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Condensations of 1,4-Cyclohexanediones and Secondary Aromatic Amines. II. *N*-Phenylation of Diarylamines

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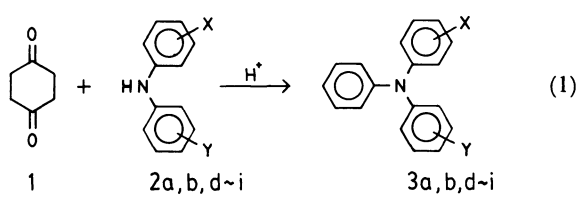
The condensations of 1,4-cyclohexanedione with several diphenylamines were investigated in order to determine the limit of the utility of this reaction for the *N*-phenylation of aromatic secondary amines. 4-Methoxy-, 4,4′-dimethyl-, and 4,4′-dibromodiphenylamines produced their *N*-phenylated compounds in fairly good yields, but 4-hydroxy-, 3-methoxy-, and 4,4′-bis(dimethylamino)diphenylamines produced poor yields. Nitro-substituted diphenylamines gave *N*-phenyl derivatives in low yields along with *N*-4-hydroxyphenyl derivatives. *N,N′*-Diphenyl-*p*-phenylenediamine and *N,N′*-diphenylbenzidine gave corresponding tetra-*N*-phenyl diamines in good yields. The condensation of *N*-phenyl-1-naphthylamine, *N*-phenyl-2-naphthylamine, di-2-pyridylamine, phenothiazine, and carbazole with 1,4-cyclohexanedione were also examined.

In a previous paper[1] the authors showed that the condensation of secondary aromatic amines with 1,4-cyclohexanedione(**1**) in the presence of *p*-toluenesulfonic acid gave *N*-phenyl derivatives. In the case of *N*-ethylaniline, a *p*-chloro or *p*-nitro substituent facilitated the reaction. Diphenylamine also reacted with the 1,4-dione to afford triphenylamine in good yield in spite of a low nucleophilicity. It would be interesting to know to what extent the *N*-phenylation of very low-nucleophilic amines proceeds since condensation with the 1,4-dione is expected to be useful for the *N*-phenylation of diarylamines under mild conditions. In this paper the condensation of several diphenylamines and some analogous amines with 1,4-cyclohexanedione are investigated, and the limit of the utility of this method for *N*-phenylation and solvent effects are discussed.

Results and Discussion

Condensation of Diphenylamines. The condensation of diphenylamines with 1,4-cyclohexanedione was carried out in the presence of *p*-toluenesulfonic acid in a manner similar to that discussed in the previous paper.[1] The results are shown in Table 1. The diphenylamines can be divided into three groups according to their reactivities. Most of diphenylamines (except nitro derivatives) gave only *N*-phenylated compounds (**3a—i**) as isolable products (Eq. 1). 4,4′-Dimethyl- and 4,4′-dibromodiphenyl-



1 2a,b,d~i 3a,b,d~i (1)

amines (**2g** and **2i**) gave the corresponding triphenylamines (**3g** and **3i**) in good yields, as did diphenylamine (**2h**).

Table 1. Condensation of Diphenylamines with 1,4-Cyclohexanedione[a]

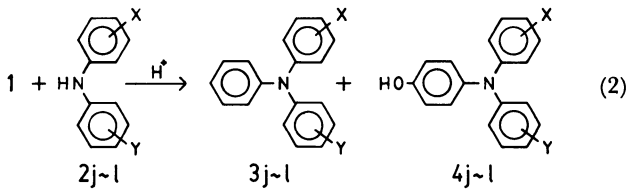
Diphenylamine			Time[b]/h	Product (Yield/%)			
	X	Y			3(Z=H)		4(Z=OH)
2a	*p*-$(CH_3)_2N$	*p*-$(CH_3)_2N$	18	**3a**	18	—	—
2b	H	*p*-HO	12	**3b**	14	—	—[c]
2c	*m*-HO	*m*-HO	12	—	—	—	—[c]
2d	H	*p*-C_2H_5O	12	**3d**	90	—	—
2e	H	*m*-C_2H_5O	11	**3e**	20	—	—[c]
2f	*m*-C_2H_5O	*m*-C_2H_5O	12	**3f**	2.8	—	—[c]
2g	*p*-CH_3	*p*-CH_3	12	**3g**	65	—	—
2h	H	H	12	**3h**	88	—	—
2i	*p*-Br	*p*-Br	12	**3i**	94	—	—
2j	H	*p*-NO_2	12	**3j**	43	**4j**	7.8
2k	*p*-NO_2	*p*-NO_2	18	**3k**	0.2	**4k**	4.2
2l	*m*-NO_2	*m*-NO_2	18	**3l**	23	**4l**	12

a) 1,4-Cyclohexanedione; 0.25 g (2.23 mmol). Diphenylamines; 2.23 mmol. *p*-Toluenesulfonic acid; 10 mg. b) The reaction was carried out in toluene (10 cm^3) at the refulux temperature. c) Resinous products were obtained.

On the other hand, strong electron-donating substituents seemed to be unfavorable for this type reaction, except for the *p*-ethoxyl group. 4-Hydroxy-, 3-ethoxy-, and 3,3′-diethoxydiphenylamines (**2b**, **2e**, and **2f**) produced triphenylamines in poor yields and 3,3′-dihydroxydiphenylamine (**2c**) gave no triphenylamine. The low yields of these *N*-phenyl derivatives may be similar to the results of the *N*-phenylation of *N*-ethylanilines. In the latter case, there was a tendency for electron-withdrawing substituents to facilitate the *N*-phenylation; *N*-ethylanilines substituted by electron-donating groups showed relatively low reactivity. These facts have been explained in terms of the acidity of the conjugate acids as the actual catalyst. However, 4-ethoxydiphenylamine

(**2d**) gave 4-ethoxytriphenylamine (**3d**) in good yield. This shows that the conjugate acid of **2d** is sufficiently acidic to catalyze the reaction. The basicity of diphenylamine, itself, is very weak. Therefore, the acidity of the conjugate acid of any diphenylamine must be strong even if it is substituted by an electron-donating group. Therefore, the low yields of the triphenylamines from **2b**, **2c**, **2e**, and **2f** must be due to side reactions. Actually, these diphenylamines produced some resinous by-products which could not be purified and remained unidentified. According to an infrared analysis, the by-products contained carbonyl groups. Also, the condensation of the secondary amines with the 1,4-dione seemed to occur at aromatic nuclei. In the case of the *p*-ethoxyl derivative (**2d**), the corresponding by-product was hardly produced. The difference between the reactivity of **2d** and that of **2e** is now under investigation. The condensation of 4,4′-bis(dimethylamino)diphenylamine (**2a**) with the 1,4-dione also gave triphenylamine **3a** in a low yield. In this case, 80% of the starting amine was recovered. The dimethylamino groups of **2a** are more basic than the inside diarylamino group; thus, protonation must occur on the dimethylamino group (the conjugate acid of **2a** is much more weak than that of diphenylamine). Therefore, the low reactivity of **2a** is due to the low activity of the conjugate acid.

The last group of diphenylamines (nitro-substituted diphenylamines) also showed a small reactivity and 4,4′-dinitrodiphenylamine (**2k**) could hardly give *N*-phenylated derivative. In these cases, by-products were isolated and identified to be 4-hydroxy-4′-nitrotriphenylamine (**4j**), 4-hydroxy-4′,4″-dinitrotriphenylamine (**4k**), and 4-hydroxy-3,3″-dinitrotriphenylamine (**4l**). The yields of these hydroxy



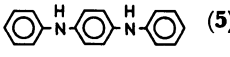
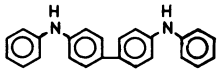
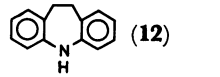
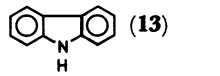
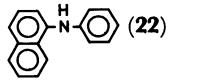
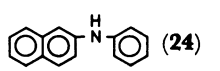
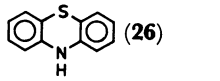
(2)

derivatives were also poor; therefore, the low yields of the triphenylamines must be due to the very low nucleophilicity of the amino groups. It is worth noting that the *p*-bromo substituent facilitated the reaction but the nitro substituent did not. That is to say, the effect of the bromo group on diphenylamines is parallel with that on *N*-ethylanilines, whereas the effect of the nitro group is opposite. This is because the decrease in the nucleophilicity of the nitro-substituted diphenylamines is more remarkable rather than an increase in the acidity of the conjugate acid.

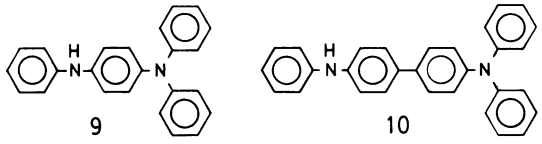
These results indicate that the reaction depends on both the necleophilicity of the amine and the acidity of the conjugate acid. Since both factors can be assumed to have a reverse tendency for many amines, they must compensate for each other in the *N*-phenylation of most aniline derivatives. If either of the two factors decreases very much, *N*-phenylation proceeds with difficulty, for example, as in the case of aliphatic amines or the dinitrodiphenylamines. Consequently, this *N*-phenylation is applicable for an aromatic secondary amine which is more nucleophilic than 4-nitrodiphenylamine; however, it is necessary to take into account the side reaction for several diphenylamines substituted by electron-donating groups. The condensation of other secondary amines analogous to diphenylamine were examined in order to determine any further utility of this reaction.

The *N*-Phenylation of Other Secondary Amines. As analogies of diphenylamine, two aromatic diamines, three cyclic amines, di-2-pyridylamine, and *N*-phenyl naphthylamines were examined for the reactivity of the *N*-phenylation. The results are shown in Table 2. *N*,*N*′-Diphenyl-*p*-phenylenediamine (**5**) and *N*,*N*′-diphenylbenzidine (**7**) gave *N*,*N*,*N*′,*N*′-tetrapheny-*p*-phenylenediamine (**6**) and *N*,*N*,*N*′,*N*′-tetraphenylbenzidine (**8**), respectively, in good yields. In these reactions, *N*,*N*,*N*′-triphenylphenylenediamine (**9**) and *N*,*N*,*N*′-triphenylbenzidine (**10**) should be formed

Table 2. Condensation of Diarylamine Other than Diphenylamines[a)]

Diarylamine	Time/h	Product (yield/%)
 (**5**)	20	*N*,*N*,*N*′,*N*′-Tetraphenyl-*p*-phenylenediamine (**6**) (80)
 (**7**)	20	*N*,*N*,*N*′,*N*′-Tetraphenylbenzidine (**8**) (78)
 (**11**)	24	No product
 (**12**)	24	No product
 (**13**)	12	*N*-Phenylcarbazole (**14**) (6.6) 1-Phenylcarbazole (**15**) (12)
 (**22**)	12	*N*,*N*-Diphenyl-1-naphthylamine (**23**) (19)
 (**24**)	12	*N*,*N*-Diphenyl-2-naphthylamine (**25**) (28)
 (**26**)	12	*N*-Phenylphenothiazine (**27**) (43)

a) The conditions were as same as that in Table 1.



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as intermediates. These compounds could not be isolated, but the formation of **6** and **8** showed that the intermediates also reacted easily with one further molecule of the 1,4-dione. On the other hand, di-2-pyridylamine (**11**) gave no tertiary amine and most of the starting materials were recovered. The facility of the *N*-phenylation of **5**, **7**, **9**, and **10** indicates that the *N*-phenylation of a polyamino aromatic compound proceeds if amino groups other than a reaction point are not more basic than the reaction point. In the case of **11**, however, both factors (nucleophilicity and acidity) which govern the reaction are under unfavorable situations. It is well known that 2- or 4-aminopyridine is more basic than aniline and that protonation occurs on the ring nitrogen,[2] and pyridine, itself, is much more basic than diphenylamine. Then, the conjugate acid of **11** is also less acidic than that of diphenylamine, but the exocyclic amino group is less nucleophilic because of the electron-withdrawing property of the pyridine ring.

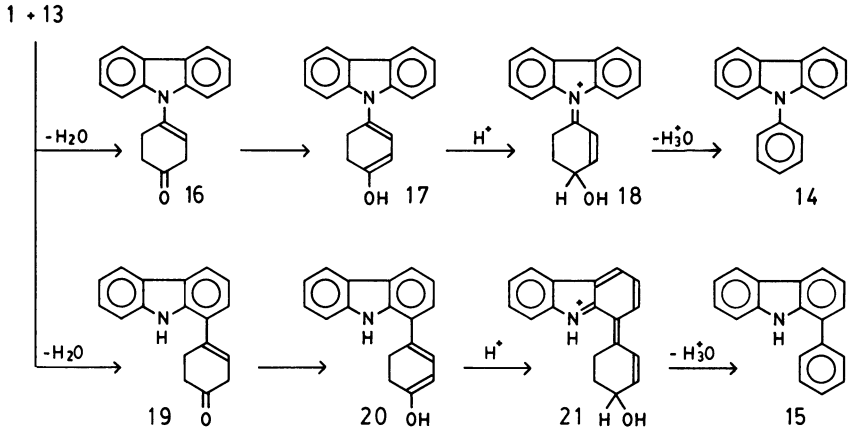
Also, 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (**12**) did not give any phenylated compound and the starting amine was recovered. The differences between **12** and diphenylamine or carbazole must be due to a steric hindrance; that is, the ethylene linkage must inhibit the nitrogen from attacking the carbonyl of the 1,4-dione.

Carbazole (**13**) had been estimated to have a very low reactivity. Actually, about 80% of **13** was recovered upon condensation with the 1,4-dione. *N*-Phenylcarbazole (**14**), however, was obtained in low yield together with 1-phenylcarbazole (**15**). The fact that *C*-phenylation is easier than *N*-phenylation in carbazole can be explained by the mechanisms shown in Scheme 1. The formation of monoenamine **16** (an intermediate of *N*-phenylation) is a reversible reaction; but the formation of **19** is irreversible and **19** easily changes to **15** under the influence of a strong acid. Comparing the stability of **18** with that of **21**, the protonation of **20** is seen to be easier than that of **17**. *C*-Phenylation could not be observed for diphenylamines. Carbazole is a much weaker base than diphenylamine.[3] This suggests that the lone-pair electrons of the nitrogen atom of carbazole are more delocalized than those of diphenylamine. Therefore, the carbocyclic rings should be more active toward an electrophilic attack than the phenyl groups of diphenylamine. In the case of diphenylamines substituted with electron-donating groups, the substituents increase the activity of the phenyl group but also increase the nucleophilicity of the nitrogen. These reactions of carbazole are very interesting, but the low reactivity of the nitrogen of carbazole also shows the limit of the utility of this method for *N*-phenylation.

N-Phenyl-1-naphthylamine (**22**) and *N*-phenyl-2-naphthylamine (**24**) gave the corresponding *N*,*N*-diphenylnaphthylamines (**23** and **25**), respectively, but in low yields. Phenothiazine (**26**) produced *N*-phenylphenothiazine (**27**) in moderate yield. These results are less satisfactory, but still show that this *N*-phenylation method is applicable to secondary amines beyond aniline derivatives.

Solvent Effect. *N*-Phenylation reactions in several polar solvents were much slower than that in aromatic hydrocarbons. In the condensation of diphenylamine (**2h**) in dimethyl sulfoxide, triphenylamine was scarcely produced. The condensation of phenothiazine (**26**) in dioxane for 24h resulted in only a 13% yield of the *N*-phenyl derivative. Carbazole (**13**) in a mixture of xylene and nitrobenzene scarcely gave *N*-phenylcarbazole.

Diphenylamines substituted with nitro groups have poor reactivities, as described above. While the



Scheme 1.

Table 3. Solvent Effect on the Condensation of 4,4′-Dinitrodiphenylamine with 1,4-Cyclohexanedione[a)]

Solvent	Catalyst /mg	Time /h	Product **3k**	(Yield/%) **4k**
Toluene	10	18	0.2	4.2
	40	18	0.6	4.6
	40	36	1.1	7.8
Toluene/DMSO	10	18	0.6	trace
(80/20)	40	18	1.9	trace
Dioxane	40	18	0.6	—
Xylene/Nitrobenzene (80/20)	40	18	—	13

a) The conditions were virtually identical with those shown in Table 1 except for the solvent and the amount of *p*-toluenesulfonic acid as the catalyst.

reactivity of **2k** is especially low, such a reaction of **2k** in high concentration could not be performed in toluene because of the poor solubility. Further, the formation of the 4-hydroxyphenyl derivatives suggests that the dehydrogenation of the monoenamines of the 1,4-dione is accompanied by their dehydration. The relative rates of these simultaneous reactions were expected to be affected by the polarity of solvent. The results of the condensation of **2k** carried out for several conditions are shown in Table 3. In toluene, an increase in the amount of the catalyst or the reaction period leads to an increase in the yields of both **3k** and **4k**; yet, their yields are very poor. In a mixture of toluene and dimethyl sulfoxide or in dioxane, **4k** was scarcely produced. In every solvent, the total yield of the two products was smaller than that in toluene. In a mixture of xylene and nitrobenzene, **3k** was not produced; however, the yield of **4k** increased. It can be said that nitrobenzene accelerated the dehydrogenation to afford **4k**, which resulted in inhibiting the formation of **3k**. This shows that an oxidizing action of a nitro group can occur in the reaction system. Therefore, dehydrogenation in the absence of nitrobenzene must be catalyzed by the nitro groups of 4,4′-dinitrodiphenylamine.

These results show that polar solvents are unfavorable and only the aromatic hydrocarbons are favorable as solvents for the condensation process.

Experimental

General. Melting points were uncorrected. ^{1}H-NMR spectra were recorded on a JNM-C-60HL spectrometer with $(CH_3)_4Si$ as an internal standard. IR spectra were taken on a JASCO Model IR-G spectrophotometer. Mass spectra were measured on a Hitachi M-80 mass spectrometer.

Materials. 4-Ethoxy-, 3-ethoxy-, and 3,3′-diethoxydiphenylamines were prepared from 4-hydroxy-, 3-hydroxy-, and 3,3′-dihydroxydiphenylamines, respectively. Ethylation was carried out using ethyl iodide in a 10% ethanolic potassium hydroxide solution. This was a modification of Houston's method[4)] for the preparation of 4-propoxydiphenylamine. 4-Ethoxydiphenylamine (**2d**) was prepared in 52% yield: Mp 71 °C. 3-Ethoxydiphenylamine (**2e**) was obtained in 80% yield: Bp 162 °C/1.5 Torr (1 Torr=133.322 Pa). 3,3′-Diethoxydiphenylamine (**2f**) was isolated by distillation and following column chromatography on silica gel: yield, 22%; bp 189 °C/1 Torr. *N*-Benzoyldiphenylamine was obtained by the usual method from diphenylamine and benzoyl chloride: Mp 175.5—176.5 °C (from ethanol). 4,4′-Dibromodiphenylamine (**2i**) was prepared by bromination of *N*-benzoyldiphenylamine in chloroform and following hydration in 3% ethanolic potassium hydroxide solution: Yield, 56%; mp 100—102 °C (lit,[5)] 105.5—107 °C). 3,3′-Dinitrodiphenylamine (**2l**) was prepared according to the method of Hodgson and Dodgson[6)]: Mp 186—187.5 °C (lit, 188 °C). 4-Nitrodiphenylamine (**2j**) was prepared from 4-bromonitrobenzene and acetanilide. The procedure was virtually identical with that of Hodgson and Dodgson for **2l** but the intermediate, *N*-acetyl-4-nitrodiphenylamine was hydrated in a 0.2% ethanolic potassium hydroxide solution since hydration in an acidic solution was difficult. Compound **2j** was obtained in 50% yield: Mp 131—132.5 °C; IR (KBr disk) 3320, 1595, 1475, 1295, 1105, 745, and 640 cm^{-1}. 4,4-Dinitrodiphenylamine (**2k**) was obtained from diphenylamine in a manner similar to that used by Chen et al.[5)]: Mp 216—218 °C (lit, 217—218 °C). All other diphenylamines and secondary amines in Table 2 were commercially available and were used after purification (if necessary).

Condensation of the Secondary Amines with 1,4-Cyclohexanedione (1). General Method: The procedure was virtually identical to that described in the previous paper.[1)] A two-necked flask was fitted with a reflux condenser and an inlet tube. In the flask, a filter paper thimble packed with $CaCl_2$ was hung under the condenser in order to dehydrate the refluxed solvent. A mixture of 0.25 g (2.23 mmol) of 1,4-cyclohexanedione, the amine (2.23 mmol) and 10 mg of *p*-toluenesulfonic acid in 10 cm^3 of toluene was refluxed. After 12 h, the solution was freed of solvent in vacuo and then the residue was separated by column chromatography on silica gel. The product was eluted with hexane–benzene.

Condensation of Diphenylamines (2a—i). The isolated products and the yields are shown in Table 1, and their properties are presented below.

4,4′-Bis(dimethylamino)triphenylamine (3a): Mp 151—152 °C (lit,[7)] 157 °C; ^{1}H NMR ($CDCl_3$) δ=2.88 (12H, broad s) and 7.30—6.52 (13H, m); IR (KBr disk) 1600, 1590, 1510, and 1490 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 331 (M^+, 100), 316 (14), and 166 (11); High-resolution mass spectra (HR-MS), *m/z* 331.2105; Calcd for $C_{22}H_{25}N_3$: M, 331.2050.

4-Hydroxytriphenylamine (3b): Mp 125.5—126.5 °C; IR (KBr disk) 3550, 1580, 1510, and 1490 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 262 (20), 261 (M^+, 100), 260 (17), 167 (6), and 77 (8); HR-MS, *m/z* 261.1117, Calcd for $C_{18}H_{15}NO$: M, 261.1154.

4-Ethoxytriphenylamine (3d): Mp 76—78 °C; NMR ($CDCl_3$), δ=1.46 (3H, t), 4.07 (2H, q), and 6.79—7.45 (14H, m); IR (KBr disk) 1580, 1485, and 1235 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 289 (M^+, 94), 260 (100), and 77 (14); HR-MS, *m/z* 289.1511; Calcd for $C_{20}H_{17}NO_2$: M,

289.1466.

3-Ethoxytriphenylamine (3e): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t), 3.89 (2H, q) and 6.38—7.38 (14H, m); IR (neat) 1580, 1490, and 1215 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 289 (M^+, 100), 260 (35), 244 (18) and 77 (21); HR-MS, *m/z* 289.1513; Calcd for $C_{20}H_{17}NO_2$: M, 289.1466.

3,3′-Diethoxytriphenylamine (3f): Light blue liquid ^{1}H NMR ($CDCl_3$) δ=1.35 (6H, t), 3.91 (4H, q) and 6.42—7.33 (13H, m); IR (neat) 1580, 1480 and 1195 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 333 (M^+, 100), 304 (6), and 276 (7); HR-MS, *m/z* 333.1634; Calcd for $C_{22}H_{23}NO_2$: M, 333.1727.

4,4′-Dimethyltriphenylamine (3g): Mp 107—108 °C; ^{1}H NMR ($CDCl_3$) δ=2.28 (6H, s) and 6.75—7.52 (13H, m); IR (KBr disk) 1593, 1507, 1490, 1320, 1290, and 1280 cm^{-1}; MS (70 eV), *m/z* (rel intensity), 273 (M^+, 100), 257 (6), and 180 (5); HR-MS, *m/z* 273.1539; Calcd for $C_{20}H_{19}N$: M, 273.1518.

4,4′-Dibromotriphenylamine (3i): Colorless viscous liquid; IR (neat) 1575, 1480, 1310, 820, and 505 cm^{-1}; MS (70 eV), *m/z* (rel intensity) 405 (51), 403 (100), and 401 (52); relative intensity of isotopic cluster calculated from $C_{18}H_{13}NBr_2$, 50.4:100:50.5 (M+4:M+2:M).

Condensation of Nitro Substituted Diphenylamines (2j, 2k, and 2l). The procedure was virtually identical with that described above. After **3j—l** were separated by column chromatography on silica gel eluted with hexane–benzene, hydroxy derivatives **4j—l** were eluted with benzene–ether. The latter compounds were further purified by chromatography on alumina. They were eluted with ethanol after elution with ether.

4-Nitrotriphenylamine (3j): Mp 138—139 °C; IR (KBr disk) 1575, 1490, 1320, and 1110 cm^{-1}; MS, *m/z* (rel intensity), 290 (M^+, 100), 244 (35), 243 (28), 242 (21), 167 (20), 166 (19), and 77 (19); HR-MS, *m/z* 290.1089; Calcd for $C_{18}H_{14}N_2O_2$: M, 290.1056.

4-Hydroxy-4′-nitrotriphenylamine (4j): Decomposed above 250 °C; IR (KBr disk) 3400, 1575, 1480, 1300, and 1110 cm^{-1}, MS, *m/z* (rel intensity), 306 (M^+, 100), 260 (23), 251 (26), and 83 (15); HR-MS, *m/z* 306.0988; Calcd for $C_{18}H_{14}N_2O_3$: M, 306.1002.

4,4′-Dinitrotriphenylamine (3k): Mp 206—207 °C; IR (KBr disk) 1585, 1575, 1500, and 1335 cm^{-1}; MS, *m/z* (rel intensity), 335 (M^+, 34), 259 (100), 223 (14), 167 (42), 166 (28), and 69 (51); HR-MS, *m/z* 335.0932, Calcd for $C_{18}H_{13}N_3O_4$: M, 335.0907.

4-Hydroxy-4′,4″-dinitrotriphenylamine (4k): Mp 243—245 °C; IR (KBr disk) 3500, 1575, 1490, 1305, and 1110 cm^{-1}; MS, *m/z* (rel intensity), 351 (M^+, 100), 259 (29), and 258 (16); HR-MS, *m/z* 351.0759; Calcd for $C_{18}H_{13}N_3O_5$: M, 351.0853.

3,3′-Dinitrotriphenylamine (3l): Mp 144.5—145.5 °C; IR (KBr disk) 1520, 1510, 1340, and 1270 cm^{-1}: MS, *m/z* (rel intensity), 335 (M^+, 100), 243 (39), 242 (39), and 241 (24); HR-MS, *m/z* 335.0929; Calcd for $C_{18}H_{13}N_3O_3$: M, 335.0907.

4-Hydroxy-3′,3″-dinitrotriphenylamine (4l): Mp 175—178.5 °C; IR (KBr disk) 3400, 1525, 1510, and 1345 cm^{-1}; MS, *m/z* (rel intensity), 351 (M^+, 100), 259 (39), 258 (26), and 257 (10); HR-MS, *m/z* 351.0915; Calcd for $C_{18}H_{13}N_3O_5$: M, 351.0854.

Condensation of Diamine 5 and 7. The procedure was virtually identical with the general method, but 1,4-cyclohexanedione was used by double molar quantity to 1 mol of the diamine.

***N,N,N′,N′*-Tetraphenyl-*p*-phenylenediamine (6):** Mp 197—198 °C; IR (KBr disk) 1590, 1505, 1493, and 1270 cm^{-1}; MS, *m/z* 412 (M^+).

***N,N,N′N′*-Tetraphenylbenzidine (8):** Mp 224—225 °C; IR (KBr disk) 1585, 1490, 1480, and 1275 cm^{-1}; MS, *m/z* 488 (M^+).

Condensation of Carbazole. The procedure was virtually identical with the general method but the column chromatograpy on silica gel with hexane was repeated several times to isolate products **14** and **15**.

***N*-Phenylcarbazole (14):** Mp 90—92 °C; Picrate, mp 127—128 °C; IR (KBr disk) 1590, 1500, 1445, and 1230 cm^{-1}; MS, *m/z* 243 (M^+).

1-Phenylcarbazole (15): Mp 129—130 °C (lit,[7] 133 °C); picrate, mp 150—151 °C (lit,[8] 151 °C); IR (KBr disk) 3320, 1620, 1590, 1500, 1410, 1320, and 1230 cm^{-1}; MS, *m/z* 243 (M^+).

Condensation of *N*-Phenyl-1-naphthylamine (22), *N*-Phenyl-2-naphthylamine (24) and Phenothiazine (26). These condensations were carried out by the general method.

***N,N*-Diphenyl-1-naphthylamine (23):** Mp, 137.5—138.5 °C; IR (KBr disk) 1590, 1490, 1390, 1290, and 1275 cm^{-1}; MS, *m/z* 295 (M^+).

***N,N*-Diphenyl-2-naphthylamine (24):** Mp, 120—121 °C; IR (KBr disk) 1620, 1590, 1490, 1275, and 755 cm^{-1}; MS, MS, *m/z* 295 (M^+).

***N*-Phenylphenothiazine (15):** Mp 93—94 °C; IR (KBr disk) 1580, 1485, 1455, and 1300 cm^{-1}; MS, *m/z* 243 (M^+).

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