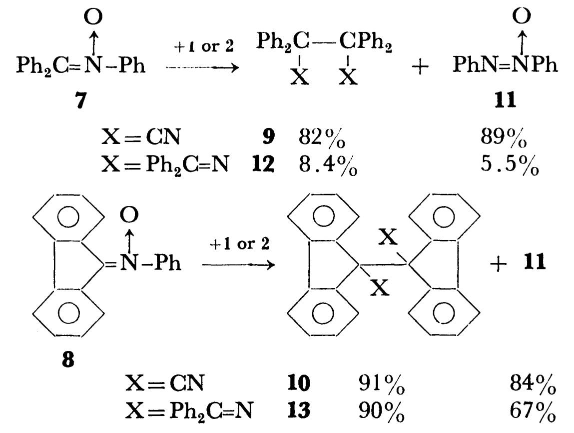
a) In the reaction at room temperature (r.t.) for 12 h **4a** was obtained in 50% yield.

TABLE 2. SPECTRAL AND ANALYTICAL DATA OF **4** AND **5**

Compd	IR/cm^{-1} $\nu_{C\equiv N}$	IR/cm^{-1} $\nu_{C=N}$	^{1}H NMR (CDCl$_3$) Si(CH$_3$)$_3$ δ/ppm	^{1}H NMR (CDCl$_3$) >CH δ/ppm	MS M$^+$ (m/e)	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
4a	2220	—	−0.22	5.12	296	68.72	6.75	9.37	68.91	6.75	9.45
4b	2230	—	−0.12	5.19	326	66.22	6.70	8.56	66.22	6.79	8.58
4c	2230	—	−0.14	5.14	330, 332	61.77	5.70	8.41	61.71	5.79	8.47
4d	2230	—	−0.12	5.32	341	59.72	5.54	12.37	59.80	5.61	12.31
5a$^{a)}$	—	1610	−0.15	5.50	450	77.42	6.79	6.26	77.29	6.71	6.21
5b	—	1610	−0.13	5.30	480	74.96	6.71	5.83	74.93	6.60	5.76
5c	—	1625	−0.12$^{b)}$	5.33$^{b)}$	470, 472$^{c)}$	71.90	5.99	5.75	71.80	6.03	5.77
5d	—	1620	−0.10	5.54	495	70.26	5.84	8.61	70.28	5.90	8.48

a) ^{13}C NMR (CDCl$_3$) δ 0.73 (Si(CH$_3$)$_3$, 86.4 (tert. **C**), 168.4 (**C**=N). b) Measured in CCl$_4$. c) No parent peaks were observed. These peaks correspond to the ions (M$^+$−Me).

On the other hand, **2** reacted with **7** or **8** in dichloromethane at room temperature to give a mixture of **11** and *N,N'*-bis(diphenylmethylene)tetraphenylethylenediamine (**12**) or 9,9'-bis(diphenylmethyleneamino)-9,9'-bifluorenyl (**13**) respectively (Scheme 2).

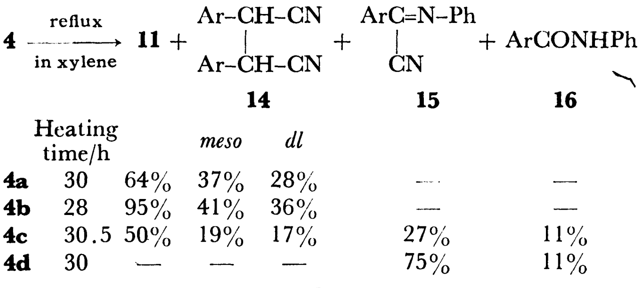


Scheme 2.

Compounds **9**, **10**, **12**, and **13** were prepared by other routes respectively, but the above reactions provide a one-pot syntheses for these compounds.

Thermal Decomposition of 1:1 Adducts. It is reasonable to assume that the reactions shown in Scheme 2 proceeded through the rupture of the C–N bonds of initial adducts of types **4** and **5**. Thus, we have investigated thermal decompositions of adducts **4** and **5**.

When a solution of **4a** or **4b** in xylene was refluxed, a mixture of **11** and stereoisomers of the corresponding 2,3-diarylsuccinonitriles (**14**) respectively. Under similar conditions **4c** afforded α-phenylimino-*p*-chlorophenylacetonitrile (**15c**) and *p*-chlorobenzanilide (**16c**) together with **11** and stereoisomers of 2,3-bis(*p*-chlorophenyl)succinonitriles (**14c**). In the thermal decomposition of **4d**, however, α-phenylimino-*p*-nitrophenylacetonitrile (**15d**) was obtained as a major product, accompanied with a small amount of *p*-nitrobenzanilide (**16d**) as shown in Scheme 3.

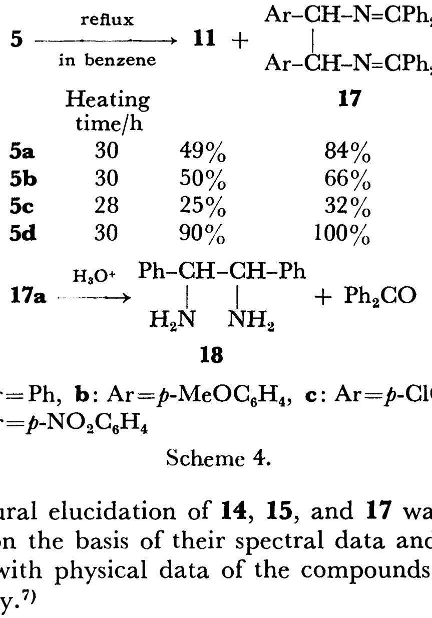


	Heating time/h		meso	dl		
4a	30	64%	37%	28%	—	—
4b	28	95%	41%	36%	—	—
4c	30.5	50%	19%	17%	27%	11%
4d	30	—	—	—	75%	11%

a: Ar=Ph, **b**: Ar=*p*-MeOC$_6$H$_4$, **c**: Ar=*p*-ClC$_6$H$_4$, **d**: Ar=*p*-NO$_2$C$_6$H$_4$

Scheme 3.

On the other hand, thermal decomposition of **5a**—**5d** in refluxing benzene afforded a mixture of **11** and the corresponding *meso-N,N'*-bis(diphenylmethylene)-1,2-diarylethylenediamines, **17a**—**17d**, respectively (Scheme 4). Hydrolysis of **17a** gave a mixture of *meso*-1,2-diphenylethylenediamine (**18**) and benzophenone.



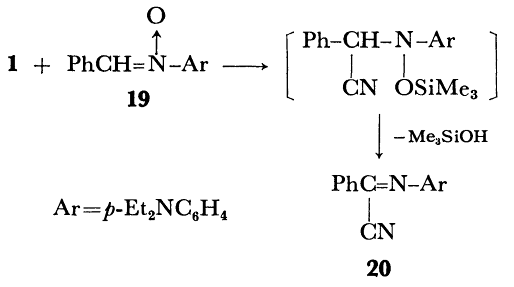
	Heating time/h		17
5a	30	49%	84%
5b	30	50%	66%
5c	28	25%	32%
5d	30	90%	100%

a: Ar=Ph, **b**: Ar=*p*-MeOC$_6$H$_4$, **c**: Ar=*p*-ClC$_6$H$_4$, **d**: Ar=*p*-NO$_2$C$_6$H$_4$

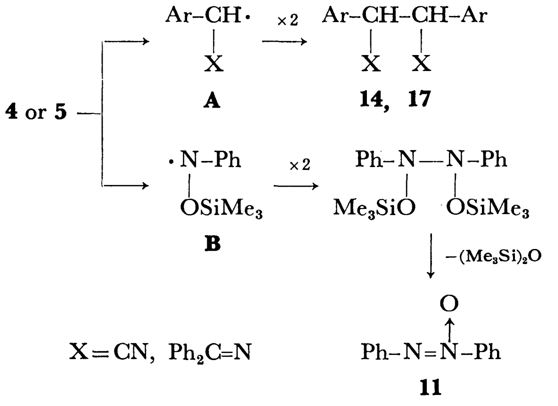
Scheme 4.

Structural elucidation of **14**, **15**, and **17** was accomplished on the basis of their spectral data and/or comparison with physical data of the compounds reported previously.[7)]

As mentioned above, α-imino nitriles **15c** and **15d** were formed in thermal decomposition of **4c** and **4d**. It is reasonable to assume that these α-imino nitriles **15** are formed by the elimination of trimethylsilanol from the corresponding **4**, because *p*-chlorophenyl and *p*-nitrophenyl groups enhance the acidity of α-hydrogen atom of **4**. Thus, it is also expected that thermal decomposition of an adduct of type **4** possessing an electron-donating group on *N*-phenyl will give an α-iminonitrile. In fact, α-(*p*-diethylaminophenylimino)phenylacetonitrile (**20**) was obtained directly even at room temperature by the reaction of **1** with *N*-(*p*-diethylaminophenyl)-*α*-phenylnitrone (**19**).



Although mechanistic considerations are still speculative, a plausible pathway for the formation of **11** and **14** or **17** from **4** or **5** is outlined in Scheme 5. The homolytic rupture of the C–N bond of **4** or **5** yields radical **A** and **B**. The radical **A** dimerizes to give **14** or **17**, and the dimerization of **B** with subsequent elimination of di(trimethyl)siloxane affords **11**.



Scheme 5.

Experimental

Melting points are uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IRA-1 spectrometer, Hitachi R-40, JEOL SX-100 spectrometers, and a Hitachi RMS-4 spectrometer, respectively. IR and NMR spectra were taken in KBr disks and $CDCl_3$ solutions respectively. Mass spectra were obtained at 70 eV.

Materials. Trimethylsilyl cyanide (**1**)[8] and *N*-(trimethylsilyl)diphenylmethyleneamine (**2**)[9] were prepared from trimethylsilyl chloride and silver cyanide or lithium diphenylmethanimine by the reported methods respectively. α-Aryl-*N*-phenylnitrones **3a**—**3d**,[10] *N*-(diphenylmethylene)aniline *N*-oxide (**7**),[11] *N*-(9-fluorenylidene)aniline *N*-oxide (**8**)[11] and *N*-(*p*-diethylaminophenyl)-α-phenylnitrone (**19**)[12] were prepared according to the reported methods respectively.

General Procedure for the Reaction of 1 with 3. A solution of **1** (0.01 mol) and **3** (0.005 mol) in benzene (5 ml) was refluxed. The reaction mixture was evaporated *in vacuo*, and recrystallization of the residue from hexane afforded the corresponding α-[*N*-(trimethylsilyloxy)phenylamino]arylacetonitrile **4**. Reaction conditions, yields, physical and analytical data for **4** are given in Tables 1 and 2.

General Procedure for the Reaction of 2 with 3. A solution of **2** (0.001 mol) and **3** (0.001 mol) in CH_2Cl_2 (20 ml) was stirred at room temperature. The reaction mixture was concentrated *in vacuo* to leave a residue. The residue was triturated with hexane to give crystals, which on recrystallization from hexane afforded the corresponding α-[*N*-(trimethylsilyloxy) phenylamino]-*N*-(diphenylmethylene) benzylamine **5**. Reaction conditions, yields, physical and analytical data for **5** are also shown in Tables 1 and 2.

Detrimethylsilylation of 4a. A solution of **4a** (1.0 g) in EtOH (25 ml) was stirred with concd HCl (20 ml) at room temperature for 1 h. The reaction mixture was poured into water (100 ml) to give solid, which on recrystallization from hexane–benzene afforded 0.69 g (91%) of α-(*N*-hydroxyphenylamino)phenylacetonitrile (**6**), mp 127.5—128.5 °C, as colorless needles. IR 3280 (OH), 2240 cm^{-1} (C≡N); ^{1}H NMR δ 5.37 (s, 1H, **>CH**), 5.50 (s, 1H, **OH**), 7.0—7.7 (m, 10H); MS *m/e* 224 (M$^+$). Found: C, 75.09; H, 5.32; N, 12.50%. Calcd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49%.

Treatment of 5a with Hydrochloric Acid in EtOH. A solution of **5a** (0.5 g) in EtOH (10 ml) was stirred with concd HCl (0.5 ml) at room temperature for 0.5 h. To the reaction mixture was added water (6 ml), and filtration gave 0.13 g (61%) of **3a**. The filtrate was extracted with $CHCl_3$, and the extract was concentrated *in vacuo* to leave 0.16 g (80%) of benzophenone.

Reaction of 1 with 7. A mixture of **1** (1.5 g, 0.15 mol) and **7** (0.5 g, 0.0018 mol) was heated at 120 °C for 2 h. The reaction mixture was concentrated *in vacuo* and the residue was triturated with hexane to give crystals, which on recrystallization from AcOEt afforded 0.28 g (82%) of tetraphenylsuccinonitrile (**9**), mp 206—208 °C (lit,[13] mp 213—215 °C), as colorless prisms. IR 2240 cm^{-1} (C≡N); ^{1}H NMR δ 7.2—7.4 (m); ^{13}C NMR δ 59.2 (quart. C), 121.0 (**C**≡N). Found: C, 87.52; H, 5.16; N, 7.33%. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29%.

The hexane filtrate was chromatographed on silica gel using hexane as eluent to give 0.16 g (89%) of azoxybenzene (**11**).

Reaction of 1 with 8. A mixture of **1** (1.5 g, 0.015 mol) and **8** (0.5 g, 0.0018 mol) was heated at 120 °C for 2 h. A similar treatment of the reaction mixture to that described above afforded 0.31 g (91%) of 9,9′-dicyano-9,9′-bifluorenyl (**10**) as colorless leaves and 0.15 g (84%) of **11**.

10: Mp 284—286 °C (lit,[14] mp 253—255 °C); IR 2240 cm^{-1} (C≡N); ^{1}H NMR δ 7.0—7.5 (m); ^{13}C NMR δ 53.6 (quart. **C**), 118.5 (**C**≡N). Found: C, 88.36; H, 4.21; N, 7.36%. Calcd for $C_{28}H_{16}N_2$: C, 88.40; H, 4.24; N, 7.36%.

Reaction of 2 with 7. A solution of **2** (1.8 g, 0.0071 mol) and **7** (1.5 g, 0.0055 mol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 21 h. The reaction mixture was concentrated *in vacuo*, and the residue was triturated with hexane to give 1.3 g (86%) of unreacted **7**. MeOH (10 ml) was added to the hexane solution to give crystals. Filtration and recrystallization of the crystals from hexane–benzene afforded 80 mg (8.4%) of *N*,*N*′-bis(diphenylmethylene)tetraphenylethylenediamine (**12**), mp 147—149 °C, as colorless prisms. IR 1620 cm^{-1} (C=N); ^{1}H NMR δ 6.4—7.6 (m); ^{13}C NMR δ 80.2 (quart. **C**), 168.1 (**C**=N). Found: C, 89.98; H, 5.73; N, 4.12%. Calcd for $C_{52}H_{40}N_2$: C, 90.17; H, 5.66; N, 4.05%.

The hexane–MeOH filtrate was concentrated *in vacuo*, and the residue was chromatographed on silica gel using hexane as eluent to give 30 mg (5.5%) of **11**.

Reaction of 2 with 8. A solution of **2** (0.5 g, 0.002 mol) and **8** (0.5 g, 0.0018 mol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 24 h. The reaction mixture was concentrated *in vacuo*, and the residue was triturated with hexane to give crystals, which on recrystallization from AcOEt-$CHCl_3$ afforded 0.55 g (90%) of 9,9′-bis(diphenylmethyleneamino)-9,9′-bifluorenyl (**13**), mp 206—207.5 °C (dec), as colorless plates. IR 1610 cm^{-1} (C=N); ^{1}H NMR δ 6.0—8.0 (m); ^{13}C NMR δ 79.9 (quart. **C**), 167.8 (**C**=N); MS *m/e* 344 ($M^+/2$). Found: C, 90.61; H, 5.29; N, 4.00%. Calcd for $C_{52}H_{36}N_2$: C, 90.66; H, 5.27; N, 4.07%.

Thermal Decomposition of ***4a***. A solution of **4a** (1.4 g) in xylene (12 ml) was refluxed for 30 h. On cooling to room temperature, crystals separated from solution. Filtration and recrystallization of the crystals from benzene–EtOH afforded 0.2 g (37%) of *meso*-2,3-diphenylsuccinonitrile (*meso*-**14a**), mp 240—242 °C (lit,[15] mp 238—239 °C), as colorless needles. IR 2240 cm^{-1} (C≡N); ^{1}H NMR δ 4.23 (s, 2H), 7.1—7.5 (m, 10H). Found: C, 82.50; H, 5.12; N, 12.19%. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06%.

The xylene filtrate was concentrated *in vacuo*, and the residue was triturated with hexane to give crystals. Recrystallization from EtOH afforded 0.15 g (28%) of *dl*-2,3-diphenylsuccinonitrile (*dl*-**14a**), mp 169—171 °C (lit,[16] mp 160 °C), as yellow prisms. IR 2250 cm^{-1} (C≡N); ^{1}H NMR δ 4.22 (s, 2H), 7.1—7.5 (m, 10H). Found: C, 82.54; H, 5.14; N, 12.00%. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06%.

The hexane solution was chromatographed on silica gel using hexane as eluent to give 0.28 g (50%) of **11**.

A similar thermal decomposition of **4b** (1.6 g) in xylene (16 ml) afforded 0.29 g (41%) of *meso*-2,3-bis(*p*-methoxyphenyl)succinonitrile (*meso*-**14b**), 0.26 g (36%) of *dl*-2,3-bis(*p*-methoxyphenyl)succinonitrile (*dl*-**14b**), and 0.46 g (95%) of **11**.

meso-**14b**: Mp 239—241 °C; IR 2260 cm^{-1} (C≡N); ^{1}H NMR δ 3.80 (s, 6H), 4.15 (s, 2H), 6.8—7.4 (m, 8H); MS *m/e* 292 (M^+), 146 ($M^+/2$). Found: C, 74.05; H, 5.61; N, 9.69%. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58%.

dl-**14b**: Mp 189—190 °C; IR 2250 cm^{-1} (C≡N); ^{1}H NMR δ 3.84 (s, 6H), 4.12 (s, 2H), 6.8—7.4 (m, 8H); MS *m/e* 292 (M^+), 146 ($M^+/2$). Found: C, 73.89; H, 5.54; N, 9.55%. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58%.

Thermal Decomposition of ***4c***. A solution of **4c** (1.9 g) in xylene (19 ml) was refluxed for 30 h. After being cooled to room temperature, filtration gave crystals which on fractional recrystallization from MeOH–$CHCl_3$ afforded 0.16 g (19%) of *meso*-2,3-bis(*p*-chlorophenyl)succinonitrile (*meso*-**14c**), mp 229—230 °C (lit,[15] mp 234—236 °C), as colorless prisms and 0.1 g (11%) of *p*-chlorobenzanilide (**16c**).

The xylene filtrate was concentrated *in vacuo*, and MeOH (12 ml) was added to the residue to give crystals. Filtration and fractional recrystallization of the crystals from MeOH afforded 0.15 g (17%) of *dl*-2,3-bis(*p*-chlorophenyl)succinonitrile (*dl*-**14c**), mp 181—183 °C, as colorless prisms and 0.38 g (27%) of α-phenylimino-*p*-chlorophenylacetonitrile (**15c**), mp 107—108 °C (lit,[17] mp 108—108.5 °C), as yellow needles. The MeOH filtrate was concentrated *in vacuo*, and the residue was chromatographed on silica gel using hexane as eluent to give 0.28 g (50%) of **11**.

meso-**14c**: IR 2250 cm^{-1} (C≡N); ^{1}H NMR δ 4.20 (s, 2H), 7.0—7.4 (m, 8H). Found: C, 63.68; H, 3.33; N, 9.23%. Calcd for $C_{16}H_{10}N_2Cl_2$: C, 63.81; H, 3.35; N, 9.30%.

dl-**14c**: IR 2225 cm^{-1} (C≡N); ^{1}H NMR δ 4.28 (s, 2H), 7.1—7.5 (m, 8H). Found: C, 63.72; H, 3.41; N, 9.18%. Calcd for $C_{16}H_{10}N_2Cl_2$: C, 63.81; H, 3.35; N, 9.30%.

15c: IR 2220 cm^{-1} (C≡N). Found: C, 69.84; H, 3.72; N, 11.56%. Calcd for $C_{14}H_9N_2Cl$: C, 69.86; H, 3.77; N, 11.64%.

Thermal Decomposition of ***4d***. A solution of **4d** (1.5 g) in xylene (16 ml) was refluxed for 30 h. On cooling to room temperature, 0.12 g (11%) of *p*-nitrobenzanilide (**16d**) crystallized out of solution. The xylene filtrate was concentrated *in vacuo*, and recrystallization of the residue from EtOH afforded 0.82 g (75%) of α-phenylimino-*p*-nitrophenylacetonitrile (**15d**), mp 121—123 °C, as yellow prisms. IR 2180 cm^{-1} (C≡N); ^{1}H NMR δ 7.2—7.6 (m, 5H), 8.4 (m, 4H). Found: C, 67.13; H, 3.55; N, 16.81%. Calcd for $C_{14}H_9N_3O_2$: C, 66.92; H, 3.61; N, 16.73%.

Thermal Decomposition of 5. A typical run is shown for the thermal decomposition of **5a**. A solution of **5a** (0.74 g) in benzene (4 ml) was refluxed for 30 h. The reaction mixture was concentrated *in vacuo*, and the residue was triturated with hexane (3 ml) to give crystals, which on recrystallization from AcOEt afforded 0.37 g (84%) of *meso-N,N′*-bis(diphenylmethylene)-1,2-diphenylethylenediamine (**17-a**), mp 238—239 °C (lit,[18] mp 228 °C), as colorless prisms. IR 1615 cm^{-1} (C=N); ^{1}H NMR δ 4.88 (s, 2H), 6.4—7.5 (m, 30H); MS *m/e* 270 ($M^+/2$). Found: C, 88.73; H, 5.96; N, 5.23%. Calcd for $C_{40}H_{32}N_2$: C, 88.85; H, 5.96; N, 5.18%.

The hexane filtrate was chromatographed on silica gel using hexane as eluent to give 79 mg (49%) of **11**.

The results on the thermal decompositions of **5b**—**5d** are shown in Scheme 4.

meso-N,N′-*Bis(diphenylmethylene)-1,2-bis(*p*-methoxyphenyl)ethylenediamine (17b)*: Mp 229—230 °C as colorless prisms; IR 1625 cm^{-1} (C=N); ^{1}H NMR δ 3.72 (s, 6H), 4.78 (s, 2H), 6.4—7.4 (m, 28H); MS *m/e* 600 (M^+), 300 ($M^+/2$). Found: C, 83.91; H, 6.07; N, 4.76%. Calcd for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.06; N, 4.66%.

meso-N,N′-*Bis(diphenylmethylene)-1,2-bis(*p*-chlorophenyl)ethylenediamine (17c)*: Mp 230—232 °C as colorless prisms; IR 1625 cm^{-1} (C=N); ^{1}H NMR δ 4.79 (s, 2H), 6.4—7.5 (m, 28H); MS *m/e* 608, 610, 612 (M^+), 304, 306 ($M^+/2$). Found: C, 78.81; H, 4.94; N, 4.50%. Calcd for $C_{40}H_{30}N_2Cl_2$: C, 78.81; H, 4.96; N, 4.60%.

meso-N,N′-*Bis(diphenylmethylene)-1,2-bis(*p*-nitrophenyl)ethylenediamine (17d)*: Mp 253—256 °C (dec) as colorless prisms; IR 1620 cm^{-1} (C=N); ^{1}H NMR δ 4.95 (s, 2H), 6.3—8.2 (m, 28H); MS *m/e* 315 ($M^+/2$). Found: C, 76.21; H, 4.75; N, 8.93%. Calcd for $C_{40}H_{30}N_4O_4$: C, 76.17; H, 4.79; N, 8.88%.

Hydrolysis of 17a. A solution of **17a** (0.48 g) in EtOH (20 ml) was stirred with 12% hydrochloric acid (3 ml) at room temperature for 25 h. The reaction mixture was poured into water and extracted with benzene. The benzene extract was concentrated *in vacuo* to give 0.11 g (34%) of benzophenone. The aqueous solution was made basic with aqueous NaOH, and then extracted with $CHCl_3$. The $CHCl_3$ extract was concentrated *in vacuo*, and recrystallization of the residue from cyclohexane afforded 0.1 g (53%) of *meso*-1,2-diphenylethylenediamine (**18**), mp 119—119.5 °C (lit,[18] mp 118 °C), as colorless plates. IR 3330, 3250 cm^{-1} (NH_2); ^{1}H NMR δ 1.35 (s, 4H, NH_2), 4.02 (s, 2H), 7.0—7.7 (m, 10H); MS *m/e* 212 (M^+). Found: C, 79.08; H, 7.67; N, 13.14%. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%.

Reaction of 1 with 19. A mixture of **1** (1.0 g, 0.01 mol) and **19** (1.0 g, 0.0037 mol) in benzene (20 ml) was stirred at room temperature for 6 h, during which time the mixture turned into a red solution. The reaction mixture was concentrated *in vacuo*, and the residue was chromatographed on silica gel using $CHCl_3$ as eluent to give 0.9 g (87%) of α-(*p*-diethylaminophenyl)iminophenylacetonitrile (**20**), mp 112—113 °C, as red prisms. IR 2210 (C≡N), 1610 cm^{-1} (C=N); ^{1}H NMR δ 1.20 (t, 6H), 3.42 (q, 4H), 7.5—8.2 (m, 9H); MS *m/e* 277 (M^+). Found: C, 77.87; H, 6.95; N, 15.15%. Calcd for $C_{18}H_{19}N_3$: C, 77.94; H, 6.91; N, 15.15%.

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7) From the analogy to reported melting points of *meso*- and *dl*-**14a**, the compound having higher melting point was assigned to be the *meso* isomer in **14b** and **14c** respectively. Compounds **17a**—**17d** were assigned to be the *meso* isomer respectively, since the melting point of **18** which was obtained by hydrolysis of **17a** agreed with that of *meso*-1,2-diphenylethylenediamine.[18]

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